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Novel Thermoset Polyimidazole Amides

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ABSTRACT: A new class of polyamides can be prepared using a solvent-free polymerization reaction. Bis(imidazoles) undergo an addition reaction with aromatic polyisocyanates to form polyamides. Since this reaction does not produce any low molecular weight volatile molecules, the reaction is suitable for the synthesis of thermoset polymers. The polyimidazole amides produced using this route have good thermal stability and mechanical properties. The toughness as measured by Izod impact was particularly high for thermoset polymers.

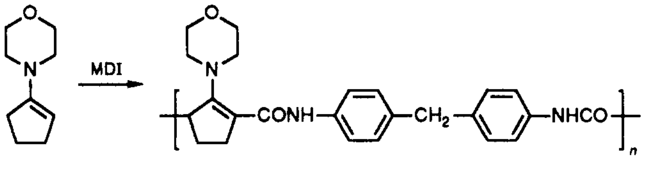
I. Introduction

Polyamides are known for their outstanding combination of physical properties, including a high degree of toughness, excellent abrasion resistance, and good resistance to a variety of solvents.[1] High molecular weight polyamides can be produced by reacting diisocyanates and dicarboxylic acids in inert solvents. However, as shown below, carbon dioxide is a byproduct of this reaction,[2] making this route unsuitable for producing polymers for certain applications.

$$n\mathrm{OCNRNCO} + n\mathrm{HOOCR'COOH} \rightarrow (\text{-NHRNHCORCO-})_n + \mathrm{CO_2}$$

However, the addition of compounds containing alkyl or aryl groups to isocyanates to form amides *without* releasing volatile compounds offers significant advantages. Such a route would allow producers to develop and use simple polyamide manufacturing processes that are similar to polyurethane or polyurea processes. In addition, a number of novel thermoset polyamide compounds could be produced by such a route.

Although this approach has been pursued by some researchers, no entirely successful example has been reported in literature. In most cases, the product yields from the model reactions were not high enough to suggest that polymerizations would be practical.[3,4] One exception was the reaction of methylenediphenyl diisocyanate (MDI) with *N*-morpholino-1-cyclopentene as shown in the following equation.[5] The resulting polymer had an intrinsic viscosity of 0.79 dL/g.



The polymer had good initial mechanical properties. Unfortunately, the polymer thermally degraded at relatively low temperatures of 60 °C. A rapid decrease in viscosity was observed when a dilute polymer solution was heated at 60 °C. The polymerization reaction was subsequently extended to permit reaction injection molding (RIM), but the polymers produced by this method had poor mechanical properties and low thermal stability.[6]

This paper reports that 1,1′-(α,ω-alkanediyl)bis(imidazole) compounds can react with aromatic polyfunctional isocyanates to produce a new class of heteroaromatic polyamides. Since no volatile compounds are produced in this reaction, this reaction is suitable for thermoset polymerization applications.

II. Experimental Section

(1) Materials. All of the solvents used in this study were purified by standard procedures.[7] Phenyl isocyanate, imidazole, 1,4-dichlorobutane, 1,6-dichlorohexane, 2-chloroethyl ether, benzothiazole, and benzoxazole were purchased from Aldrich Chemical Co. MDI and PAPI 580 polymeric MDI (equivalent weight of 136.8 g/mol)[8] were obtained from The Dow Chemical Co., Texas Division. Laboratory quantities of these compounds are available from Polysciences, Inc. 1-Methylbenzimidazole was prepared according to the procedure outlined by Kikugawa.[9]

(2) Measurements. Transmission IR spectra were produced on a Perkin-Elmer 590 infrared spectrophotometer. Attenuated total reflectance IR was generated on a Nicolet analytical instruments 170SX Model with KRS-5 crystal. NMR spectra were determined on a Varian VXR300 NMR. Thermal gravimetric analysis (TGA) was performed using a Du Pont 951 thermogravimeter analyzer at 10 °C/min. Differential scanning calorimetry (DSC) was carried out using a Du Pont 912 differential scanning calorimeter under atmospheric conditions. Gas chromatography (GC) was carried out with a Hewlett-Packard 5840A gas chromatograph equipped with a 15-m J&W DB-5 megabore capillary column. Mass spectroscopy (MS) was run on a Finnigan Model 4600 quadruple mass spectrometer.

