Synthesis and Characterization of Polyamides Containing Imidazole: Intramolecular Hydrogen Bonding and Constitutional Isomerism

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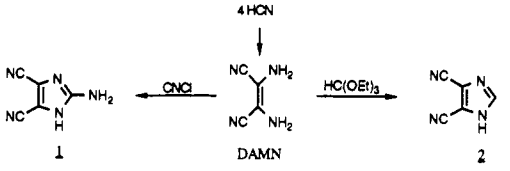
ABSTRACT: Polyamides derived from 1-methyl-4,5-imidazoledicarboxylic acid and aliphatic diamines such as hexamethylenediamine, neopentylenediamine, and ethylenediamine are synthesized and characterized. The polymers have inherent viscosities up to 0.56 dL/g, are amorphous, have good thermal stability, and are soluble in a wide range of solvents. The amide proton of the carboxamide at the 5-position of the imidazole intramolecularly hydrogen bonds to the carbonyl oxygen at the 4-position. There is little or no evidence of intermolecular hydrogen bonding occurring in the polyamides. The nonsymmetric diacid creates constitutional isomerism in the polymers. This isomerism can be detected at various levels, by NMR spectroscopy, in the polyamides depending on the diamine portion and the solvent used.

Introduction

Polymers derived from cyanoimidazoles are of interest for a number of reasons. The high nitrogen and low hydrogen content of such materials is expected to provide thermal stability and low flammability. The various functional groups of cyanoimidazoles provide routes to monomers leading to different types of polymers, including polyamides and polyimides. Dicyanoimidazoles are synthesized from diaminomaleonitrile (DAMN; Scheme I), which is a tetramer of hydrogen cyanide. Numerous dicyanoimidazoles can be derived from DAMN depending on the condensing agent used. For example, DAMN can be condensed with cyanogen chloride to give 2-amino-4,5-dicyanoimidazole (**1**)[1] or with triethyl orthoformate to give 4,5-dicyanoimidazole (**2**).[2] Our group has previously

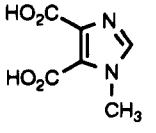
Scheme I
Synthesis of Dicyanoimidazoles



1 2

reported on AB and AAB type monomers synthesized from **1** leading to polyamides[3] and polyimides.[4] The AA monomer 1-methyl-4,5-imidazoledicarboxylic acid (**3**), synthesized from **2**, has been the subject of earlier studies.[5]

Aliphatic–aromatic polyamides are of interest because these materials can offer a wide range of properties including transparency, thermal stability, good barrier properties, and solvent resistance. Two aliphatic–aromatic polyamides that are of commercial importance are Du Pont's Selar and Dynamit Nobel's Trogamide T. We report here the synthesis and characterization of polyamides derived from **3** and hexamethylenediamine, neopentylenediamine, and ethylenediamine.



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Experimental Section

General Methods. All glassware was oven dried. Diamines were distilled prior to use. All other reagents and solvents were purified by standard methods. ^{1}H NMR analyses were run at 360 MHz and ^{13}C NMR analyses were run at 90 MHz on a Bruker AM-360 spectrometer. The spectra were referenced to residual protonated solvent. Inherent viscosities were measured at a concentration of 0.5 g/dL in concentrated H_2SO_4 at 30 °C. Gel permeation chromatography was conducted in hexafluoroisopropyl alcohol using nylon 6,6 molecular weight standards. Differential scanning calorimetry was conducted on a Perkin-Elmer DSC 7 with a heating rate of 20 °C/min. Decomposition temperatures, defined as the temperature at which the onset of decomposition began, were determined by thermogravimetric analysis on a Perkin-Elmer TGA 7 with a heating rate of 40 °C/min. Molecular modeling was conducted with the program Sybyl (Sybyl Tripos Associates, St. Louis, MO), using the Del Re method to determine electrostatic charges.

1-Methyl-4,5-imidazoledicarbonyl Chloride (5). A 500-mL Schlenk flask, equipped with a magnetic stirring bar, was charged with 8.02 g (0.047 mol) of **3**, 60 mL (0.12 mol, 2.55 equiv) of 2.0 M oxalyl chloride ($(COCl)_2$) in methylene chloride (CH_2Cl_2), and a catalytic amount of dimethylformamide (DMF). The mixture was stirred overnight at room temperature. The excess $(COCl)_2$ and solvent were removed in vacuo, and the resulting solid was dissolved in anhydrous ether. The insolubles were filtered under nitrogen, and the ether was evaporated to leave 9.31 g (0.045 mol) of a slightly yellow solid (96%). The product can be recrystallized from ether/pentane at low temperature to give white needle crystals, which turn yellow once they are isolated from the mother liquor: mp 40–42 °C (lit.[5a] mp 42–43 °C); IR (CH_2Cl_2) 1776, 1744 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.69 (s, 1 H), 3.85 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 162.25, 158.05, 141.01, 140.51, 128.33, 34.83; MS (EI) *m/z* 206, 208 (M, M + 2), 171 (100%), 143, 115, 80, 52, 42, 38. Anal. Calcd for $C_6H_4N_2O_2Cl_2$: C, 34.81; H, 1.95; N, 13.53. Found: C, 34.64; H, 2.07; N, 13.54.

Polymerization. A 250-mL three-neck round-bottomed flask, equipped with a magnetic stirring bar, N_2 inlet, solid addition funnel, and rubber septum, was charged with 15–20 mmol of hexamethylenediamine (HMDA), neopentylenediamine (NPDA), or ethylenediamine (EDA), 25–100 mL of methylene chloride or *N*-methylpyrrolidinone (NMP), and 2.0 equiv of triethylamine. After the solution was cooled to 0 °C, 1.0 equiv of **5** was added via the addition funnel, over a 2–3-min period. The reaction mixture was kept at 0 °C for 30 min and then allowed to warm to room temperature over an additional 30-min to 1-h period. Polymerization conducted in CH_2Cl_2: The mixture was diluted with CH_2Cl_2 to dissolve the triethylamine hydrochloride, washed with H_2O and brine, dried ($MgSO_4$), and filtered. The solution was concentrated by rotary evaporation, and the polymer was

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precipitated in cold ether and collected. Polymerization conducted in NMP: The polymer was precipitated by pouring the polymerization mixture into methanol (MeOH). The polymer was collected and washed with MeOH and acetone. The polymer was dried under vacuum at 50–60 °C for 14–17 h to give isolated yields of 28–58%.

Poly(hexamethylene 1-methyl-4,5-imidazoledicarboxamide) (6-IM): IR (KBr) 3396, 3012, 2931, 2857, 1662, 1638, 1539, 1550, 1511 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.27 (br s, 1 H), 8.53 (br s, 1 H), 7.80 (s, 1 H), 3.85 (s, 3 H), 3.20 (br m, 4 H), 1.45 (br s, 4 H), 1.27 (br m, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.50, 159.64, 138.71, 134.81, 127.75, 29.19, 26.68, 26.57, 26.47. Anal. Calcd for $C_{12}H_{18}N_4O_2$: C, 57.57; H, 7.26; N, 22.39. Found: C, 57.25; H, 7.09; N, 22.39. **Poly(neopentylene 1-methyl-4,5-imidazoledicarboxamide) (NEO-IM)**: IR (KBr) 3395, 3062, 2961, 2931, 2873, 1665, 1643, 1589, 1511 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.28 (br s, 0.5 H), 11.18 (br s, 0.5 H), 8.92 (br s, 0.5 H), 8.60 (br s, 0.5 H), 7.86 (br s, 1 H), 3.87 (br s, 3 H), 3.13 (br s, 4 H), 0.85 (br s, 6 H); ^{13}C NMR (DMSO-d_6) δ 163.83, 163.45, 159.24, 158.78, 139.94, 134.29, 134.17, 126.74, 126.65, 46.77, 46.24, 45.84, 45.31, 39.96, 36.28, 35.57, 35.02, 23.85, 23.14, 22.99, 22.85. Anal. Calcd for $C_{11}H_{16}N_4O_2$: C, 55.91; H, 6.84; N, 23.71. Found: C, 55.96; H, 6.85; N, 23.38.

