Synthesis and Characterization of Poly(piperazinenaminonitriles)

J. A. Moore* and Sarjit Kaur†

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

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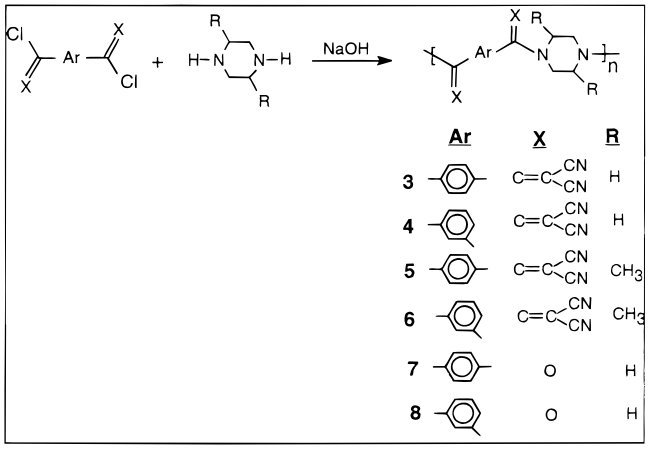
ABSTRACT: Poly(piperazinenaminonitriles), analogs of poly(piperazinamides), were synthesized by interfacial polycondensation of piperazine or 2,5-dimethylpiperazine (cis or trans) with bis-electrophilic monomers (1,3- or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene). Because of the absence of hydrogen bonding, poly(piperazinenaminonitriles) showed limited solubility in dipolar aprotic solvents and, compared to poly(piperazinamides), gave lower molecular weight materials of lower thermal stability. The barrier to internal rotation of enaminonitrile groups, measured using dynamic NMR spectroscopy of model compounds, was comparable to the barrier to internal rotation measured for amide groups.

Introduction

In contrast to the limited solubility of aramids,[1] improved solubility and high molecular weight polymers have been reported for poly(enaminonitriles) (PEANs), where the dicyanovinylidene group ($C{=}C(CN)_2$) is substituted for the carbonyl group of the amide linkage. PEANs are soluble in many organic solvents such as dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), pyridine, glymes, and tetrahydrofuran (THF).[2] The solubility of PEAN has been speculated to be a consequence of weaker interchain hydrogen-bonding interactions as compared to polyamides, which are highly self-associated through strong intermolecular hydrogen bonds. Because of the weaker intermolecular hydrogen bonding, PEANs have a decreased tendency toward self-association and are solubilized through hydrogen bonding with proton-accepting solvents.[2a] Among the factors that may contribute to weaker hydrogen bonds in PEAN is the presence of the rather bulky and polar enaminonitrile groups in the backbone, which may sterically prevent strong hydrogen bonding and/or reduce crystallinity. Other factors (electronic) that may contribute to weaker intermolecular interactions in enaminonitriles are the lower electronegativity of nitrogen atoms relative to oxygen atoms and the reduced ability of the nitrogen lone pair electrons of the cyano groups (sp hybridization) to donate electrons for hydrogen bonding as compared to the oxygen atom of the carbonyl group (sp^2).

As a confirmation of the role of hydrogen bonding in the solubility of PEANs, the piperazine ring was utilized to prepare poly(piperazinenaminonitriles), PPEANs, to examine the solubility properties of the enaminonitrile unit in the absence of hydrogen bonding (Scheme 1). Incorporation of piperazine in the polymer backbone confers chain stiffness in the absence of hydrogen bonding, and as shown for poly(piperazinamides),[3] these polymers retain high thermal stability and excellent mechanical properties. However, poly(piperazinamides) exhibited no improvement in solubility upon the removal of intermolecular hydrogen-bonded interactions; they remain relatively insoluble in conventional organic solvents. The lack of solubility of poly(piperazinamides)

