^{13}C and ^{15}N Solid-State NMR of Partially Methyl Substituted Polyazines

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ABSTRACT: The partially methylated polyazine series, which varies the number of methyl groups along the polyazine backbone, has been prepared. The number and substitution pattern of methyl groups were altered via a condensation reaction between an α,β-dicarbonyl and an α,β-dihydrazone using glyoxal, pyruvic aldehyde, 2,3-butanedione, glyoxal dihydrazone, pyruvic aldehyde dihydrazone, and 2,3-butanedione dihydrazone. All combinations of the above reagents were used, leading to nine different polymers. The polymers prepared with glyoxal dihydrazone exhibit hydroxy-bearing defects like those in the unsubstituted polyazine. In contrast, the polymers prepared with 2,3-butanedione dihydrazone were essentially defect-free, like the permethyl and higher alkyl polyazines. However, the polymers prepared with pyruvic aldehyde dihydrazone failed to follow a simple trend.

Introduction

Conducting polymers have been of great interest since the late 1970s when doped polyacetylene was found to be highly conductive.[1-12] Since this discovery, a number of other polymeric systems have been introduced, polypyrrole,[13-16] polythiophene,[17-24] and polyaniline[25-34] to name a few. Polyacetylene, $[-CH{=}CH-CH{=}CH-]_x$, is the prototype and simplest conjugated polymer. If an azine bond, $=N-N=$, replaces a dimeric unit, $=CH-CH=$, at every other site, unsubstituted polyazine, $[-N{=}CH-CH{=}N-]_x$, is the product. The presence of the nitrogen in polyazines stabilizes them in air; i.e., they are not oxidized by oxygen. Polyazines are synthesized via an acid-catalyzed condensation reaction between an α,β-dihydrazone and an α,β-dicarbonyl. A number of polymers prepared from α,β-dihydrazones and α,β-dicarbonyls can be prepared, but this paper concentrates only on the partially methylated polyazines.

Polyazines, $[-N{=}C(R_1)-C(R_2){=}N-]_x$, where $R_1 = R_2 = CH_3$ or $R_1 = R_2 = H$, have been previously characterized.[35-40] The linear defect-free permethyl derivative can be oxidized to show moderate levels of conductance.[35] On the other hand, the defect-containing unsubstituted polyazine shows conductivity measurements 5 orders of magnitude lower than that of the permethyl derivative.[39] The unsubstituted polyazine, R = H, is of interest because it is formally isoelectronic and isostructural to *trans*-polyacetylene. Unfortunately, the unsubstituted polyazine possesses defects in the form of 2,3,5,6-tetrahydroxypiperazine (THP). Since the removal of all pendant methyl groups incorporated defects into the polymer, the partially methylated polyazine series was prepared. The purpose of this research is to investigate how the defect structures are incorporated into the polyazines.

Some of the partially methylated polyazines show defects. However, two types of defects are present: THP and α,α'-dihydroxy tertiary amine (DHTA). All of the polymers prepared with glyoxal dihydrazone (GDH) mimic the unsubstituted polymer; the polymers prepared with 2,3-butanedione dihydrazone (BDDH) are essentially defect-free and imitate the permethyl polyazine. The polymers prepared from pyruvic aldehyde dihydrazone (PADH) do not follow a simple trend. Rather, the members of this series exhibit defects, but the nature of the defect is dependent upon the starting materials.

Since long-chain polyazines are insoluble, solid-state NMR is a valuable technique to investigate these conjugated systems. The ^{13}C NMR probes the imine, defect, and methyl regions of the spectrum. The ^{15}N spectra also directly probe the imine region and should correlate with the ^{13}C data. Moreover, ^{15}N spectra will confirm the presence of an amine and the nature of the proposed defect sites. Since the spectral dispersion for ^{15}N is large, primary amines are distinguishable from tertiary amines. This partially methyl substituted polyazine series will help determine the reasons defects are incorporated into the polymer lattice. Specifically, the type of defect that occurs and the rationale as to why defects are formed are examined by using ^{13}C and ^{15}N solid-state NMR.

Experimental Procedures

Solid-state NMR spectra were obtained at Lehigh University on General Electric NMR instrument GN-300 operating at 75.4 MHz for ^{13}C and at 30.4 MHz for ^{15}N. A 7-mm Doty Scientific, Inc., probe was utilized at ambient temperature with sapphire rotors and Kel-F endcaps containing a sample volume of up to 0.35 cm^3. Spectra were obtained with cross polarization[41] and magic angle sample spinning.[42] Spinning speeds were measured between 2.5 and 5.3 kHz. Typical conditions included a single cross-polarization contact time of 1.0 ms and an acquisition time of 40 ms. Signal averaging of approximately 1000–20 000 transients improved the signal-to-noise ratio with a 2–4-s recycle time. Exponential line broadening equivalent to 150–200 Hz was applied before zero-filling and Fourier transformation. Maximum radio frequency field strengths were 1.6, 6.3, and 12.9 mT for protons, carbon, and nitrogen, respectively. ^{13}C chemical shifts are relative to TMS referenced to external adamantane,[43] with an estimated error of ±0.2 ppm for narrow peaks. For the broader peaks, chemical shift errors are correspondingly larger. ^{15}N chemical shifts are relative to solid $^{15}NH_4Cl$.