Poly(ethylene 1-methyl-4,5-imidazoledicarboxamide) (2-IM): IR (KBr) 3385, 3380, 3008, 2951, 2879, 1661, 1637, 1589, 1548, 1511 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.28 (br s, 0.5 H), 11.19 (br s, 0.5 H), 8.77 (br s, 0.5 H), 8.71 (br s, 0.5 H), 7.82 (s, 1 H), 3.84 (s, 3 H), 3.35 (br s, 4 H); ^{13}C NMR (DMSO-d_6) δ 163.75, 163.67, 159.21, 140.23, 134.45, 134.34, 126.96, 38.61, 38.12, 36.55, 35.33. Anal. Calcd for $C_8H_{10}N_4O_2 \cdot {}^2/_3H_2O$: C, 46.59; H, 5.55; N, 27.17. Found: C, 46.16; H, 5.09; N, 27.08.

***N*-Isobutyl-1-methyl-4,5-imidazoledicarboximide (12).** A 25-mL two-neck round-bottomed flask, equipped with a magnetic stirring bar, N_2 inlet, and rubber septum, was charged with 0.170 g (1.0 mmol) of **3**, 2.5 mL (5.0 mmol, 5.0 equiv) of 2.0 M $(COCl)_2$ in CH_2Cl_2, and a catalytic amount of DMF. The mixture was stirred at room temperature for 30 min. The excess $(COCl)_2$ and solvent were removed in vacuo, and 5 mL of CH_2Cl_2 were added to the oil. After the yellow solution was cooled to 0 °C, a solution containing 0.1 mL (1.0 mmol, 1.0 equiv) of isobutylamine, 0.28 mL (2.0 mmol, 2.0 equiv) of Et_3N, and 5 mL of CH_2Cl_2 was added over a 3–4-min period. The reaction mixture was kept at 0 °C for 30 min and then allowed to warm to room temperature. The crude mixture was analyzed without purification: IR (KBr disk) 1784, 1725, 1677, 1651 cm^{-1}; ^{1}H NMR (DMSO-d_6) showed a 6:5 of imide to diamide. Distinguishable imide signals: δ 9.27 (s, 1 H), 3.99 (s, 3 H). HRMS (CI with ammonia). Calcd for $C_{10}H_{14}N_3O_2$ (MH^+): 208.1086. Found: 208.1079.

***N,N'*-Bis[(1-methyl-4-cyano-5-imidazolyl)carbonyl]neopentylenediamine (19).** A 25-mL two-neck round-bottomed flask, equipped with a magnetic stirring bar, N_2 inlet, and rubber septum, was charged with 0.756 g (5.0 mmol) of 1-methyl-4-cyano-5-imidazolecarboxylic acid (**17**),[6] 6 mL of 2.0 M $(COCl)_2$ in CH_2Cl_2, and a catalytic amount of DMF. The mixture was stirred at room temperature for 1–2 h. The excess $(COCl)_2$ and solvent were removed in vacuo, and 5 mL of CH_2Cl_2 were added. After the yellow solution was cooled to 0 °C, a solution containing 0.26 g (2.5 mmol, 0.5 equiv) of neopentylenediamine, 0.7 mL (5.0 mmol, 1.0 equiv) of triethylamine, and 5 mL of CH_2Cl_2 was added over a 2–3-min period. The mixture was kept at 0 °C for 30 min and then allowed to warm to room temperature over an additional 1-h period. The reaction mixture was diluted with 10 mL of CH_2Cl_2 and was washed with 10% HCl (1 × 5 mL), H_2O (1 × 5 mL), 10% NH_4OH (1 × 5 mL), H_2O (1 × 5 mL), and brine (1 × 5 mL), dried ($MgSO_4$), and filtered. The solvent was removed, and the resultant solid was recrystallized from 95% ethanol giving 0.310 g (0.84 mmol) of the white solid (34%): mp 228–229 °C; IR (KBr) 3257, 3098, 2235, 1676, 1658, 1556, 1509 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.81 (t, J = 6.2 Hz, 2 H), 7.98 (s, 2 H), 3.77 (s, 6 H), 3.22 (d, J = 6.2 Hz, 4 H), 0.95 (s, 6 H); MS (DCI) m/z 368 (M^+), 205, 164 (100%), 107, 79. HRMS. Calcd for $C_{17}H_{20}N_8O_2$: 368.1709. Found: 368.1706. Anal. Calcd for $C_{17}H_{20}N_8O_2$: C, 55.41; H, 5.48; N, 30.42. Found: C, 55.29; H, 5.55; N, 30.68. ***N,N'*-Bis[(1-methyl-5-cyano-4-imidazolyl)carbonyl]neopentylenediamine (20)** was similarly prepared from 1-methyl-5-cyano-4-imidazolecarboxylic acid (**18**):[6] mp 239–240 °C; IR (KBr) 3414, 3355, 2966, 2928, 2933, 1663, 1576, 1571, 1506 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.60 (t, J = 6.6 Hz, 2 H), 8.06 (s, 2 H), 3.79 (s, 6 H), 3.03 (d, J = 6.6 Hz, 4 H), 0.82 (s, 6 H); MS (DCI) m/z 368 (M^+), 205, 163, 149, 134 (100%), 107, 49. HRMS. Calcd for $C_{17}H_{20}N_8O_2$: 368.1709. Found: 368.1699. Anal. Calcd for $C_{17}H_{20}N_8O_2 \cdot H_2O$: C, 52.84; H, 5.74; N, 28.00. Found: C, 52.57; H, 5.34; N, 26.68.

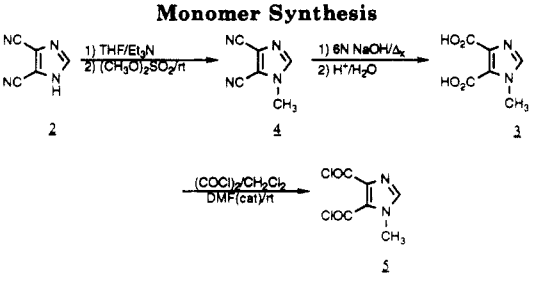
***N,N'*-Bis[(1-methyl-4-carboxamido-5-imidazolyl)carbonyl]neopentylenediamine (21).** A 10-ml one-neck round-bottom flask, equipped with magnetic stirring bar and reflux condenser, was charged with 0.184 g (0.5 mmoles) of **19**, 0.18 ml (0.5 mmoles, 1.0 eq) of 40% w/w Et_4NOH, and 5 ml of H_2O. The mixture was refluxed overnight. The precipitate that formed upon cooling was collected giving 0.037 g (0.09 mmoles) of white solid (18%). IR (KBr) 3457, 3414, 3218, 3213, 2962, 1649, 1588, 1509 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.15 (br. s, 2 H), 7.60 (br. s, 2 H), 7.37 (s, 2 H), 6.19 (br. s, 2 H), 3.99 (s, 6 H), 3.36 (d, J = 5.4 Hz, 4 H), 1.13 (s, 6 H); ^{13}C NMR (DMSO-d_6) δ 166.01, 159.02, 140.34, 134.42, 127.31, 46.84, 35.62, 35.55, 23.03; MS (DCI) m/z 404 (M^+), 223 (100%), 181, 152 (100%), 134, 109; HRMS. Calcd for $C_{17}H_{24}N_8O_4$: 404.1921. Found: 404.1917. ***N,N'*-Bis[(1-methyl-5-carboxamido-4-imidazolyl)carbonyl]neopentylenediamine (22)** was similarly prepared from **20**: IR (KBr) 3384, 1671, 1660, 1610, 1556, 1514 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.11 (s, 2 H), 8.38 (br s, 2 H), 7.42 (s, 2 H), 5.61 (br s, 2 H), 3.98 (s, 6 H), 3.23 (d, J = 6.7 Hz, 4 H), 0.98 (s, 6 H); ^{13}C NMR (DMSO-d_6) δ 163.87, 160.64, 140.45, 134.70, 126.72, 45.35, 37.37, 35.39, 23.48; MS (DCI) m/z 404 (M^+), 223 (100%), 206, 182, 168, 152, 134, 109, 42. HRMS. Calcd for $C_{17}H_{24}N_8O_4$: 404.1921. Found: 404.1908.