Scheme 1



has been attributed to the presence of a relatively rigid backbone and intermolecular dipole−dipole interactions in the polymers, similar to those of aramids.[3] Although hydrogen-bonded interactions are removed with incorporation of the piperazine ring, the rigidity of the polymer backbone in aromatic poly(piperazinamides) possibly remains relatively unchanged in comparison to aramids and, therefore, solubility is not improved because there is no accompanying increase in the flexibility of the polymer backbone. The piperazine ring is also expected to be in its chair conformation and, consequently, is not expected to interfere sterically with the resonance delocalization of the amide group (−N−C═O). It is possible, then, that poly(piperazinamides) can remain strongly associated through dipole−dipole interactions despite the absence of intermolecular hydrogen bonds. Both lines of reasoning imply that the rigidity and dipole−dipole interactions of aramids may not be disturbed with the incorporation of the piperazine ring. Consequently, incorporation of the piperazine ring in the backbone of PEANs is not expected to decrease the rigidity of the polymer backbone and change the dipole−dipole interactions to the extent of influencing solubility properties significantly. Any difference in solubility between PPEAN and PEAN should, therefore, be related to differences in hydrogen-bonded interactions.

Resonance delocalization in enaminonitrile groups, ($NH{-}C{=}C(CN)_2$, results in partial double bond character of the C−N bond, analogous to amide groups, and a barrier to internal rotation about the C−N bond is

† Current address: Department of Chemistry, Vassar College, Poughkeepsie, NY 12601.

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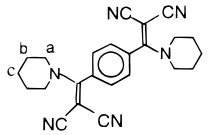
observed in PEAN, as measured by dynamic NMR spectroscopy. Of the two factors that influence the height of the barrier to internal rotation, namely steric and inductive effects, the steric factor is considered a minor contributor when a $C(CN)_2$ group replaces oxygen in the amide group.[4] Breneman[5] has also observed that the steric differences between amide and enaminonitriles are most likely minimal, based on molecular modeling studies of planar conformations of model compounds containing amide and enaminonitrile groups. Consequently, a comparison of the barriers to internal rotation between amide and enaminonitrile groups may provide a comparison of their respective inductive effects. To this end, the measurements of barriers to rotation using dynamic NMR spectroscopy were carried out for model compounds **1** and **2** to ascertain if there was a measurable difference in the inductive behavior between the carbonyl and dicyanovinylidene groups.



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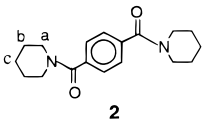

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Experimental Section

Materials. NMP was stirred over anhydrous barium oxide for 48 h and distilled under reduced pressure. Methylene chloride and dichloroethane were stirred over calcium hydride and fractionally distilled. DMAP, isophthaloyl chloride and terephthaloyl chloride, piperidine, NaOH, and $Ca(OH)_2$ were used as received from Aldrich. 1,3- and 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene were prepared as described in the literature.[2a] Piperazine and 2,5-dimethylpiperazine (cis and trans) were sublimed under reduced pressure. The presence of charred residue from thermally stable structural moieties in the polymers generally causes lower carbon values. Consequently, elemental analyses of polymers were not performed.

Techniques. All melting points (mp) and glass transition temperatures (T_g) were determined under nitrogen using differential scanning calorimetry (DSC) at a heating rate of 10 °C/min) on a Perkin-Elmer System 7 instrument. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Model 1800 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on either Varian XL-200 (200 MHz ^{1}H; 50.3 MHz ^{13}C) or Varian 500 (500 MHz ^{1}H; 125 MHz ^{13}C) spectrometers. Solutions for dynamic NMR studies were made from 20 mg in 0.8 mL of deuterated DMSO. ^{1}H NMR data were collected after equilibration for 1 min at the stated temperatures: model compound **1** (22.0, 29.4, 35.0, 40.0, 45.0, 47.5, 50.0, 52.5, 55.0, 57.5, 62.4, 65.0, 67.5, and 70.0 °C); model compound **2** (22.0, 29.3, 34.5, 37.3, 49.8, 42.3, 45.0, 47.3, 59.9, 50.9, 51.9, 53.9, and 55.9 °C). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Viscosity measurements were made at 25.00 °C with a Cannon-Ubblelohde viscometer (75 E 198).