Solutions of 40% glyoxal in water, 40% pyruvic aldehyde solution in water, 2,3-butanedione, and hydrazine hydrate were purchased from Aldrich and used as received. Solvents were of reagent grade and, unless otherwise noted, were used as received. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. All elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

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Glyoxal dihydrazone (GDH),[44,45] pyruvic aldehyde dihydrazone (PADH),[44,46] 2,3-butanedione dihydrazone (BDDH),[35] and $(-C_4H_6N_2-)_x$ [$(-N{=}C(CH_3)-C(CH_3){=}N-)_x$, 2M][35] were prepared according to literature procedures.

$(C_2H_2N_2)_x$ $(-N{=}CH-CH{=}N-)_x$ (2H). Two drops of glacial acetic acid was added to a stirring solution of 0.264 g (3.07 mmol) of GDH in approximately 25 mL of 95% ethanol in a 100-mL round-bottom flask. The stirring solution had a yellowish tint to it. A solution of 0.45 mL (3.9 mmol) of 40% glyoxal in approximately 10 mL of 95% ethanol was added dropwise over a 30-min period. A precipitate formed about 10 min after the final addition of the ethanolic glyoxal solution. The solution was stirred an additional 12 h, cooled on ice, filtered, and washed with hexanes. The precipitate was dried under vacuum overnight. Yield: 0.358 g (6.62 mmol), 108%. Upon heating, the polymer began to darken at 130 °C and turned black (decomposed) at 208 °C. Anal. Calcd for $C_2H_2N_2$: C, 44.44; H, 3.73; N, 51.83. Found: C, 37.46; H, 4.81; N, 46.48.

The same procedure was used for each polymerization; the amounts of reagents and analytical data are listed below.

$(-C_5H_6N_4-)_x$ $(-N{=}CH-CH{=}N-N{=}CH-C(CH_3){=}N-)_x$ (2HHM). Amounts: 0.337 g of GDH (3.92 mmol); 0.67 mL (4.1 mmol) of 40% pyruvic aldehyde solution. Yield: 0.410 g (3.35 mmol), 85.5%. Upon heating, the polymer began to darken at 130 °C and turned black (decomposed) at 213 °C. Anal. Calcd for $C_5H_6N_4$: C, 49.17; H, 4.95; N, 45.88. Found: C, 42.19; H, 5.59; N, 44.84.

$(-C_5H_6N_4-)_x$ $(-N{=}CH-C(CH_3){=}N-N{=}CH-CH{=}N-)_x$ (HM2H). Amounts: 0.53 g of PADH (5.3 mmol); 0.60 mL (5.3 mmol) of 40% glyoxal solution. Yield: 0.71 g (5.8 mmol), 109%. Upon heating, the polymer began to darken at 130 °C and turned black (decomposed) at 218 °C. Anal. Calcd for $C_5H_6N_4$: C, 49.17; H, 4.95; N, 45.88. Found: C, 44.52; H, 5.69; N, 42.88.

$(-C_6H_8N_4-)_x$ $(-N{=}CH-CH{=}N-N{=}C(CH_3)-C(CH_3){=}N-)_x$ (2H2M). Amounts: 0.464 g of GDH (5.39 mmol); 0.47 mL (5.6 mmol) of 2,3-butanedione. Yield: 0.387 g (2.85 mmol), 52.9%. Upon heating, the polymer began to darken at 123 °C and turned black (decomposed) at 140 °C. Anal. Calcd for $C_6H_8N_4$: C, 52.93; H, 5.92; N, 41.15. Found: C, 42.42; H, 5.69; N, 46.26.

$(-C_6H_8N_4-)_x$ $(-N{=}C(CH_3)-C(CH_3){=}N-N{=}CH-CH{=}N-)_x$ (2M2H). Amounts: 0.468 g of BDDH (4.10 mmol); 2.5 mL (4.1 mmol) of 9% glyoxal solution. Yield: 0.49 g (3.6 mmol), 88%. Upon heating, the polymer began to darken at 152 °C and turned black (decomposed) at 228 °C. Anal. Calcd for $C_6H_8N_4$: C, 52.93; H, 5.92; N, 41.15. Found: C, 51.46; H, 6.15; N, 37.52.

$(-C_3H_4N_2-)_x$ $(-N{=}CH-C(CH_3){=}N-)_x$ (HM). Amounts: 0.37 g of PADH (3.7 mmol); 0.61 mL (3.80 mmol) of 40% pyruvic aldehyde solution. Yield: 0.12 g (1.8 mmol), 48%. Upon heating, the polymer began to darken at 137 °C and turned black (decomposed) at 201 °C. Anal. Calcd for $C_3H_4N_2$: C, 52.93; H, 5.92; N, 41.15. Found: C, 49.76; H, 6.09; N, 37.52.

$(-C_7H_{10}N_4-)_x$ $(-N{=}CH-C(CH_3){=}N-N{=}C-(CH_3)-C(CH_3){=}N-)_x$ (HM2M). Amounts: 0.44 g of PADH (4.4 mmol); 0.40 mL (4.6 mmol) of 2,3-butanedione. Yield: 0.50 g (3.3 mmol), 75%. Upon heating, the polymer began to darken at 124 °C and turned black (decomposed) at 209 °C. Anal. Calcd for $C_7H_{10}N_4$: C, 55.98; H, 6.71; N, 37.31. Found: C, 54.14; H, 7.13; N, 38.02.