Isomeric Mixtures. A 25-mL two-neck round-bottomed flask, equipped with a magnetic stirring bar, N_2 inlet, and rubber septum, was charged with equal amounts of **17** and **18**, 2.0 M $(COCl)_2$ (10 mol equiv) in CH_2Cl_2, and a catalytic amount of DMF. The mixture was stirred at room temperature for 2–3 h. The excess $(COCl)_2$ and solvent were removed in vacuo, and CH_2Cl_2 was added. After the yellow solution was cooled to 0 °C, a solution containing 1.0 equiv of HMDA, NPDA, or EDA, 2.0 equiv of triethylamine and CH_2Cl_2 was added over a 2–3-min period. The mixture was kept at 0 °C for 30 min, and then it was allowed to warm to room temperature over an additional 30-min period. The mixture was washed with 10% HCl, H_2O, 10% NH_4OH, H_2O, and brine, dried ($MgSO_4$), and filtered. The solvent was evaporated to leave the crude isomeric mixture. **HMDA isomers (23a–c)**: IR (KBr) 2234, 1661, 1575, 1507, 1311, 1263 cm^{-1}; ^{1}H NMR (DMSO-d_6) amide region, δ 8.78, 8.35; MS (EI) m/z 382 (M^+), 324, 164, 134 (100%), 106, 42. **NPDA isomers (24a–c)**: IR (KBr) 2235, 1666, 1574, 1508, 1472, 1312, 1262 cm^{-1}; ^{1}H NMR (DMSO-d_6) amide region, δ 8.91, 8.75, 8.61, 8.40; MS (CI ammonia) m/z 386 (MNH_4^+), 369 (MH^+), 168 (100%), 151, 136, 108, 102. **EDA isomers (25a–c)**: ^{1}H NMR (DMSO-d_6) amide region, δ 8.89, 8.83, 8.48; MS (CI ammonia) m/z 344 (MNH_4^+), 327 (MH^+), 168, 151, 136 (100%), 108, 102.

Results and Discussion

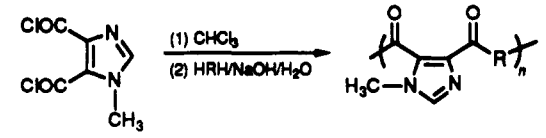
Monomer and Polymer Synthesis. The diacid monomer **3** is synthesized (Scheme II) by alkylating **2**, giving 1-methyl-4,5-dicyanoimidazole (**4**),[7] followed by basic

Scheme II
Monomer Synthesis



hydrolysis.[8] The diacid **3** is converted to the diacid chloride **5** using oxalyl chloride ($(COCl)_2$) and a catalytic amount of dimethylformamide (DMF) at room temperature. The diacid chloride **5** has been prepared previously using

Table I
Previously Reported Polyamides Synthesized from 5



5

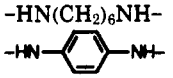
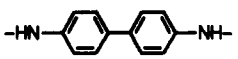
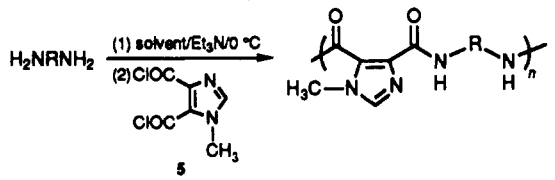
R	η_{inh}	ref
$-HN(CH_2)_6NH-$	0.21	5a
	0.19	5a
	0.20	5a
	0.83	5b

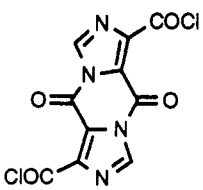
Table II
Polyamides Synthesized from 5



5

R	solvent	polymer	isolated yield, %
$-(CH_2)_6-$	CH_2Cl_2	6-IM	45–58
	CH_2Cl_2	NEO-IM	42–61
$-(CH_2)_2-$	CH_2Cl_2	2-IM	28
$-(CH_2)_2-$	NMP	2-IM	59

thionyl chloride,[5] but we found using oxalyl chloride was easier and faster.[9] The 1-position of the imidazole must be blocked in order to avoid the formation of the diketopyrazine derivative 6[10] during the preparation of the diacid chloride.



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The diacid chloride 5 has been previously polymerized with various diamines. Takahashi and co-workers[5a] interfacially polymerized 5 with the first three diamines shown in Table I, obtaining polyamides of low to moderate molecular weights. Researchers at Du Pont polymerized 5 with *trans*-2,5-dimethylpiperazine, obtaining high polymer.[5b]

We have repeated the polymerization of 5 with HMDA, giving the polyamide designated as 6-IM. We also have polymerized 5 with NPDA, to give the polymer designated NEO-IM, and EDA, giving the polyamide 2-IM. We used low-temperature (0 °C) solution polymerization methods to prepare our polyamides using methylene chloride (CH_2Cl_2) as the solvent (Table II). In the case of 2-IM, the polymer precipitated when the polymerization was conducted in CH_2Cl_2, giving a yield of 28% and an inherent viscosity of 0.30 dL/g. Using *N*-methylpyrrolidinone (NMP) as the solvent doubled the yield, but the viscosity was unchanged. The isolated yields of the polymerizations, after fractionation, ranged from roughly 30 to 60%.

Polymer Characterization. A summary of the polymer properties is shown in Table III. The inherent viscosities of the polyamides ranged from 0.30 to 0.56 dL/g. The number-average molecular weight (M_n) of the polymers, as determined by gel permeation chromatography, was found to be 6500 for 6-IM and 4500 for NEO-IM. The molecular weight distributions (M_w/M_n or MWD) were quite broad. Takahashi and co-workers obtained an inherent viscosity of 0.21 dL/g when they synthesized 6-IM interfacially,[5a] while we obtained a viscosity of 0.56 dL/g using solution conditions. Typically, the molecular weights of aliphatic–aromatic polyamides are the highest when they are prepared by interfacial methods. For example, the inherent viscosity of nylon 4-T prepared under interfacial[11] conditions was twice that of the material polymerized in solution[12] (Table IV). We also prepared NEO-IM interfacially and found that the molecular weight was significantly less compared to the solution polymerization results (0.22 versus 0.42 dL/g).[13] For these particular polyamide systems, solution polymerization conditions are evidently more suitable than interfacial.