Synthesis of 1,4-Bis(2,2-dicyano-1-vinylpiperidyl)benzene (1). To a solution of piperidine (0.227 g, 2.7 mmol) and DMAP (0.318 g, 2.83 mmol) in 50 mL of dichloroethane was added 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (0.4045, 1.34 mmol) slowly as a solid under nitrogen. The reaction mixture turned red and was stirred overnight at room temperature, followed by heating at 50−55 °C for 24 h. The solvent was removed on a rotary evaporator, and addition of water gave a viscous liquid that solidified slowly. The yellow solid was redissolved in DMF and reprecipitated from water (0.23 g, 43.4%). The crude product was recrystallized from acetone and dried in vacuo (2−3 Torr) at 100 °C over P_2O_5 for 48 h, mp 301 °C (DSC). FT-IR (KBr): 3126, [2956, 2950, 2930, 2862] (aliphatic C−H stretch), [2206, 2192] (CN), 1562, 1468, 1450, 1426, 1400, 1366, 1290, 1260, 876, 838 cm^{-1}. ^{1}H NMR (DMSO−d_6): 1.40−1.90 (m, 12H, protons b and c of the piperidine ring), [3.08, 3.92] (broad singlets, 8H, protons a of the piperidine ring; two resonance peaks are observed because of the presence of a rotational barrier), 7.70 ppm (s, 4H, aromatic H). ^{13}C NMR (DMSO−d_6): 168.3 (C=C(CN)$_2$), 136.0 (aromatic tertiary carbon atoms), 129.3 (protonated aromatic carbon atoms), [116.6, 117.4] (CN), 52.6 (br, C=C(CN)$_2$), [22.8, 25.8, 30.5] ppm (piperidine ring carbon atoms). Anal. Calcd for $C_{24}H_{24}N_6$: C, 72.73; H, 6.06; N, 21.2. Found: C, 72.70; 6.32; N, 20.98.

Synthesis of 1,1′-(1,4-Phenylenedicarbonyl)dipiperidine (2). To a solution of piperidine (0.5678 g, 6.8 mmol) and DMAP (0.4088 g, 3.34 mmol) in 15 mL of NMP was added a solution of terephthaloyl chloride (0.6780, 3.34 mmol) in 10 mL of NMP under nitrogen. The reaction mixture was stirred overnight at room temperature, and a crude solid was obtained upon precipitation into water. The product was dried in vacuo (2−3 Torr) over P_2O_5 at 75 °C for 24 h (0.53 g, 58.4%). The crude product was recrystallized from DMSO, washed in acetone, and dried in vacuo at 80 °C for 24 h. Two endotherms at 180 and 207 °C were observed by DSC. Crystals of the product were observed on a hot-stage microscope under cross-polarized light. At the first endotherm, a bright birefringence was observed and was attributed to a crystal−crystal transformation; no fluidity was observed, and liquid crystalline behavior was ruled out. The second endotherm was a transition to an isotropic phase between 205 and 207 °C (lit.[6] 203−205 °C). FT-IR (KBr): [2992, 2957, 2935, 2921, 2856] (aliphatic and aromatic C−H stretch), 1616 (C=O), 1508, 1451, 1440, 1286, 1273, 1124, 1115, 1023, 1002, 886, 854, 844, 730 cm^{-1}. ^{1}H NMR (DMSO-d_6): 4.0−1.70 (m, 12H, protons b and c of the piperidine ring), [3.25, 3.56] (broad singlets, 8H, protons a of the piperidine ring; the protons are split because of the presence of a rotational barrier), 7.34 ppm (s, 4H, aromatic H). ^{13}C NMR (DMSO-d_6): 168.3 (C=O), 137.3 (substituted aromatic carbon atom), 125.8 (aromatic protonated carbon atoms), [48.1, 42.4] (carbons a of the piperidine ring), [25.3, 26.0] (carbons b of the piperidine ring), 24.1 ppm (carbon c of the piperidine ring).

Preparation of Polymers 3 and 4. In a typical interfacial polycondensation 10 mmol of piperazine was dissolved in 13 mL of aqueous NaOH (∼6.5 mmol) in a blender. The solution was stirred vigorously, and a solution of 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (equimolar to piperazine) in 13 mL of methylene chloride was added in a single portion. A white precipitate formed immediately, and the mixture was stirred at maximum speed for 1−4 min. The precipitate was collected by filtration, washed well with water, and dried in vacuo (2−3 Torr) for 24 h at 80 °C. The polymers were insoluble in dioxane, *m*-cresol, NMP, or THF and showed limited solubility in DMSO and DMF.