(3) Synthesis of 1-Methyl-2-[(*N*-phenylamino)carbonyl]imidazole (1) (Model Reaction). Phenyl isocyanate (11 g, 0.093 M) was poured into a 100-mL flask containing 1-methylimidazole (7.62 g, 0.093 M) at room temperature. A white solid was formed almost immediately. The solid was heated to its melting point, and the temperature was then increased to 180 °C. Using a magnetic stirring bar, the temperature was sustained at 180 °C for 2 h. A light yellow solid (18.6 g) was obtained, and the following properties were determined: mp 101–103 °C;[10] IR (nujol) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.93 (s, 3, CH_3), 6.70–7.50 (m, 7), 8.8–9.2 (br, 1, NH); MS *m/e* (relative intensity) 201 (M^+, 100), 109 (60), 82 (55), 81 (74).

(4) Synthesis of 1,1′-(1,4-Butanediyl)bis(imidazole) (6). Imidazole (68 g, 1 M), a 50% NaOH solution (80 g, 1 M), toluene (120 mL), and DMSO (120 mL) were added to a flask. With a Dean–Stark apparatus connected to the flask, the mixture was heated until all of the water was removed by means of azeotropic distillation. 1,4-Dichlorobutane (63.5 g, 0.5 M) was added, and the mixture was stirred at 60 °C for 2 h. After the removal of sodium chloride and DMSO by filtration and distillation, respectively, the resulting liquid was poured into 300 mL of water. A white solid formed immediately which weighed 93 g (95% recovery) after drying and had the following properties: mp 83–86 °C; IR (nujol) 1520 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.55–1.95 (m, 4, $-CH_2CH_2-$), 3.75–4.05 (m, 4, NCH_2), 6.70 (s, 2), 6.87 (s, 2), 7.25 (s, 2); MS *m/e* 190 (M^+), 123.

(5) Synthesis of 1,1′-(1,2-Phenylene)bis(imidazole). *o*-Dibromobenzene (39 g, 0.165 M), imidazole (28 g, 0.41 M), potassium carbonate (46 g, 0.33 M), and cupric oxide (1.3 g) were heated

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while stirring in 150 mL of DMSO at 150 °C for 48 h. The resulting slurry was cooled to room temperature, and solids were removed by filtration. DMSO of the filtrate was removed by distillation under reduced pressure. Methylene chloride was added to the remaining filtrate, and the mixture was then washed with water and dried over sodium sulfate. The methylene chloride was then removed. The 1,1′-(1,2-phenylene)bis(imidazole) was further purified by sublimation at 0.4 Torr. A white solid weighing 28 g was obtained (81%). The melting point, as recorded by DSC, was 134.3 °C, and mass spectroscopy produced the following result: MS *m/e* (relative intensity) 210 (M^+, 100), 182 (33), 102 (16). The 1,1′-(1,4-phenylene)bis(imidazole) was synthesized using the same method; however, purification by sublimation failed.

(6) Synthesis of 1,1′-(1,4-Butanediyl)bis(benzimidazole). Powdered KOH (15.7 g, 0.39 M) and benzimidazole (7 g, 0.06 M) were added to 100 mL of acetone in a flask. After 5 min, 1,4-diiodobutane (9.27 g, 0.03 M) was added. A solid appeared after about 1 h. After the solid had been recovered, washed with water, and crystallized in ethanol, the following properties were measured: ^1H NMR ($CDCl_3$) δ 1.60–2.00 (m, 4, $-CH_2CH_2-$), 4.10–4.45 (m, 4, NCH_2), 7.00–7.80 (m, 8), 8.20 (s, 2); MS *m/e* (relative intensity) 290 (M^+, 100), 183 (45), 107 (61). Yield of the purified solid was 7.5 g (86%).

(7) Synthesis of Polyamide from 1,1′-(1,4-Butanediyl)bis(imidazole) and a 2 to 1 Mixture of MDI and PAPI 580. 1,1′-(1,4-Butanediyl)bis(imidazole) (51.57 g, 0.27 M, 0.54 equiv) was heated to 80 °C and held under vacuum for 24 h and then heated to 130 °C to ensure the removal of any residual water. MDI (45 g, 0.18 M, 0.36 equiv) and PAPI 580 polymeric MDI (24.6 g, 0.18 equiv) were mixed, heated to the melting point, and added to the bis(imidazole). A solid formed almost immediately. The solid was heated to its melting point (150 °C) and then degassed under vacuum. The temperature was increased to 180 °C, and, after 5 min, the melt became viscous. It was poured into a 3.5 in. × 6 in. mold for additional curing. Timing for resin transfer is important. The mold was heated at 220 °C and held under pressure at that temperature for 2.5 h; before the pressure was released, the mold was allowed to cool. The molded plaque of polyamide was then removed, and testing bars were made.