The moderate molecular weights of the polyamides combined with the geometry of 3 raise the question of whether imidization is occurring. No imides based on 3 have been reported. In work conducted on the related polyimide 8, synthesized from 1-methyl-2-amino-4,5-imidazoledicarboxylic acid (7), Kim and Rasmussen report that imidization began to occur at room temperature, but only in the solid state (Scheme III).[4] However, MacDonald and Sharkey report the formation of the thiadiazoleimide 10 along with the bisamide 11 from the corresponding diacid chloride 9 in solution at 0 °C (Scheme IV).[14]

In order to determine if imidization was occurring in our polyamide systems, we ran model reactions under conditions where imidization would be favored. The model reactions were conducted by adding 1 equiv of isobutylamine to a dilute solution of 5 (0.1 M) at 0 °C (Scheme V). A number of reactions were carried out under these conditions, and the resultant mixtures were analyzed by IR, ^1H NMR, and GC/MS or direct probe MS. Many of the reactions showed evidence of imidization, particularly by IR spectroscopy, but no confirmation was seen by MS using electron impact (EI) ionization. Only by using chemical ionization (CI) were we able to detect the presence of the imide 12. Analysis of the reaction mixture by ^1H NMR showed a 6:5 ratio of 12 to the diamide 13.[15] When the reaction mixture was washed with water, in a similar manner to the polymerizations, the ratio of the products became 1:3. Apparently 12 readily hydrolyzes due to the strain in the imide ring, as was observed for the polyimide 8.[4] The resultant amide acid is evidently washed away. Acid end groups are clearly seen in the IR spectra of the polyamides. Figure 1 shows the IR spectrum of 6-IM as a typical example with a carboxylic acid C=O stretch at 1725 cm^{-1}.[16]

The fact that imidization is occurring during the polymerizations explains why the yields and molecular weights of the polyamides were moderate and why the MWD were broad. Interfacial polymerization conditions apparently are more conducive to imidization, causing a decrease in the molecular weight of these polymers. MacDonald et al. were able to get high polymer with *trans*-2,5-dimethylpiperazine since using a secondary diamine prevents imidization. They report that conducting polymerizations with 5 and primary diamines gave lower molecular weight polyamides in a fashion similar to research they conducted on 9.[5b] However, they do not report any imides derived from 5, as they did with 9.[14]

Table III
Polymer Characterization

polymer	η_{inh}	M_n	M_w	M_w/M_n	T_g (°C)	T_m	T_d in N_2 (°C)	T_d in air (°C)
6-IM	0.56	6500	31 400	4.9	86	none	454	436
NEO-IM	0.42	4500	30 750	6.8	152	none	419	420
2-IM	0.30				189	none	428	421

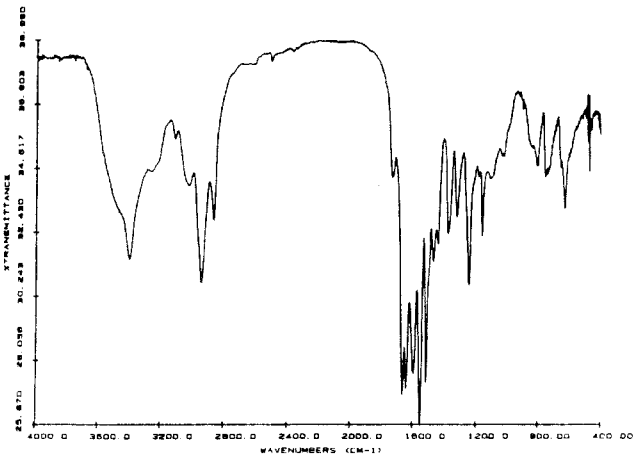
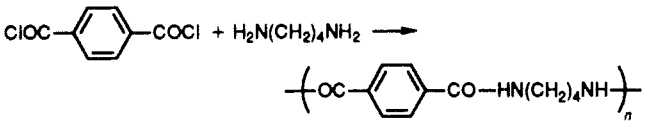


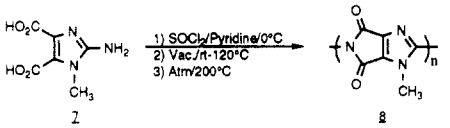
Figure 1. IR spectrum of 6-IM.

Table IV
Synthesis of Nylon 4-T

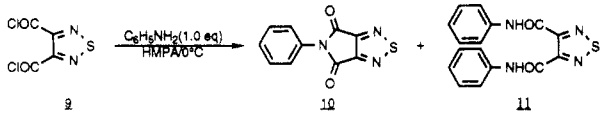


polymzn method	η_{inh}	ref
interfacial	1.20	11
solution	0.58	12

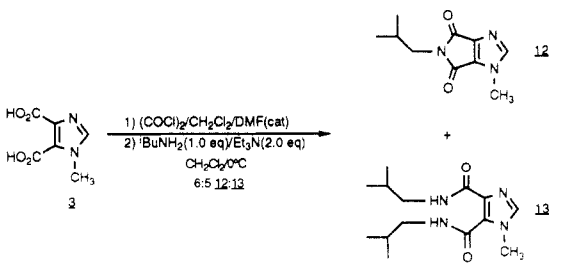
Scheme III



Scheme IV



Scheme V



The glass transition temperatures (T_g) of the polyamides ranged from 86 to 189 °C (Table III). The 6-IM polymer has the lowest T_g, 86 °C, due to the relatively long and flexible diamine portion. The shorter aliphatic chain in 2-IM reduces the polymer chain flexibility, producing a T_g of 189 °C. The 152 °C T_g of NEO-IM is due to a combination of the shorter aliphatic chain and the geminal dimethyl substituents reducing the rotational freedom of the diamine portion. None of the polyamides showed any evidence of crystallinity by DSC analysis or by X-ray

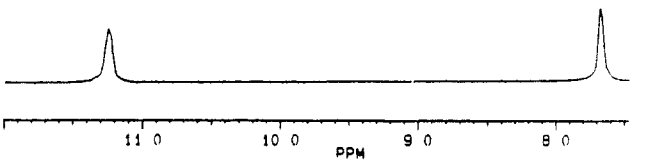
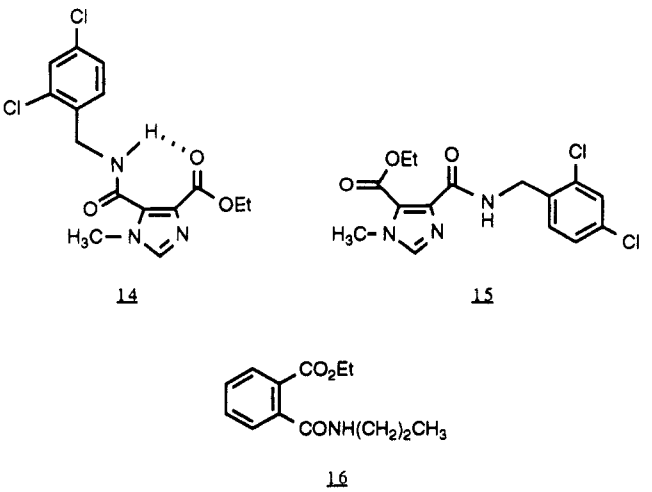


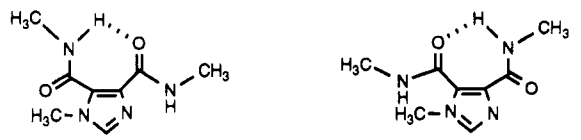
Figure 2. ^1H NMR spectrum of 6-IM in $CDCl_3$.

powder diffraction. Transparent films of the polyamides can be cast from solution. However, since the polymers are of moderate molecular weight, the films become brittle as the solvent evaporates. The polymers are thermally stable to temperatures equal to, or in excess of, 419 °C. The decomposition temperature (T_d) of NEO-IM is the same under nitrogen as in air, demonstrating the oxidative stability of the neopentyl group. In contrast, the T_d of 2-IM polyamide was slightly less in air than in nitrogen (421 versus 428 °C), and 6-IM decomposed 18 °C lower in air than under nitrogen (436 versus 454 °C). The polymers are at least partially soluble in a wide range of solvents, from chlorinated solvents, such as CH_2Cl_2 and chloroform, to polar aprotic solvents, such as DMF and NMP. Quantitatively, 6-IM is soluble to at least 20–25% in CH_2Cl_2.