3: 86% yield; inherent viscosity = 0.17 dL/g (1.0 g/dL in concentrated sulfuric acid) at 25.00 °C; FT-IR (KBr) 2929 (aliphatic C−H), 2205 (CN), 1540 (br), 1440, 1365, 1285, 1268, 1010, 885 cm^{-1}; ^{1}H NMR (DMSO-d_6) 7.76 (br, s, central aromatic ring), 3.2−4.5 ppm (br, m, piperazine ring).

4: 83% yield; inherent viscosity = 0.14 dL/g (0.59 g/dL in concentrated sulfuric acid) at 25.00 °C; FT-IR (KBr) 2929 (aliphatic C−H), 2205 (CN), 1540 (br), 1440, 1365, 1285, 1268, 1010, 885 cm^{-1}; ^{1}H NMR (DMSO-d_6) 7.81 (br, s, central aromatic ring), 3.2−4.5 ppm (br, m, piperazine ring).

Preparation of Polymers 5 and 6. $Ca(OH)_2$ (12 mmol) was added to a solution of 2,5-dimethylpiperazine (2.1 mmol) in 10 mL of chloroform. 1,3-Bis(1-chloro-2,2-dicyanovinyl)-benzene or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (2.1 mmol) in 10 mL of chloroform was added slowly (N_2). The reaction mixture was stirred for 18 h at room temperature, and a yellow precipitate was obtained upon evaporation of chloroform. The yellow solid was washed in water, 2% HCl, water, and acetone and dried over P_2O_5 at 80 °C in vacuo (2−3 Torr) for 24 h. The polymers were insoluble in chloroform, THF, and acetone and showed limited solubility in DMF and DMSO.

5: 52% yield; inherent viscosity = 0.09 dL/g (1.000 g/dL in concentrated sulfuric acid) at 25.00 °C; FT-IR (KBr) 2984 (aliphatic C−H), 2213 (CN), 1539 (br), 1436, 1387, 1340, 1285, 1160, 1102, 875, 840 cm^{-1}; ^{1}H NMR (DMSO-d_6) 7.81 (br, s,

Table 1. Characterization Data for Polymers 3−8

polymer	% yield	inherent viscosity[a]	5% wt loss, nitrogen, °C	5% wt loss, air, °C	50% wt loss, nitrogen, °C
3	86	0.17 (i)	350	340	>700
4	86	0.23 (ii)	360	350	>700
5	52	<0.1 (i)	340	340	>700
6	62	0.14 (i)	335	340	>700
7	85	0.51(iii)	435	400	450
8	78	0.54 (iii)	400	400	415

[a] (i) 25.00 °C, 1.00 g/dL in concentrated sulfuric acid. (ii) 25.00 °C, 0.59 g/dL in concentrated sulfuric acid. (iii) intrinsic viscosities in concentrated sulfuric acid, 25.00 °C.

central aromatic ring), 3.2−5.0 (br, m, piperazine ring), 0.8−1.8 ppm (m, 6H, CH_3).

6: 62% yield; inherent viscosity = 0.13 dL/g (1.000 g/dL in concentrated sulfuric acid) at 25.00 °C; FT-IR (KBr) [2981, 2938] (aliphatic C−H), 2214 (CN), 1530 (br), 1439, 1386, 1340, 1268, 1165, 1101, 1062, 823, 708 cm^{-1}; ^1H NMR (DMSO-d_6) 7.81 (br, s, central aromatic ring), 3.2−5.1 (br, m, piperazine ring), 0.9−1.9 ppm (m, 6H, CH_3).

Preparation of Polymers 7 and 8. The polymers were synthesized by interfacial polycondensation,[3,7] as described for polymers **3** and **4**, with the following materials: piperazine (10 mmol), 100 mL of NaOH solution (22 mmol), isophthaloyl or terephthaloyl chloride (10 mmol).

7: 85% yield; intrinsic viscosity = 0.55 dL/g (concentrated sulfuric acid) at 25.00 °C; no T_g was detected up to 350 °C (DSC); FT-IR (KBr) [2919, 2860] (aliphatic C−H), 1635 (br, C═O), 1507, 1419, 1359, 1280, 1251, 1153, 999, 896, 841, 720 cm^{-1}.