$(-C_7H_{10}N_4-)_x$ $(-N{=}C(CH_3)-C(CH_3){=}N-N{=}CH-C-(CH_3){=}N-)_x$ (2MHM). Amounts: 0.501 g of BDDH (4.39 mmol); 0.71 g (4.37 mmol) of 40% pyruvic aldehyde solution. Yield: 0.561 g (3.74 mmol), 85.6%. Upon heating, the polymer began to darken at 155 °C and turned black (decomposed) at 265 °C. Anal. Calcd for $C_7H_{10}N_4$: C, 55.98; H, 6.71; N, 37.31. Found: C, 54.13; H, 7.18; N, 35.97.

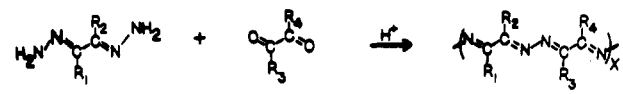
The calculated values for elemental analysis do not match the experimental values in any case. This occurs for two reasons: (1) The calculated values are for infinite chain polymers while all the polymers prepared have chain lengths of less than 20 repeat units. (2) Most of the polymers have an unknown percentage of oxygen-bearing defects.

Table I
Explanation of the Nomenclature

polymer	ideal structure
2H	$(-N{=}CH-CH{=}N-)_x$
2HHM	$(-N{=}CH-CH{=}N-N{=}CH-C(CH_3){=}N-)_x$
HM2H	$(-N{=}CH-C(CH_3){=}N-N{=}CH-CH{=}N-)_x$
2H2M	$(-N{=}CH-CH{=}N-N{=}C(CH_3)-C(CH_3){=}N-)_x$
2M2H	$(-N{=}C(CH_3)-C(CH_3){=}N-N{=}CH-CH{=}N-)_x$
HM	$(-N{=}CH-C(CH_3){=}N-)_x$
HM2M	$(-N{=}CH-C(CH_3){=}N-N{=}C(CH_3)-C(CH_3){=}N-)_x$
2MHM	$(-N{=}C(CH_3)-C(CH_3){=}N-N{=}CH-C(CH_3){=}N-)_x$
2M	$(-N{=}C(CH_3)-C(CH_3){=}N-)_x$

Results

A condensation reaction between an α,β-dihydrazone and an α,β-dicarbonyl



in an acidic media results in the formation of a polyazine. Glyoxal, CHOCHO, pyruvic aldehyde, CH_3COCHO, 2,3-butanedione, $CH_3COCOCH_3$, and their respective dihydrazones were utilized to vary the number of methyl groups along the polymer backbone.

Table I lists all of the polymers with their ideal structures. The nomenclature for the abbreviations in Table I is H = hydrogen and M = methyl. Further, the first two characters in the sequence refer to the dihydrazone and the last two characters to the α,β-dicarbonyl that was used in the polymerization. For example, 2M2H breaks down into two parts, where 2M denotes BDDH (2,3-butanedione dihydrazone) and 2H represents glyoxal. If there are only two characters listed, the dihydrazone of the α,β-dicarbonyl and the identical α,β-dicarbonyl were used in the polymerization. The nomenclature tells what starting materials were used, the length of the repeat unit, and the nature of the ideal polymerization product.

Theoretically, three pairs of identical polymers were synthesized: 2HHM and HM2H, HM2M and 2MHM, and 2H2M and 2M2H. The last pair should have an isomer, HM. The difference will be in the placement of the methyl groups: the methyl groups are paired in 2H2M and 2M2H, $=C(CH_3)-C(CH_3)=$, whereas HM alternates a hydrogen and a methyl, $=CH-C(CH_3)=$. ^{13}C and ^{15}N solid-state NMR spectra show that all three pairs of potentially equivalent polymers are not identical. One pair, 2H2M and 2M2H, gives distinctly different products; the other two cases give comparable but distinguishable products.

Two examples of defect-free PAZs are the permethyl derivative[35,36,47,48] (2M) and the propyl–methyl polyazine.[48,49] Polyazines prepared from diketones and associated dihydrazones do not exhibit defects, whereas polyazines prepared from aldehydes and associated dihydrazones[37-40] exhibit defects. The defect structure incorporated into the 2H polymer is believed to be a 2,3,5,6-tetrahydroxypiperazine (THP).[37,39]

^{13}C Solid-State NMR. The solid-state NMR spectra of 2M[35] and 2H[39] were previously reported. The spectrum of 2M with a chain length of ~45 repeat units shows two primary resonances: one due to methyl groups on the chain at 12.6 ppm and the other due to a single imine at 155.2 ppm. In contrast to 2M, the unsubstituted polyazine exhibits two peaks due to imines, at 162 and 137 ppm. 2H also exhibits a peak at 75 ppm, due to a sp^3 C, suggestive of a saturated defect. With the presence of saturated sites in the polymer, the two types of imines are assigned