Hydrogen Bonding Behavior. Hydrogen bonding in polymers, including natural proteins, polyurethanes, and synthetic polyamides, is of great interest since it plays an important role in determining molecular structure and, hence, polymer properties. Many aspects of hydrogen bonding have been comprehensively reviewed.[17] Figure 2 shows the ^1H NMR spectrum of 6-IM in deuterated chloroform ($CDCl_3$). One amide proton signal is shifted downfield to 11.3 ppm while the other amide proton peak appears at 7.7 ppm. Yasuda and co-workers[18] determined that the amide proton in the ester amide **14** intramolecularly hydrogen bonds to the ester carbonyl oxygen, causing the amide proton signal to be shifted downfield to 10.7 ppm in the NMR spectrum. They report that the same was not true for the regioisomer **15**, which has an amide proton signal at 8.1 ppm, or for the ester-substituted benzamide **16**, which shows an amide signal at 5.9 ppm.



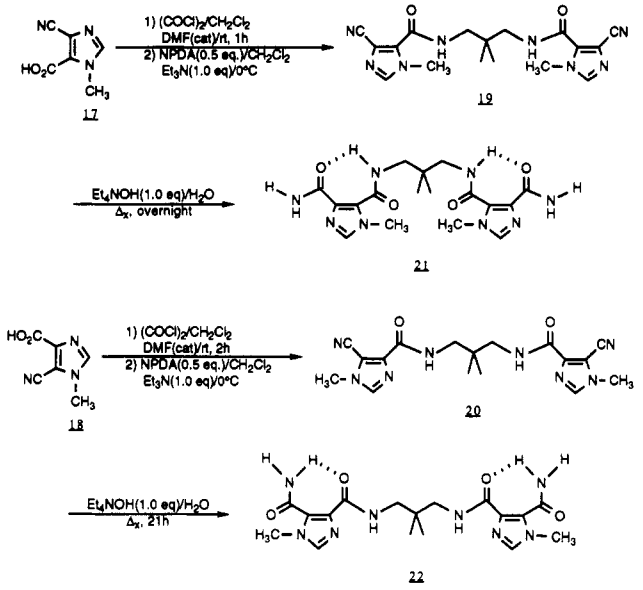
Yasuda et al. suggest that the selective hydrogen bonding in **14** is due to steric effects as well as resonance stabilization



a b

Figure 3. Hydrogen-bonding patterns used in molecular modeling calculations.

Scheme VI
Synthesis of Model Compounds



with the imidazole ring. They support their resonance stabilization hypothesis by reporting that **14** absorbs at a longer wavelength in the UV absorption spectrum than **15**.[18] However, since a similar resonance form can be constructed for **15**, with the amide proton of the carboxamide at the 4-position hydrogen bonded to the carbonyl oxygen at the 5-position, we were interested in investigating the basis of the preferential hydrogen bonding further. We computer modeled the two hydrogen-bonded forms of the methyl-substituted diamide (Figure 3). We constrained the seven-membered ring containing the hydrogen bond to remain coplanar with the imidazole ring in accordance with Yasuda and co-workers' UV data. The calculations showed that when the amide proton of the carboxamide at the 4-position is hydrogen bonded to the carbonyl oxygen at the 5-position (Figure 3b), the amide proton of the carboxamide at the 5-position sterically interacts with the methyl group at the 1-position, contributing to an increase in energy of 5–6 kcal/mol, relative to the other form (Figure 3a). This steric interaction can only be avoided if the carbonyl groups are allowed to bend out of the plane of the imidazole ring. Therefore, we concur with Yasuda et al. that the exclusive hydrogen bonding between the amide proton of the carboxamide at the 5-position and the carbonyl oxygen at the 4-position is due to a combination of electronic and steric interactions.

We synthesized the model amides **21** and **22** from the cyanoimidazole acids **17** and **18** (Scheme VI) to verify that the same exclusive hydrogen bonding was taking place in our polyamides. We used NPDA as the diamine since it would be the most sterically restricted of the three diamines studied. By conducting ^{1}H homonuclear decoupling NMR experiments on the model compounds,[19] we were able to confirm that the same hydrogen-bonding pattern exists in our polyamides as Yasuda and co-workers observed in their ester amides.[20] The intramolecular hydrogen bonding is not influenced by whether the amide is a primary or secondary amide nor by the geminal dimethyl groups on the diamine portion. This intramolecular hydrogen bonding is evidently very stable. Conducting NMR of the polyamides and model compounds in DMSO-d_6, even at probe temperatures up to 175 °C, did not disrupt the intramolecular hydrogen bonding.

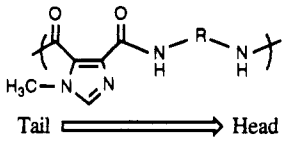


Figure 4. Schematic representation of the head and tail designation of the polyamide repeat unit.

The hydrogen-bonding behavior of polyamides has been extensively studied by IR spectroscopy.[21] Even in amorphous aliphatic–aromatic polyamides, such as Du Pont's Selar, nearly all of the amide linkages are involved in hydrogen bonding, giving rise to one N–H stretch near 3300 cm^{-1} and one C=O stretch near 1640 cm^{-1}. At most, slight shoulders can be observed near 3440 and 1660 cm^{-1} due to free, or non-hydrogen-bonded, amide groups.[21d] As mentioned earlier, the IR spectra of our polyamides are very similar in appearance to each other. Figure 1 shows the IR spectrum of 6-IM as a typical example with amide I bands, of nearly equal intensities, near 1660 and 1640 cm^{-1}. A non-hydrogen-bonded N–H stretch appears as a broad shoulder near 3500 cm^{-1}, while a more resolved hydrogen-bonded N–H stretch appears near 3390 cm^{-1}.[22] The IR data suggest that there is little or no intermolecular hydrogen bonding occurring in the polyamides, which is unusual even for amorphous aliphatic–aromatic polyamides. We have seen evidence of intramolecular hydrogen bonding occurring between the amide proton of the carboxamide at the 4-position and the 3-position imidazole nitrogen, in various model compounds.[13] However, since there is a strong non-hydrogen-bonded N–H stretch in the IR spectra, this particular interaction is apparently disrupted in the polyamides.

Constitutional Isomerism. Constitutional isomerism arises in AA–BB type step-growth polymers if at least one of the monomers is nonsymmetrical, as is the case with **3**. Various aspects of constitutional isomerism of such step-growth polymer systems have been investigated.[23,24] Constitutional isomerism affects polymer properties such as solubility and crystallinity. These properties can be manipulated to some extent if the constitutional isomerism is controlled.[23] The constitutional isomerism of our polymers is uncontrollable under the polymerization conditions we used.

Defining a head-to-tail direction for the repeat unit, as shown in Figure 4, gives three diad structures. The three diads, which are shown schematically along with their corresponding structures in Figure 5, give rise to four distinct amide linkages.[25] However, in our polyamide systems the ability to detect the four amide protons of the diads, by ^{1}H NMR, is dependent on the diamine portion.