(8) Synthesis of Polyamide from 1,1′-(1,6-Hexanediyl)bis(imidazole) and a 2 to 1 Mixture of MDI and PAPI 580. 1,1′-(1,6-Hexanediyl)bis(imidazole) (40.6 g, 0.372 equiv; made using essentially the same procedure used to make 1,1′-(1,4-butanediyl)bis(imidazole) with the exception of 1,6-dichlorohexane being used as a starting material) was heated to 90 °C under vacuum for 17 h to ensure the removal of any residual water. The temperature was then raised to 140 °C. MDI (31 g, 0.248 equiv) and PAPI 580 polymeric MDI (16.9 g, 0.124 equiv) were melted and mixed together, and the isocyanate mixture was poured into the hot 1,1′-(1,6-hexanediyl)bis(imidazole). The reaction mixture was heated and stirred. When the temperature reached 150 °C, vacuum was applied. A time interval of 10 min was necessary for the temperature to reach 178 °C, at which time the mixture became very viscous. The viscous liquid was poured into a 3.5 in. × 6 in. mold, and the mold temperature was increased, over a 20-min interval, from 170 to 205 °C, under 0.2 ton of pressure. Polymerization was completed at 205 °C for 3 h. The molded plaque of polyamide was then removed, and testing bars were made.

(9) Synthesis of Polyamide from 1,1′-(Oxydi-2,1-ethanediyl)bis(imidazole) and PAPI 580. 1,1′-(Oxydi-2,1-ethanediyl)bis(imidazole) (40.2 g, 0.39 equiv), made from 2-chloroethyl ether and imidazole, was heated at 60 °C under vacuum for 24 h. The temperature was then increased to 120 °C. A mixture of MDI (32.5 g, 0.26 equiv) and PAPI 580 polymeric MDI (17.8 g, 0.26 equiv) was added. The reaction mixture was then stirred and degassed at 120 °C, poured into a 3.5 in. × 6 in. mold, and cured under pressure at 210 °C for 2.5 h.

(10) Attempted Synthesis of Polyamide from MDI and 1,1′-(1,2-Phenylene)bis(imidazole). Freshly distilled MDI (2.443 g, 9.77 mM) and 1,1′-(1,2-phenylene)bis(imidazole) (2.052 g, 9.77 mM) were mixed and heated. A homogeneous solution was obtained at 140 °C. The solution became viscous after it was heated at 190 °C. It was subsequently degassed under vacuum for 15 min, transferred to a 1 in. × 3 in. die, heated to 210 °C, and held at that temperature for 1.5 h. An infrared spectrum of the brittle polymer showed absorption bands that were consistent with amide (1670–1690 cm^{-1}) and isocyanate (2260 cm^{-1}) groups. Although heating continued for an additional 5 h, the polymer remained brittle and IR analysis again indicated the presence of residual isocyanate.

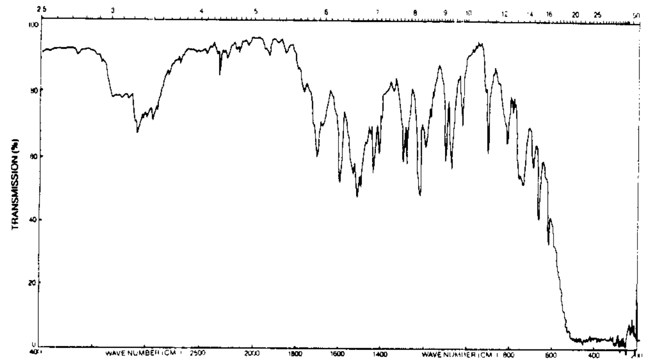


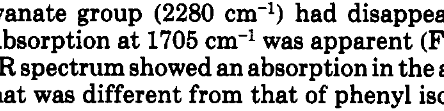
Figure 1. IR of the solid from a 1 to 1 mixture of phenyl isocyanate and 1-methylimidazole after they were stirred at 25 °C for 3 min.