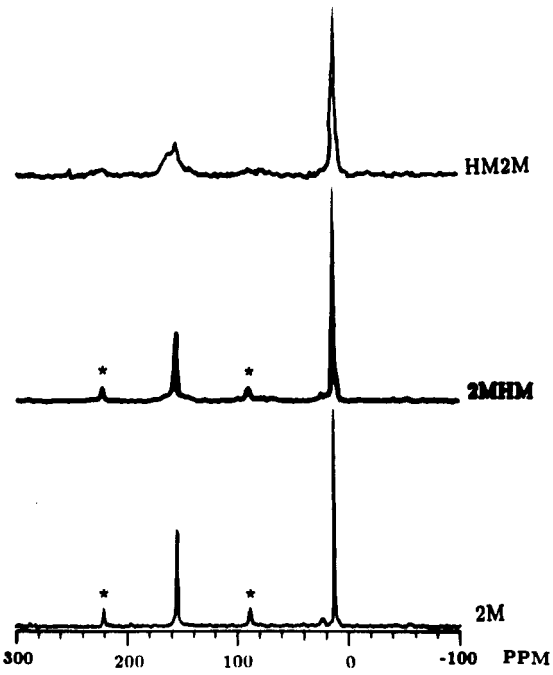


Figure 1. ^{13}C solid-state NMR spectra of HM2M, 2MHM, and 2M. Starred peaks are rotational sidebands.

as one in bulk (162 ppm) and one near the saturated sites (137 ppm). Previously we reported two possible types of defect structures,[39] 2,3,5,6-tetrahydroxypiperazine (THP) or α,α'-dihydroxy tertiary amine (DHTA). Both defect structures, if isolated as low molecular weight compounds, would be expected to be unstable. Thus, the polymer stabilizes these unusual chemical species, and model compounds for both defect structures have been difficult to produce.

The ^{13}C solid-state NMR spectra of HM2M, 2MHM, and 2M are compared in Figure 1. HM2M exhibits a broad resonance due to two different imines, $-C(CH_3)=N-$, at 156 ppm, and $-CH=N-$, at 166 ppm. The other peak in the spectrum at 12.8 ppm is due to the methyl carbons, with a shoulder at approximately 9.0 ppm. Two major absorptions are seen in the 2MHM spectrum, a narrow peak due to imines with its maximum at 156 ppm and a peak due to methyl carbons at 12.7 ppm with a shoulder at approximately 9.5 ppm. The lack of a second peak in the imine region for 2MHM is surprising, since it should be identical with HM2M. This is probably due to a relaxation effect. The 9.5 ppm shoulder is due to endgroups of oligomeric moieties contained within the sample.[36] 2MHM and HM2M both mimic the permethyl polymer, 2M. The weak peaks seen in these spectra at 24 and 198 ppm are due to carbonyl endgroups.

The ^{13}C solid-state spectra of 2H, 2HHM, and HM2H are shown in Figure 2. A large broad band near 75 ppm is present in each spectrum. This peak is associated with the defect structure incorporated in the polymer. 2HHM has its peaks at 161 and 138 ppm assigned to imines, the 73 ppm peak is assigned to the defect structure, the 19 ppm peak due to methyls is unassigned, and the 12.8 ppm peak is due to the methyls on the main chain. Similar peaks are seen in the HM2H spectrum. Two resonances due to imines are observed at 163 and 143 ppm, one resonance due to defects is seen at 73 ppm, and two peaks due to methyls are found at 12.7 and 18 ppm. With the exception of the additional methyl peak, 2HHM and HM2H imitate the unsubstituted polymer, 2H. The other high-field–low-intensity peaks are due to solvent inclusion and endgroups.[39]

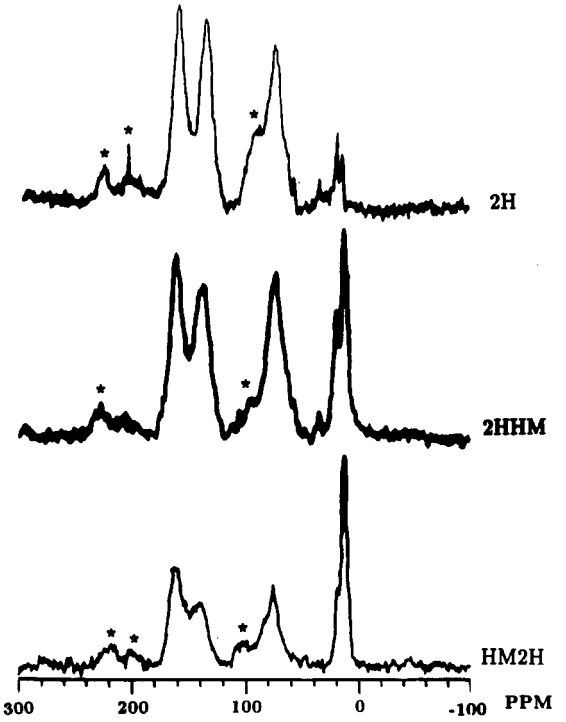


Figure 2. ^{13}C solid-state NMR spectra of 2H, 2HHM, and HM2H. Starred peaks are rotational sidebands.