In order to illustrate this dependence, we synthesized (Scheme VII) the three sets of isomers **23–25** to emulate the diads of the three polyamides. The ^{1}H NMR spectra of the isomeric mixtures are shown in Figure 6. The spectrum of the isomers containing HMDA (Figure 6a) only shows two amide protons, while the ^{1}H NMR spectrum of the isomers containing NPDA (Figure 6b) shows all four of the amides in the isomers **24a–c**. The shorter aliphatic chain allows the amide groups at opposite ends of the chain to inductively effect each other. In addition, the geminal dimethyl groups of NPDA significantly reduce

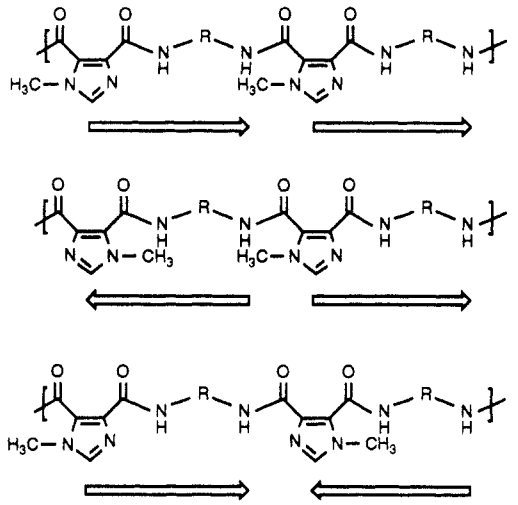


Figure 5. Schematic representation of polyamide diads.

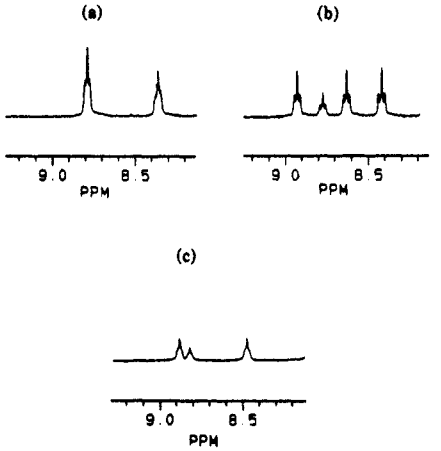
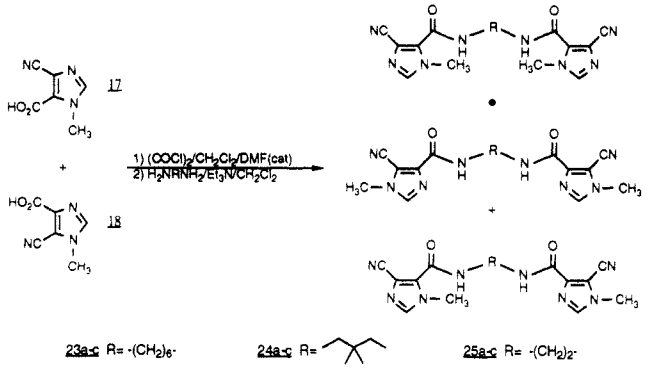


Figure 6. ^{1}H NMR spectra of isomeric mixtures in DMSO-d_6: (a) HDMA isomers **23a–c**; (b) NPDA isomers **24a–c**; (c) EDA isomers **25a–c**.

Scheme VII
Synthesis of Isomeric Mixtures



the rotational freedom of the aliphatic chain. The combination of these two factors allows for the four different amides to be observed. The ^{1}H NMR spectrum of the isomers containing EDA, **25a–c**, shows three amide signals (Figure 6c). The shorter chain of EDA allows for inductive effects but is more flexible than NPDA, and so only three of the four types of amides are observed.

The ^{1}H NMR spectra of the polyamides in DMSO-d_6 are shown in Figure 7. In a manner similar to that of the isomeric mixtures, the spectrum of 6-IM (Figure 7a) shows the structure of the repeat unit of the polymer and no constitutional isomerism, while the spectrum of NEO-IM shows the constitutional isomerism at the diad level (Figure 7b). In spite of the ^{1}H NMR spectrum of the EDA isomers

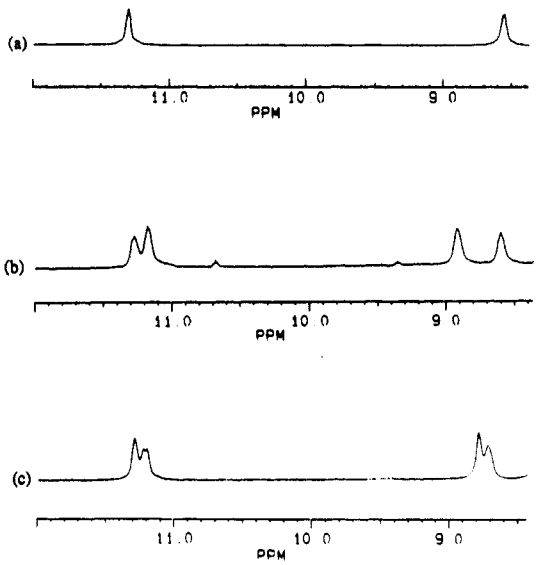


Figure 7. ^{1}H NMR spectra of polyamides in DMSO-d_6: (a) 6-IM; (b) NEO-IM; (c) 2-IM.

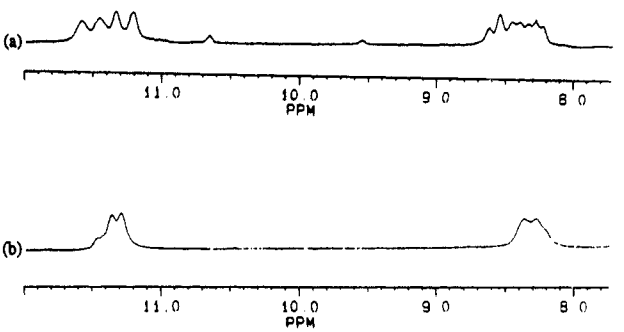


Figure 8. ^{1}H NMR spectra of polyamides in $CDCl_3$: (a) NEO-IM; (b) 2-IM.

25a–c only showing three of the four types of amides, the ^{1}H NMR spectrum of 2-IM (Figure 7c) shows the four amide signals of the diads. The four amide proton peaks in the 2-IM spectrum are not as well separated as they are in the NEO-IM spectrum.

The ^{1}H NMR spectrum of NEO-IM in $CDCl_3$ (Figure 8a) is more complex than the corresponding spectrum in DMSO-d_6 (Figure 7b). The possibility that this ^{1}H NMR spectrum shows diad constitutional isomerism combined with amide conformational effects was considered. However, the ratio of cis to trans conformers would not be expected to be 1:1, as the integration of the four proton signals near 11.5 ppm suggests. In addition, the energy required to overcome the intramolecular hydrogen bonding makes amide conformational changes highly unlikely. Thus, amide conformational contributions were ruled out. The additional amide signals in the $CDCl_3$ ^{1}H NMR spectrum are due to the constitutional isomerism at the triad level. In most AA–BB step-growth polymer systems, with one nonsymmetrical monomer, it is usually only possible to observe the isomerism of the diads.[24c–e] However, in NEO-IM the intramolecular hydrogen bonding combined with the low rotational freedom of the diamine portion allows for the triads to be observed. The four triads of NEO-IM are shown in Figure 9.