8: 78% yield; intrinsic viscosity = 0.54 dL/g (concentrated sulfuric acid) at 25.00 °C; T_g = 237 °C (DSC, second run); FT-IR (KBr) [2920, 2860] (aliphatic C−H), 1653 (br, C═O), 1456, 1419, 1251, 1244, 1164, 730 cm^{-1}.

Results and Discussion

Poly(piperazinamides) and Poly(piperazinenaminonitriles). Poly(piperazinamides), **7** and **8**, were synthesized by interfacial polycondensation, as reported by Morgan.[7] The poly(piperazinenaminonitriles), PPEAN, were also prepared by interfacial polycondensation by reaction of 1,3- or 1,4-bis(1-chloro-2,2-dicyanovinyl)-benzene with piperazine or *cis*/*trans*-2,5-dimethylpiperazine. Optimization of the syntheses of PPEAN was attempted by variation of the molar concentrations used in interfacial polycondensation, but no significant improvement in inherent viscosities was observed. Scheme 1 outlines the polymers prepared.

The PPEANs (**3**−**6**) obtained were insoluble in chloroform, THF, acetone, DMF, dioxane, and pyridine but showed limited solubility in NMP, DMAC, and DMSO. These results are in contrast to PEANs, which are easily soluble in NMP, DMSO, and DMAC. PEANs contain NH sites, which permit both intermolecular hydrogen bonding and interactions with proton-accepting solvents.[2b] With the incorporation of piperazine in PPEAN, hydrogen bonding is no longer available and the reduced solubility of these polymers can be correlated to the absence of hydrogen-bonded interactions with polar aprotic solvents.

The characterization data for polymers **3**−**8** are reported in Table 1. Low molecular weight polymers were obtained in the synthesis of **3** and **4**, as evidenced by the low inherent viscosities. The corresponding polyamides, **7** and **8**, were obtained with reasonably good molecular weights even though the polymers showed negligible solubility in NMP, DMF, DMAC, or DMSO. The low molecular weights of polymers **3** and **4** are possibly the consequence of both low solubility and steric hindrance from the presence of the bulkier dicyanovinylidene groups as compared to the carbonyl group. To improve solubility, a substituted diamine, 2,5-dimethylpiperazine (cis, trans), was used but even lower molecular weight polymers were obtained (**5** and **6**). Both solution condensation and interfacial polycondensation were attempted. Although negligible improvement in solubility was observed for **5** and **6**, the substituted diamine is likely to increase the steric hindrance during polycondensation of piperazine with enaminonitriles. The results, therefore, suggest that steric hindrance is also a reason for the reduced molecular weights of PPEAN, along with the low solubility of the polymers.

Despite the low molecular weights of PPEANs, the thermal stability is good with 5% weight loss ranging between 335 and 360 °C, in both air and nitrogen (Table 1). However, the thermal stabilities of PPEAN are lower than those of the corresponding amide polymers, which range between 400 and 435 °C. This difference is larger than observed for PEAN and polyamides that contain NH sites. The lower thermal stabilities of PPEAN relative to PEAN may be due to the low molecular weight of PPEAN. A second reason is the observation that curing of the enaminonitrile group is absent in PPEAN because of the lack of NH groups that can add to the cyano functionality. The absence of curing is confirmed by the fact that there is no exothermic transition observed by DSC up to degradation temperatures of 350 °C. PEAN polymers containing NH−C═C$(CN)_2$ moieties generally show an exothermic curing process between 300 and 370 °C, which has been proposed to be linked to inter- and intrachain cyclization processes.[2] The thermal stability of polymers containing enaminonitrile groups is probably enhanced through intramolecular cyclization and intermolecular cross-linking processes.