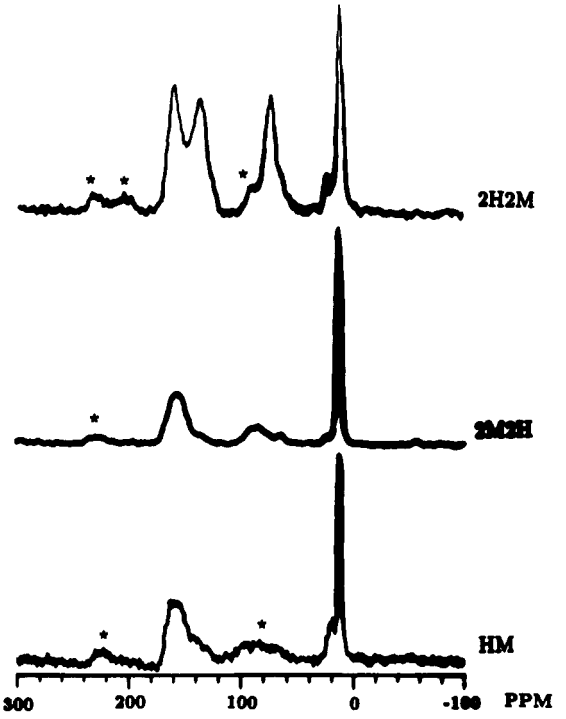


Figure 3. ^{13}C solid-state NMR spectra of 2H2M, 2M2H, and HM. Starred peaks are rotational sidebands.

Figure 3 shows the ^{13}C solid-state spectra of 2H2M, 2M2H, and HM. 2H2M has five major features: two resonances due to imines at 161 and 137 ppm, a peak due to defects at 74 ppm, a line due to a methyl carbonyl endgroup at 24.4 ppm, and a peak due to chain methyls at 12.8 ppm. 2H2M looks like 2H. In contrast, 2M2H exhibits four major peaks: a reasonance at 158 ppm due to imines, a low-intensity absorption at 75 ppm due to defects, a peak due to a methyl carbonyl endgroup at 24 ppm, and a feature due to a chain methyl at 13.1 ppm. The spectrum looks like that of 2M with a much smaller amount of defect. As expected, HM is different from its isomers. HM exhibits four major features: a resonance due to an imine

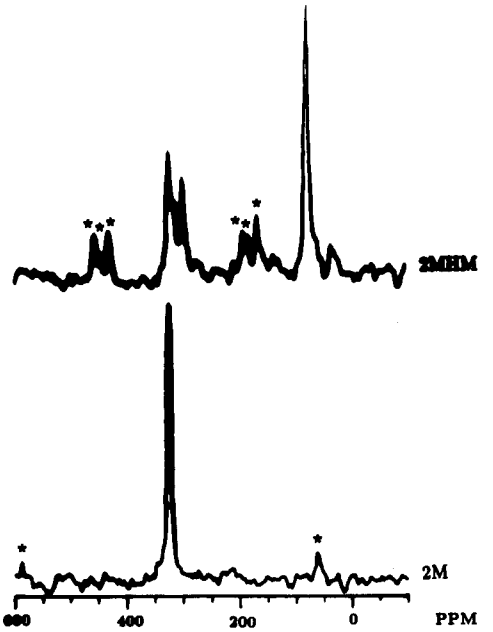


Figure 4. ^{15}N solid-state NMR spectra of 2MHM and 2M. Starred peaks are rotational sidebands.

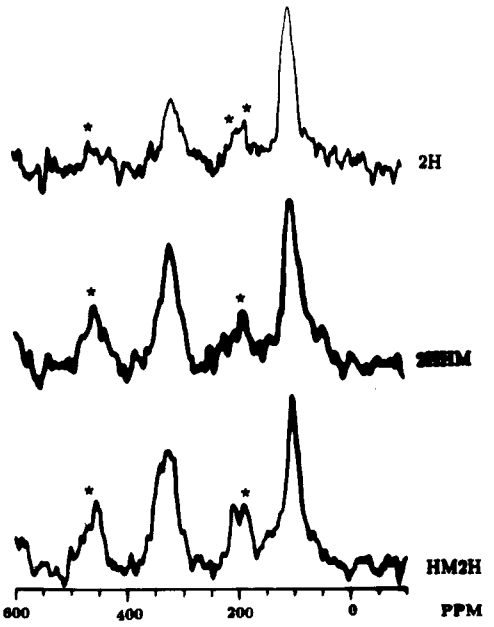


Figure 5. ^{15}N solid-state NMR spectra of 2H, 2HHM, and HM2H. Starred peaks are rotational sidebands.

at 164 ppm, a broad and rather weak absorption due to the defect at 84 ppm, a feature due to methyl groups associated with the defect at 19 ppm, and a peak due to methyl groups on the chain at 12.6 ppm.

^{15}N Solid-State NMR. The natural abundance ^{15}N spectra of 2MHM and 2M are shown in Figure 4. 2M exhibits a single resonance at 324.8 ppm, due to an imine, in agreement with the ^{13}C which also displayed only one type of imine. In 2MHM, the appearance of three peaks due to imine nitrogens at 300, 315, and 325 ppm suggests that this sample is probably an oligomeric mixture. There is also a very narrow peak at 75 ppm, indicative of a primary amine, which must be a hydrazone endgroup. Since a significant amount of endgroup was detected, this is further evidence that the material is of low molecular weight.