(11) Synthesis of Polyamide from 1,1′-(1,4-Butanediyl)bis(benzimidazole) and PAPI 580. 1,1′-(1,4-Butanediyl)bis(benzimidazole) (4.3 g, 0.03 equiv) was dried under vacuum at 100 °C for 24 h and then at 170 °C for 2 h. PAPI 580 polymeric MDI (4.1 g, 0.03 equiv) was added, and the mixture was stirred and degassed at 180 °C. The mixture became very viscous after 10 min. It was poured into a mold and heated at 200 °C under 3 tons of pressure for 0.5 h. The temperature was increased stepwise to 210 °C (1 h), 220 °C (1.5 h), and 230 °C (1.5 h). The T_g of the polymer was 170 °C.

(12) Attempted Synthesis of Linear Polyamides from 1,1′-(1,4-Butanediyl)bis(imidazole) and MDI in DMSO. 1,1′-(1,4-Butanediyl)bis(imidazole) was crystallized in acetonitrile and dried at 100 °C under vacuum for 48 h. The bis(imidazole) (8.829 g, 0.0465 M) was dissolved in a mixture of 50 mL of toluene and 80 mL of DMSO. The toluene was subsequently removed by Dean–Stark distillation. Freshly distilled MDI (11.617 g, 0.0465 M) was dissolved in 60 mL of DMSO. The solution was added dropwise to the bis(imidazole) solution, which was maintained at 50 °C. After the addition was complete and the solution had been stirred for an additional 10 min, gel formation was observed. The gel did not dissolve even at refluxing temperature.

III. Results and Discussion

(1) Model Reaction. Papadopoulos reported that 1-methylimidazole reacted with aromatic isocyanates in refluxing nitrobenzene to form amides in 82–92% yield according to the following reaction.[11]



1: R = Me, R′ = Ph

It was found that when equimolar quantities of 1-methylimidazole and phenyl isocyanate were mixed in the *absence* of a solvent, a light yellow solid was formed almost immediately. The IR spectrum of the solid indicated that the isocyanate group (2280 cm^{-1}) had disappeared and that an absorption at 1705 cm^{-1} was apparent (Figure 1). The NMR spectrum showed an absorption in the aromatic region that was different from that of phenyl isocyanate (Figure 2). Neither IR nor NMR analysis suggested the formation of phenyl isocyanate dimer or trimer.[12] NMR indicated that the chemical shifts of the protons on the methyl group and the protons on the ring were identical to those of 1-methylimidazole.

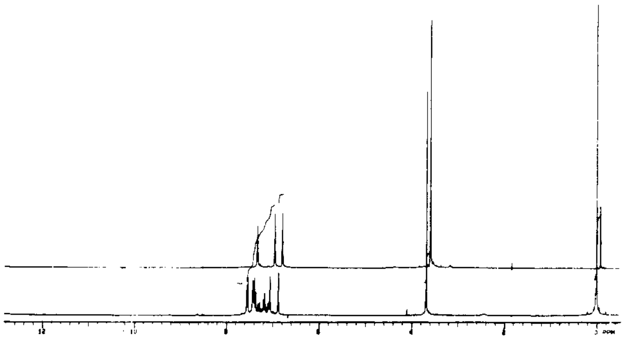


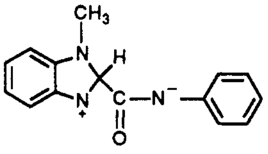
Figure 2. NMR ($CDCl_3$) of the solid from a 1 to 1 mixture of phenyl isocyanate and 1-methylimidazole after they were stirred at 25 °C for 3 min. The NMR spectrum of 1-methylimidazole in $CDCl_3$ with the scale shifted to the right is shown for comparison.

The solid reaction intermediate was dissolved in chloroform and analyzed by gas chromatography (GC). Analysis of the chromatogram suggested that the solid was 3% 1-methyl-2-[(*N*-phenylamino)carbonyl]imidazole (1), while the rest was starting material. The nature of the solid intermediate was not clear. It appeared that a very high percentage of the solid intermediate converted back to the starting materials under GC conditions. Upon heating, the solid melted at approximately 110 °C. The melted solid was then further heated to 180 °C and held for 2 h. At this point, a GC chromatogram indicated 1 was the only material present. Spectroscopic data and the melting point were consistent with those reported by Papadopoulos, who also synthesized 1 by an independent route to confirm its structure. The study showed that a solvent was not necessary for the reaction to proceed to high conversion and that the high product selectivity is practical for polymerization reactions.