There are some observable differences in the degradation patterns between PPEAN and poly(piperazinamides). In nitrogen, a precipitous weight loss of ∼60% was observed at 450 and 415 °C for **7** and **8**, respectively. By comparison, PPEANs retain 50% of their original weight up to 700 °C. These results are consistent with earlier comparisons between aromatic polyamides and PEANs where the presence of dicyanovinylidene groups increases the char yield observed at elevated temperatures in nitrogen.[2] The high char yield of PEANs was postulated to be the result of possible cross-linking/curing processes that reduce the amount of volatile products. Although no curing processes are detected for PPEANs, the presence of dicyanovinylidene groups leads to an increase in the char yield. It is observed that once degradation starts in aramids, subsequent weight loss is accelerated, as compared to PEANs and PPEANs. One possible explanation for this behavior is that the products from the degradation of aramids contain amino and carboxylic end groups that arise from scission of the amide bonds in the main chain. The presence of amino and carboxylic end groups have been reported to reduce thermal stabilities in aromatic model compounds by inducing acidolysis or aminolysis of the remaining amide bonds.[8] Of the two groups, the amide group is possibly more susceptible to hydrolysis than enaminonitrile groups because the oxygen atom (sp^2 hybridization) of the amide group is more basic and, thus, more easily protonated by acidic end groups (promoting acidolysis) than the less basic nitrogen atoms (sp hydridization) of the cyano groups in enaminonitriles. Consequently, amino and carboxylic acid end

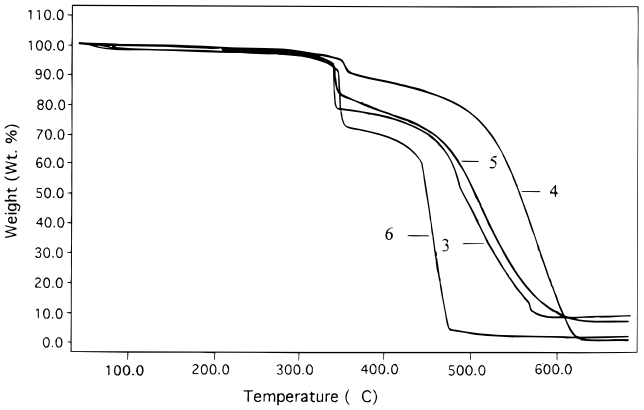

Figure 1. Thermogravimograms of polymers **3**−**6** in air.

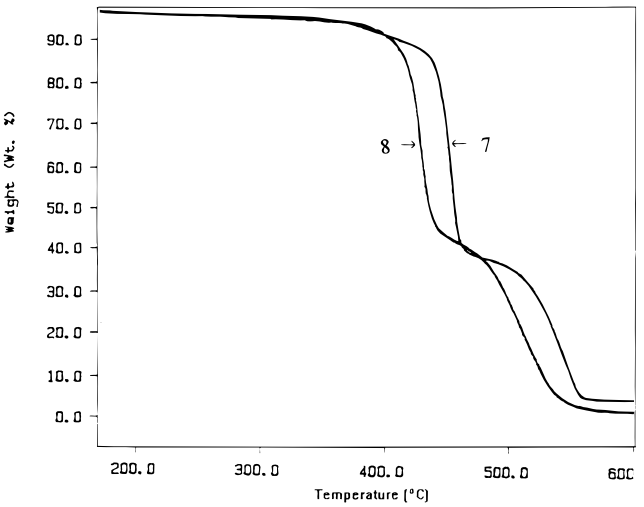

Figure 2. Thermogravimograms of polymers **7** and **8** in air.

groups formed during the initial stages of polyamide degradation promote, catalytically, further hydrolysis of amide bonds, leading to a greater weight loss in polyamides than enaminonitriles, while the latter are more resistant to acid-catalyzed hydrolysis.[9]

Both PPEANs and poly(piperazinamides) undergo a two-step degradation in air (Figures 1 and 2). The onset of degradation in the first step occurs at a higher temperature for poly(piperazinamides) than PPEANs, indicating greater thermal stability. However, greater weight losses are observed for poly(piperazinamides) in the first degradation step, by as much as 35−55%, than for PPEAN. In general, PPEANs show lower thermal stabilities than poly(piperazinamides) but retain a higher char yield.

The first degradation steps of PPEANs all occur at ∼300 °C, but there is a noticeable variation in the second degradation step for polymers **3**−**6**. The degradation temperatures of the second step range between 450 and 530 °C and appear to be correlated with the amount of weight lost in the first degradation step. Polymers showing less weight loss in the first step are observed to have the onset of the second degradation occurring at higher temperatures. This variation is not apparent in poly(piperazinamides) **7** and **8**.