The natural abundance ^{15}N spectra of 2H, 2HHM, and HM2H are shown in Figure 5, and all are similar. Each of these polyazines exhibits one broad peak near 320 ppm

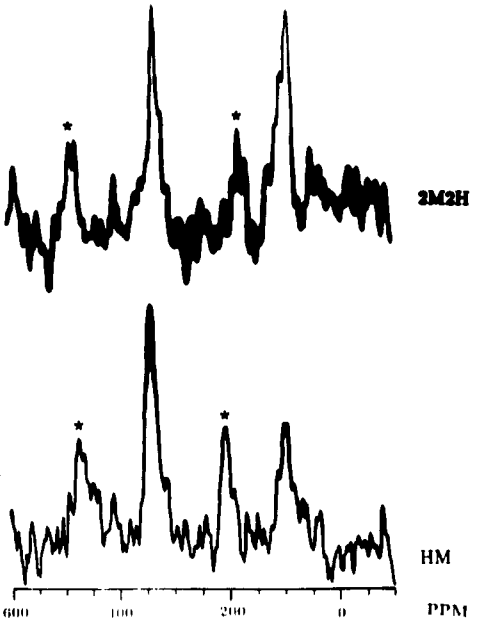


Figure 6. ^{15}N solid-state NMR spectra of 2M2H and HM. Starred peaks are rotational sidebands.

and one broad peak near 100 ppm. Peaks near 320 ppm (2H, 320; 2HHM, 322; HM2H, 320) are due to imine nitrogens; resonances near 100 ppm (2H, 103; 2HHM, 102; HM2H, 98) are due to tertiary sp^3 hybridized nitrogens, associated with the defect structure in the polymer.

The natural abundance ^{15}N spectra of 2M2H and HM are shown in Figure 6. The peaks at 328 ppm with a shoulder at 321 ppm in 2M2H are due to imines, indicating that both types of nitrogens are detected, $-C(CH_3)=N-$ (328) and $-CH=N-$ (321). A large amine resonance is seen with a peak maximum at 86 ppm and a significant asymmetry to the low-field side of the peak. This is assigned to a mixture of tertiary nitrogens. As expected from the ^{13}C spectrum, the ^{15}N spectrum of HM was different. Two imine features are present, one at 338 ppm with a shoulder at 312 ppm. The defect peak of HM, at 95 ppm, indicative of a tertiary amine, is slightly more shielded than 2H, by under 10 ppm.

Discussion

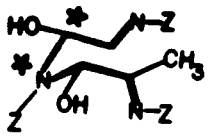
Permethyl and other higher alkyl polyazines are defect-free, whereas defects are present within unsubstituted polyazine. With unanticipated peaks in the ^{13}C and ^{15}N sp^3 regions of the spectra an inquiry was conducted to determine why defects formed. The mixed methyl polyazine series can be partitioned into two classes: defect-containing and defect-free. The NMR spectra suggest arranging this polymer series by their respective dihydrazones. All of the polymers that utilize glyoxal dihydrazone (GDH) exhibit similar NMR spectra; the same trend is seen in the 2,3-butanedione dihydrazone (BDDH) series. The use of GDH fosters defect formation, whereas the use of BDDH does not. However, when pyruvic aldehyde dihydrazone (PADH) is utilized, the ensuing chemistry is different. Here, the α,β-dicarbonyl unit seems to determine the final polymerization product. HM2H is much like the GDH series, HM2M is much like the BDDH series, and HM is unique.

Of the polymers that contain defects, two different hydroxy-bearing defects are proposed: 2,3,5,6-tetrahydroxypiperazine (THP) and α,α'-dihydroxy tertiary amine (DHTA). The major difference between THP and DHTA is that THP is a cyclic defect, whereas DHTA is acyclic.

THP has the conjugation broken by four sp^3 atoms, whereas DHTA has two sp^3 atoms. Both defect structures contain a tertiary amine, but in different environments. The two defects, THP and DHTA, should have similar properties but different and distinguishable NMR spectra.

The assignments of both ^{13}C and ^{15}N chemical shifts of the defect structures which need to be addressed are shown as the starred atoms in the structures. The saturated

THP

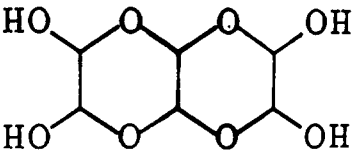


DHTA

carbon in THP is detected at ~75 ppm, whereas the DHTA carbon is at ~85 ppm. Each carbon has an α-tertiary nitrogen and a β-carbon bearing a hydroxyl group. The difference arises from what chemical species is α' to the starred carbon. THP has a sp^3 carbon with a hydroxyl, while DHTA has an imine. Knowing that an imine shields more than a hydroxyl ($H_3C^*CH_2OH$, C* = 19 ppm, vs $H_3C^*C{=}N$, C* = 12 ppm), an explanation as to why the ring carbons in the THP are more shielded than the saturated carbon bearing a OH in DHTA is necessary. A likely explanation lies in the nature of the defect: cyclic vs acyclic. When a substituted straight-chain alkane, i.e., 3-hexanol, is compared to cyclohexanol, the ^{13}C chemical shift difference is ~10 ppm with the carbon bearing the hydroxyl group in the cyclohexane being more shielded, the γ-effect associated with six-membered rings, attributed to steric hinderance.[50,51] Thus, THP experiences the γ-effect, causing shielding, whereas DHTA does not feel this effect.