1-Methylbenzimidazole, benzothiazole, and benzoxazole reacted with phenyl isocyanate to give 1-methyl-2-[(*N*-phenylamino)carbonyl]benzimidazole (92% by GC chromatograph; other peaks not identified), 2-[(*N*-phenylamino)carbonyl]benzothiazole (91%), and 2-[(*N*-phenylamino)carbonyl]benzoxazole (65% yield), respectively. Lower product yields for these compounds, as compared to 1-methylimidazole, may be attributed to the disruption of the aromaticity in the resonance structures 2 and 3 shown for the reaction intermediate of 1-methylbenzimidazole and phenyl isocyanate. The resonance structures 4 and 5 from the reaction of 1-methylimidazole and phenyl isocyanate are more stable.

Table I
Glass Transition Temperatures of Polyamides from 6 and Different Ratios of MDI and PAPI 580 Polymeric MDI

polymer	T_g, °C
6 with PAPI 580 polymeric MDI	160
6 with a 1:1 ratio of MDI to PAPI 580	148
6 with a 2:1 ratio of MDI to PAPI 580	131
6 with a 6:1 ratio of MDI to PAPI 580	109
6 with MDI	105



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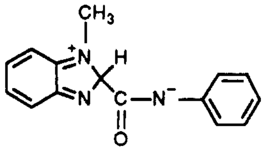

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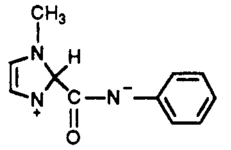

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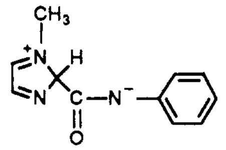

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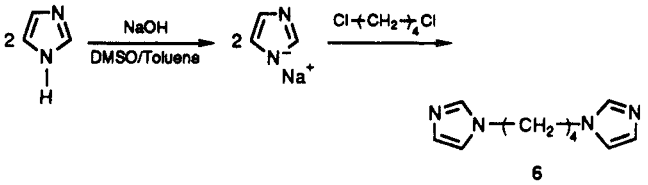
(2) Preparation of Bis(imidazoles). 1,1′-(1,4-Butanediyl)bis(imidazole) (6) was prepared from 1,4-dichlorobutane and 2 mol of imidazole in dimethyl sulfoxide (DMSO) according to the following reaction.



The yield of this reaction was 95%. 1,1′-(1,4-Butanediyl)bis(benzimidazole), 1,1′-(1,6-hexanediyl)bis(imidazole), and 1,1′-(oxydi-2,1-ethanediyl)bis(imidazole) were successfully prepared using similar reactions. It appears that the two imidazole groups can be linked with any α,ω-

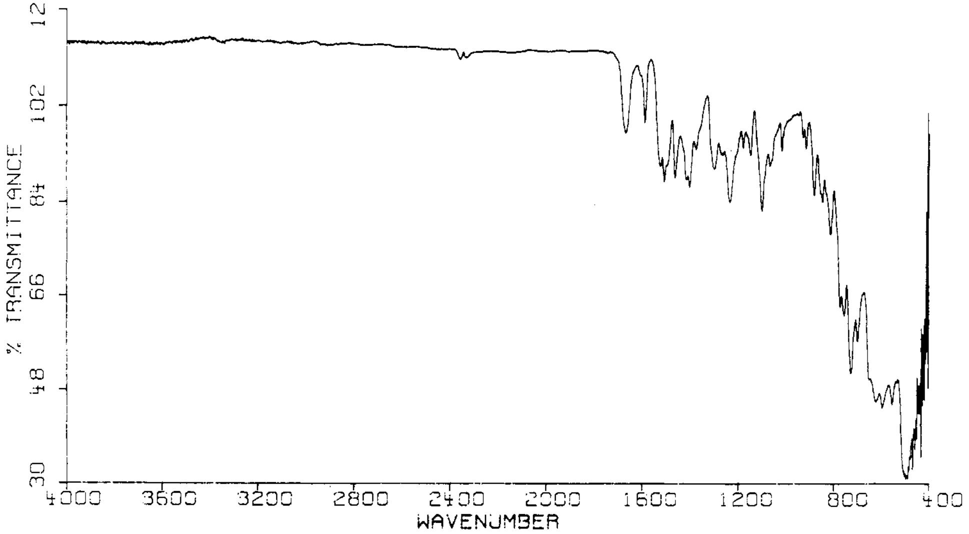


Figure 3. Attenuated total reflectance IR of a film made from 1,4-tetramethylene-*N*,*N*′-bis(imidazole) and a 2 to 1 mixture of MDI and PAPI 580.