The four different amide protons at the 5-position of the NEO-IM triads are clearly seen near 11.5 ppm in the ^{1}H NMR spectrum (Figure 8a), while the four amide protons at the 4-position appear as a large complex peak around 8.5 ppm. The amide protons at the 5-position are more distinct because they are locked in place by the intramolecular hydrogen bonding. The ^{1}H NMR spectrum

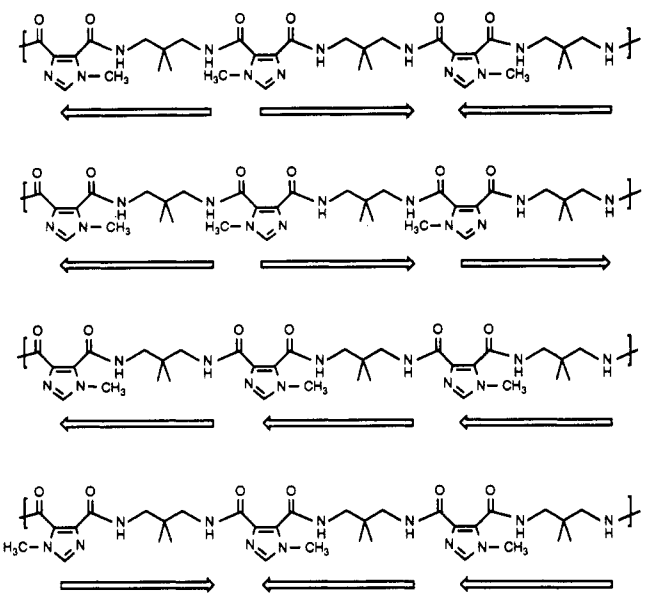


Figure 9. Schematic representation of NEO-IM triads.

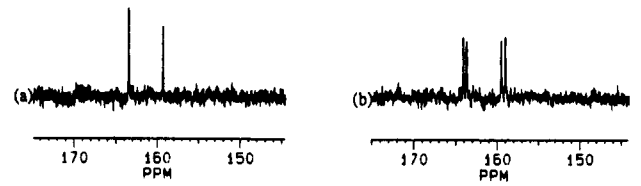


Figure 10. ^{13}C NMR spectra of polyamides: (a) 6-IM in $CDCl_3$; (b) NEO-IM in DMSO-d_6.

of 2-IM in $CDCl_3$ (Figure 8b) does not show the isomerism of the triads and differs only slightly from the spectrum in DMSO-d_6 (Figure 7c), showing a shoulder on the amide proton peak near 11.5 ppm and a broader more nondescript peak at 8.3 ppm. This again shows that the geminal dimethyl groups in the diamine portion of NEO-IM play a vital role in the elucidation of the constitutional isomerism. The triad isomerism of NEO-IM is most likely not detectable in DMSO-d_6 because of greater solvent–polymer interaction compared to $CDCl_3$.

As with the ^1H NMR spectra, ^{13}C NMR spectra of the polyamides illustrate the various levels of constitutional isomerism. Figure 10 shows the carbonyl carbon region of the ^{13}C NMR spectra of 6-IM and NEO-IM. The ^{13}C NMR spectrum of 6-IM (Figure 10a) shows the two types of carbonyl carbons present in each repeat unit, just as the corresponding ^1H NMR spectrum (Figures 2 and 7a) showed the two amide protons. Likewise, Figure 10b shows the four carbonyl carbon signals of the NEO-IM diads. The carbon signal of the carbonyl at the 4-position of the imidazole is shifted downfield due to the intramolecular hydrogen bonding.

The scale of the ^{13}C NMR spectrum of NEO-IM in $CDCl_3$ must be expanded to see all eight carbonyl carbons of the triads (Figure 11a). The spectrum shows four broad carbonyl signals centered around 160 ppm and four more near 165 ppm. The four peaks near 165 ppm can be resolved further using resolution enhancement (Figure 11b), while the signals near 160 ppm are resolved to show finer structure.[26] The four carbonyl peaks at the 4-position of the triads are more distinct due to the intramolecular hydrogen bonding.

In spite of the ^1H NMR spectra of 2-IM and NEO-IM in DMSO-d_6 being similar (Figure 7b,c), the ^{13}C NMR spectrum of 2-IM in DMSO-d_6 contrasts significantly to the corresponding spectrum of NEO-IM. The carbonyl region of the ^{13}C NMR spectrum of NEO-IM in DMSO-d_6

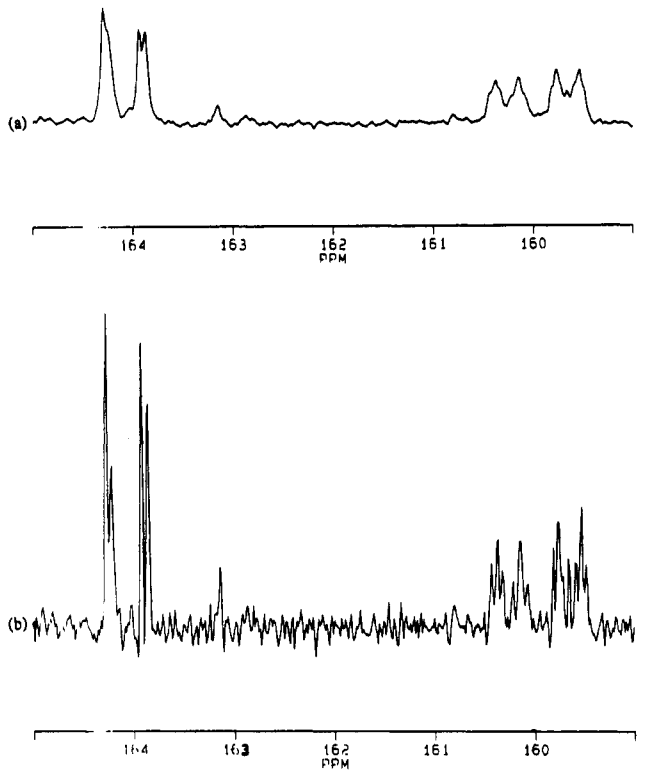


Figure 11. (a) ^{13}C NMR spectra of NEO-IM in $CDCl_3$. (b) Resolution enhanced.

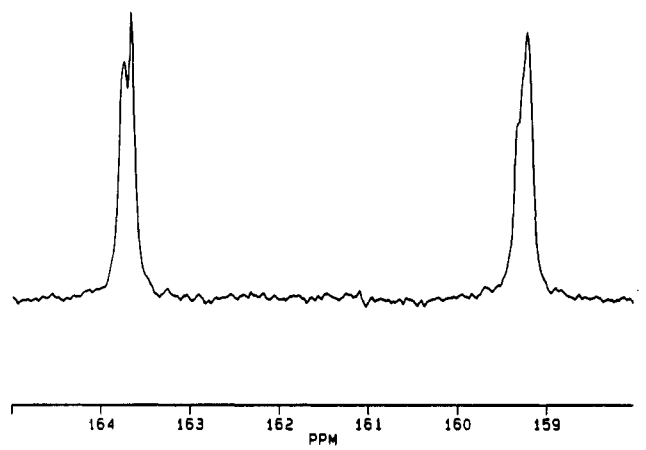


Figure 12. ^{13}C NMR spectra of 2-IM in DMSO-d_6.

(Figure 10b) shows the four distinct carbon signals of the diads. However, even on an expanded scale, the 2-IM spectrum only shows two peaks near 164 ppm and a peak with some fine structure located near 159 ppm (Figure 12). Resolution enhancement failed to resolve the peaks of the diads. Although the diads of 2-IM are clearly seen by ^1H NMR in DMSO-d_6 (Figure 7c), they are not so easily observed by ^{13}C NMR.