Conjugated unsubstituted imines have ^{15}N resonances around 320 ppm, with the peak moving to 325 ppm when a methyl group is on the carbon. The imine peak in 2H is assigned at 320 vs 338 and 312 ppm peaks for the imines in HM. However, for an imine to have a resonance at 338 ppm implies that a functional group which has great deshielding effects must be present and close in proximity. The structure of DHTA has a hydroxyl group β to the nitrogen. The presence of the hydroxyl group β to the imine nitrogen deshields the imine. The assignment of THP defects to 2H and other related polymers and DHTA defects to HM is consistent with the solid-state NMR data.

The polymerization conditions were such that the α,β-dihydrazone was placed in acidic ethanol. The presence of the acid catalyst caused some of the dihydrazone to undergo hydrolysis, but the products of the α,β-dihydrazone hydrolysis are dependent upon which α,β-dicarbonyl was employed. In the case of BDDH, the dione product is protonated 2,3-butanedione monohydrazone,[52] a product that does not promote defect formation. If BDDH is placed in a slightly acidic media, the monohydrazone is formed and reacts with itself or free BDDH, forming oligomeric products. In the case of GDH, the hydrolysis product is the trimeric dihydrate form of glyoxal:[52]



Upon reaction with aqueous acid, PADH hydrolyzes to give products that lead to both imine and defect formation. Preliminary results[52] suggest that the aldehyde carbon is hydrolyzed to the acetal, but it is unclear if the ketone carbon is hydrolyzed. Like GDH, the presence of an aldehyde leads to defect formation under these synthetic conditions.

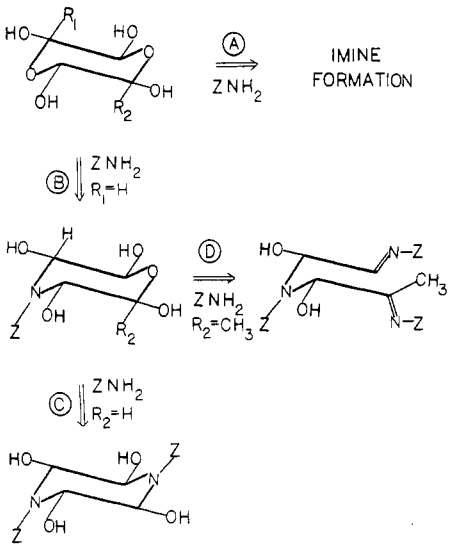
The hydrolysis of the dihydrazones can complicate the polymerizations. The polymers prepared from BDDH exhibit no defects, independent of the dicarbonyl used; the hydrolysis products of BDDH do not directly affect the polymerization. However, this is not the case with GDH or PADH. Hydrolysis of GDH yields glyoxal in the form of a cyclic adduct (as well as hydrazine) which allows defects to be incorporated into the polymer. The polyazines prepared with PADH display different defects, which are dependent upon starting materials. The type of defect formed is primarily influenced by the dihydrazone used and sometimes the α,β-dicarbonyl unit. Moreover, it is the products of the hydrolysis, specifically the α,β-dicarbonyl unit, that directly influence the polymerization.

An examination of the addition–elimination mechanism associated with the condensation reaction reveals how the defect can be incorporated into the polymer foundation. The nature of the R group on the α,β-dicarbonyl affects the rate of dehydration. If the R group is an electron-donating group, as in the case of a methyl group, dehydration is fast and always occurs before any other reaction can. But if R is a hydrogen, two possible pathways exist: (1) dehydration to form an imine or (2) defect formation.

Scheme I shows how the two defect species are formed. A primary amine, ZNH_2, undergoes reaction at a carbon in the aldehyde oxidation state. In pathway A, an imine forms and another repeat unit is incorporated into the polymer chain. However, if imine formation does not occur, a tetrahydroxymorpholine[53] ring can form. The reaction can be viewed as a replacement of the oxygen with a nitrogen (pathway B). In the case of glyoxal, R_2 = H, if another mole of ZNH_2 reacts in the same fashion and substitutes for the oxygen, THP has been made and interjected into the polymer (pathway C). In the case of 2H, the polymer is still linear but now a "bubble" has been incorporated into its structure. If $R_2 = CH_3$, the morpholine ring breaks open upon the attack of ZNH_2 and an imine forms as in the case of pyruvic aldehyde (pathway D). Thus, DHTA is incorporated into the polymer system, introducing a cross-link into the polymer.

Due to the presence of the methyl group, monosubstituted and disubstituted THPs cannot form. The electron-donating effect of the methyl group causes imine formation before any other reaction can proceed. The morpholine ring system will always open, and DHTA defects are interjected into the polymer. The more methyl groups present (and consequently the more ketones present and fewer acetal rings), the lower the chance of defects forming. The lower the number of alkyl groups present, the more likely it is that defects will form. For glyoxal, there is a low probability that DHTA will form because the molecule

Scheme I



is competing between imine formation (hence cross-linking) and ring formation, which is a favorable process. Ring formation is favored over cross-linking in the 2H polymer.

Table II lists the ^{13}C and ^{15}N data for the mixed methyl polymer series. The polymer series is divided into three groups: (A) 2M, 2MHM, 2M2H, and HM2M; (B) HM; and (C) 2H, 2HHM, 2H2M, and HM2H. Group A represents the mostly defect-free polymers; groups B and C represent the defect-containing polymers. Group C is representative of THP defects, while group B is DHTA defects.