Internal Rotation in Enaminonitriles Using Dynamic NMR Spectroscopy. The rotational barrier of the amide group has been shown to vary when oxygen is replaced by other groups such as S, $C(CN)_2$, or $CH(NO_2)$.[10] Previous reports have indicated that such substituents decreased the rotational barrier, and assuming no steric hindrance was involved, the decrease in the rotational barrier was correlated with a reduction in the double bond character of H*N*−*C*═C. The reduction in double bond character was attributed to the lower electron withdrawal ability of the $C(CN)_2$ group as compared with oxygen.[10] However, the experimental error for determining rotational barriers using coalescence peaks from dynamic NMR experiments is on the order of 8−15 kJ/mol, and the difference between the rotational barriers of CH_3N−CH═O ($\Delta G^* = 90$ kJ/mol) and CH_3N−CH═$C(CN)_2$ ($\Delta G^* = 75$ kJ/mol) is too small to be conclusive.

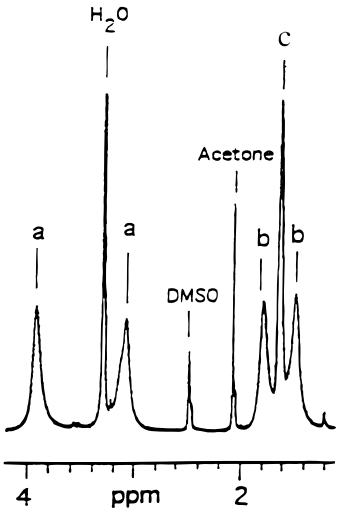

Figure 3. ^{1}H NMR spectrum of model compound **1** at room temperature.

The rotational barriers for **1** and **2** were obtained by dynamic ^{1}H NMR spectroscopy, and Figure 3 shows the ^{1}H NMR spectrum for model compound **1**. At room temperature, protons α (a) and β (b) to nitrogen each show two proton resonances (indicating different conformers as a result of the barrier to rotation about *C*−*N*). As the temperature is raised, the two peaks for (a) start to merge; the two peaks for (b) behave similarly. The coalescence temperature (T_c) is obtained when the width of the coalesced peak at half height corresponds to the difference in the chemical shift ($\Delta\nu$) of the two conformers at room temperature. The rotational barrier (ΔG^*) is then calculated from the modified Eyring[11] equation:

$$\Delta G^* = 4.57T_c[9.97 + (T_c/\Delta\nu)]$$

The results obtained for the rotational barriers of **1** and **2** are 64 and 63 kJ/mol, respectively. A rotational barrier of 62 kJ/mol has been previously reported for **2**.[12] There is little difference between the rotational barriers for enaminonitrile and amide groups in the absence of hydrogen bonding. The results show that both enaminonitrile and amide groups have similar inductive effects, if the steric factor is truly negligible. Rotational barriers of 50−67 kJ/mol have been reported for aromatic model compounds containing dicyanovinylidene groups with hydrogen bonding.[13] These results indicate that the rotational barriers are almost the same with or without hydrogen bonding.

Conclusions

In the absence of hydrogen bonding, poly(piperazinenaminonitriles) showed reduced solubility in polar aprotic solvents, which confirms the supposition that the solu-

bility of poly(enaminonitriles) is dependent on hydrogen-bonded interactions with solvents. The low molecular weights of PPEANs are attributed to both the low solubility of the polymers and possible steric hindrance from the dicyanovinylidene groups during polycondensation. The thermal stabilities of PPEANs are lower than those of the corresponding poly(piperazinamides), but the char yields of PPEANs are higher. The reduced thermal stabilities of PPEANs are most likely the result of low molecular weight materials and the absence of curing processes in the enaminonitrile group because there are no NH groups. The higher char yields of PPEANs, relative to those of the corresponding poly(piperazinamides), are speculated to be the consequence of the greater hydrolytic stability of enaminonitriles to bond scission caused by initial degradation products.

The inductive abilities of amide and enaminonitrile groups were determined to be comparable by dynamic ^{1}H NMR spectroscopy, and consequently, PEANs are likely to exhibit inductive properties, such as dipole−dipole interactions and resonance delocalization, comparable to those of aramids.

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