Although the ^1H NMR spectra of 2-IM (Figures 7c and 8b) did not drastically differ from each other, the ^{13}C NMR spectra are significantly different. Just like the ^{13}C NMR spectra of NEO-IM, the ^{13}C NMR spectrum of 2-IM in $CDCl_3$ is more complex than the corresponding DMSO-d_6 spectrum (Figure 12). The expanded spectrum of 2-IM (Figure 13) is similar to the NEO-IM spectrum (Figure 11a), illustrating the constitutional isomerism at the triad level. Resolution enhancement failed to resolve the signals near 164 ppm as it did with NEO-IM, once again indicating the significance of the geminal dimethyl groups in accentuating the constitutional isomerism.

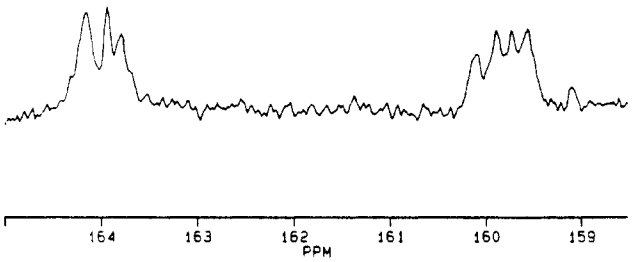


Figure 13. ^{13}C NMR spectra of 2-IM in $CDCl_3$.

Conclusion

We have improved the molecular weight of the polyamide 6-IM, first reported by Takahashi and co-workers,[5a] and synthesized two new polyamides, NEO-IM and 2-IM. The molecular weights of the polyamides are moderate due to imidization occurring during the polymerization. The polymers are amorphous, thermally stable to temperatures in excess of 419 °C, and soluble in a wide range of solvents.

The amide proton of the carboxamide at the 5-position of the imidazole intramolecularly hydrogen bonds to the carbonyl oxygen at the 4-position. This exclusive hydrogen bonding is due to a combination of electronic and steric interactions. There is little or no evidence that intermolecular hydrogen bonding is occurring in the polymer systems.

We found that the ability to detect the constitutional isomerism that arises from the random placement of the nonsymmetrical diacid 3, by NMR spectroscopy, is dependent on the structure of the diamine portion and the solvent. Thus, we have found that the constitutional isomerism is undetectable in 6-IM but is detectable at the diad level in NEO-IM, in DMSO-d_6, and at the triad level in $CDCl_3$. The diads of 2-IM are observed by ^1H NMR in DMSO-d_6 but not so clearly seen by ^{13}C NMR. In contrast, the triads of 2-IM are more noticeable by ^{13}C NMR in $CDCl_3$ than by ^1H NMR.

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References and Notes

(1) Webster, O. W. U.S. Patent 3,882,140, 1975.
(2) Woodward, D. W. U.S. Patent 2,534,331, 1950; *Chem. Abstr.* **1951**, *45*, 5191d.
(3) (a) Allan, D. S.; Rasmussen, P. G. *J. Polym. Sci. Polym. Chem. Ed.* **1992**, *30*, 1413. (b) Thurber, E. L.; Rasmussen, P. G. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(4) Kim, Y. K.; Rasmussen, P. G. *Macromolecules* **1991**, *24*, 6357.
(5) (a) Takahashi, K.; Suzuki, K.; Ishiguro, H.; Zaima, T.; Mitsuhashi, K. *J. Jpn. Chem. Soc.* **1974**, *4*, 801. (b) MacDonald, R. N.; Cairncross, A.; Seija, J. B.; Sharkey, W. H. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 663.
(6) Subrayan, R. P.; Rasmussen, P. G., unpublished results from this laboratory.
(7) Apen, P. G.; Rasmussen, P. G. *Heterocycles* **1989**, *25*, 1325.
(8) O'Connel, J. F.; Parquette, J.; Yelle, W. E.; Wang, W.; Rapoport, H. *Synthesis* **1988**, *10*, 767.
(9) Although the acid chloride reaction was typically conducted overnight for large-scale preparations, it was usually complete in as little as 20 min on smaller scales.
(10) (a) Yasuda, N. *J. Heterocycl. Chem.* **1985**, *22*, 413. (b) Yasuda, N.; Iwagami, H.; Nakanishi, E.; Nakamiya, T.; Sasaki, Y.; Murata, T. *J. Antibiot.* **1983**, *36*, 242.
(11) Shashoua, V. E.; Eareckson, W. M. *J. Polym. Sci.* **1959**, *40*, 343.
(12) Aubineau, C.; Audebert, R.; Champetier, G. *Bull. Soc. Chim. Fr.* **1970**, 533.
(13) Bouck, K. J. Ph.D. Thesis, The University of Michigan, Ann Arbor, MI, 1992.
(14) MacDonald, R. N.; Sharkey, W. H. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2519.
(15) The ratio of the products is based on the integration of the imidazole methyl groups. The methyl group of the imide appears at 3.99 ppm, and the methyl group of the diamide appears at 3.89 ppm.[13]
(16) By ^{13}C NMR, weak signals corresponding to methylene carbons adjacent to amine end groups are observed.
(17) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: New York, 1991.
(18) Yasuda, N.: Nakamura, A.; Tsuboi, M. *J. Heterocycl. Chem.* **1987**, *24*, 303.
(19) Homonuclear decoupling experiments of the model compounds were conducted by selectively irradiating individual amide proton signals and observing the effect on the methylene proton signal.
(20) We[13] and Yasuda et al.[18] have synthesized a number of diamides which possess the same hydrogen-bonding patterns as well.
(21) (a) Garcia, D.; Starkweather, H. W., Jr. *Polym. Sci. Technol.* **1987**, *36*, 213. (b) Colman, M. M.; Skrovanek, D. J.; Painter, P. C. *Makromol. Chem., Macromol. Symp.* **1986**, *5*, 21. (c) Skrovanek, D. J.; Painter, P. C.; Colman, M. M. *Macromolecules* **1986**, *19*, 699. (d) Skrovanek, D. J.; Howe, S. E.; Painter, P. C.; Colman, M. M. *Macromolecules* **1985**, *18*, 1676.
(22) The broad stretch around 3500 cm^{-1} is not believed to be due to the presence of water. The elemental analyses of 6-IM and NEO-IM were in agreement with the calculated values, and no water was observed in the ^1H NMR spectra of these polyamides. In the case of 2-IM it was necessary to add $^2/_3$ mol of water per repeat unit to fit the elemental analysis data. However, this water is attributed to end groups since no water peaks were observed in the ^1H NMR spectra of 2-IM.
(23) For a recent review on constitutional isomerism of step-growth polymers, see: Gentile, F. T.; Suter, U. W. In *Comprehensive Polymer Science*; Allen, G., et al., Eds.; Pergamon: New York, 1989; Vol. 5, p 97.
(24) (a) Gentile, F. T.; Meyer, W. R.; Suter, U. W. *Macromolecules* **1991**, *24*, 633. (b) Gentile, F. T.; Suter, U. W. *Makromol. Chem.* **1991**, *192*, 663. (c) Meyer, W. R.; Gentile, F. T.; Suter, U. W. *Macromolecules* **1991**, *24*, 642. (d) De La Campa, J. G.; De Abajo, J. *Eur. Polym. J.* **1983**, *19*, 667. (e) Murano, M. *Polym. J.* **1972**, *6*, 663.
(25) The intramolecular hydrogen-bonding interactions have been omitted for simplicity.
(26) Resolution enhancement was conducted using Gaussian multiplication.