The members of group A consist of the polymers prepared with BDDH and HM2M. The only member of this set that exhibits a minimal amount of defect is 2M2H. The defect comes about from the use of the aqueous glyoxal (as required by the synthesis) and not from the hydrolysis of the BDDH starting material. All other members of group A do not have defects for the following reasons: (1) the hydrolysis products of the α,β-dicarbonyl do not lead to defect structures and (2) the presence of alkylcarbonyls forces imine formation and does not allow a tertiary amine to enter into the polymer backbone. Despite the fact the 2M2H contains a limited amount of defects, the other spectral characteristics show that 2M2H belongs in this category. Otherwise, each member of this group exhibits either one or two imines in the ^{13}C spectra; one or two imines are seen in the ^{15}N spectra if the material has sufficient chain length.

Group C contains all of the polymers synthesized from GDH plus HM2H. 2H, 2HHM, 2H2M, and HM2H all exhibit defect peaks around 74 ppm in the ^{13}C spectra; the ^{15}N spectra also exhibit a peak around 100 ppm, indicative of a tertiary amine. The ^{15}N spectrum only showed one peak in the imine region, but this was sufficiently broad to be the result of two or more imine sites. Our assignment of the THP defect structure is consistent with the data.

In principle, 2HHM and HM2H may have two different defects, THP and DHTA, whereas 2H2M and 2H can only have THP defects. A comparison of the ^{13}C spectra of 2HHM and HM2H with the spectrum of 2H shows that the spectra are very similar and only differ in the methyl region, which is expected. If the same two spectra are compared with the spectrum of HM, vast differences are noticeable. Therefore, the principal defect contained in 2HHM and HM2H is THP.

Group B, consisting of only one polymer, HM, is the final group to be discussed. The spectral properties are

Table II
^{13}C and ^{15}N Solid-State NMR Data

		imine region		defect region	
group	polymer	^{13}C	^{15}N	^{13}C	^{15}N
A	2M	155.2	324.8		
	2MHM	156	325, 320, 300		
	2M2H	164, 158	328, 321 (sh)	75	86, 103 (sh)
	HM2M	166, 156			
B	HM	164	338, 312 (sh)	84	95
C	HM2H	163, 143	322	73	102
	2H2M	161, 137		74	
	2HHM	161, 138	320	73	98
	2H	162, 137	320	75	103

significantly different from those of any of the other polyazines. HM is defect-containing but the defect is not THP. The ^{13}C spectrum is different from that of the other polymers since the peak in the defect region has shifted to 84 ppm. The ^{15}N sp^3 peak is also shifted, to 95 ppm. The imine region of both the ^{13}C and ^{15}N spectra is also distinctly different. The peak due to the imine nitrogen has been deshielded by more than 10 ppm, in comparison to 2H and 2M. Defect formation for HM must follow pathway D, requiring DHTA defects as indicated by the NMR. Further evidence for DHTA is chemical. We have found one powder sample that annealed into a hard glassy substance, typical of a cross-link. Another indication that HM possesses a different defect structure is that HM complexes to Co^{2+}, whereas 2H and 2M will not. The metal-containing product is water soluble. The properties of the glassy polyazine and the metalated polyazine are currently being studied and will be reported elsewhere.

Conclusion

The mixed methyl polyazine series gives two types of polyazines: defect-free and defect-containing. Of the defect-containing polymers, two different defects exist, 2,3,5,6-tetrahydroxypiperazine and α,α'-dihydroxy tertiary amine. The formation of defects comes about due to an intermediate which does not promote imine formation, but rather a saturated site. For THP defects to form, the following sequence must be followed: (1) attack of a primary amine on the aldehyde carbon with subsequent exchange with an oxygen, forming a morpholine ring; (2) attack of another primary amine on the morpholine ring and again exchange with an oxygen, forming a substituted 1,4-diazocyclohexane. This sequence can only happen with glyoxal as the cyclic dialdehyde; if any other aldehyde is employed, imine formation will occur at the second step and the defect site will be DHTA. Glyoxal dihydrazone promotes defect formation and gives THP defects, pyruvic aldehyde dihydrazone gives DHTA defects, and 2,3-butanedione dihydrazone yields essentially defect-free polymerization products.

The more "ketone-like" the environment, the less apt it is that the resulting polymer will possess defects. Likewise, the more aldehydic the surroundings, the greater the chance for defect formation. The choice of the aldehyde will determine the nature of the defect. To rid the system of defects that use aldehydic starting materials, other synthetic routes need to be employed. Such possible avenues are currently under investigation.

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(53) The ring system is a morpholine, a saturated six-membered ring with an oxygen at the 1-position and a nitrogen at the 4-position. However, due to the hydroxy substituents, each of the ring carbons is in the aldehyde oxidation state. The morpholine name just describes the ring system.

Registry No. 2H (copolymer), 129571-97-7; 2H (SRU), 85772-00-5; 2HHM (copolymer), 133271-89-3; HM2H (copolymer), 133271-90-6; 2H2M (copolymer), 133271-91-7; 2H2M (SRU), 133271-96-2; 2M2H (copolymer), 133271-92-8; HM (copolymer), 133271-93-9; HM2M (copolymer), 133271-94-0; 2MHM (copolymer), 133271-95-1; 2M (copolymer), 122408-43-9; 2M (SRU), 54047-69-7.