Table II
Mechanical Properties of Polyamides from a 2:1 Ratio of MDI and PAPI 580 and Different Bis(imidazoles)

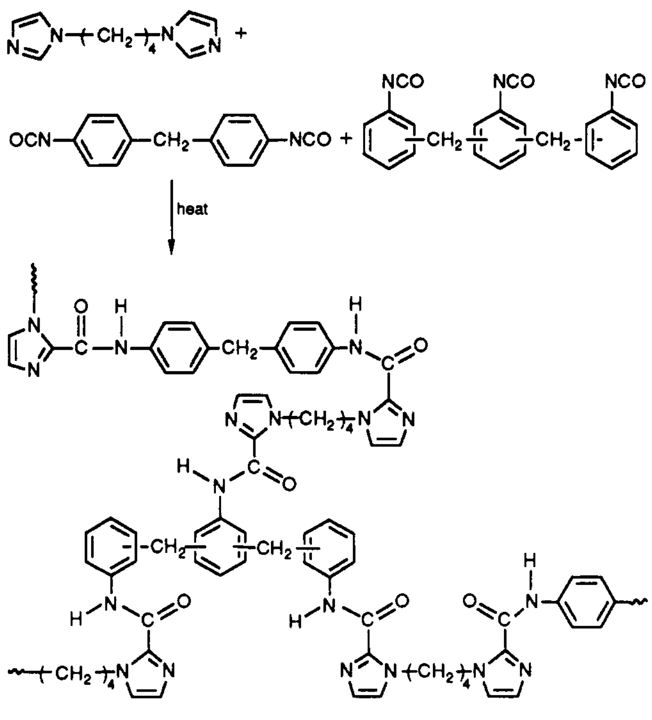
polymer[a]	flexural modulus, ksi	flexural strength, ksi	tensile modulus, ksi	tensile strength, ksi	elongation at break, %	Izod impact, ft·lb/in.
A	438	16.1	200	4	2.2	0.8
B	380	17.3	390	5.6	1.5	0.74
C	450	16.7	320	5.2	1.9	0.85
DGEBA	390	17.0	360	9.5	4.5	0.40

[a] Polymers A–C were made with 1,1′-(1,4-butanediyl)bis(imidazole), 1,1′-(1,6-hexanediyl)bis(imidazole), and 1,1′-(oxydi-2,1-ethanediyl)bis(imidazole), respectively. DGEBA is diglycidyl ether of Bisphenol A cured with 4,4′-methylenedianiline.

group. The use of a phenyl group for the linkage was investigated by preparing 1,1′-(1,2-phenylene)bis(imidazole).

(3) Polymerization Reactions. The polymerization reacted the bis(imidazoles) prepared earlier with mixtures of aromatic polyfunctional isocyanates. The most extensively studied bis(imidazole) was **6**.

When **6** was mixed with a blend of MDI and PAPI 580 polymeric MDI, a solid formed almost immediately. The solid was subsequently heated to its melting point, and the polymerization reaction was completed with additional heating. The resulting polymer was insoluble in the common organic solvents such as methylene chloride, chloroform, acetone, or methanol. The structure of this polyimidazole amide is shown below:



Attenuated total reflectance IR of a film made from **6** and a 2 to 1 mixture of MDI and PAPI 580 showed the absence of isocyanurate, and amide was essentially the only linkage: 3340, 1650, 1550, 1300 cm^{-1} (Figure 3).

A thermoset polymer was obtained by reacting 1,1′-(1,4-butanediyl)bisbenzimidazole with PAPI 580 polymeric MDI. The polymer had a glass transition temperature (T_g) of 170 °C, but the test bar was too brittle to obtain any mechanical property testing.

Attempts to make a linear polymer from **6** and MDI with DMSO as the solvent did not produce a high molecular weight linear polymer. Gel formation was observed shortly after the components were mixed in the solvent. The gel collected by filtration was insoluble in chloroform, dimethylacetamide, or *m*-cresol.

The reaction of 1,1′-(1,2-phenylene)bis(imidazole) with MDI was very slow. Free isocyanate was observed by IR even after 7 h at 210 °C. Mechanical properties were not able to be tested due to the unavailability of good specimens. This suggests that bis(imidazoles) linked with a phenyl group are not good candidates for this polymerization.

(4) Properties of the Polyamides. Thermal gravimetric analysis (TGA) of the polyamide prepared from **6** and a 2 to 1 ratio of MDI and PAPI 580 polymeric MDI showed no weight loss at 300 °C in the presence of either nitrogen or air. A 2% weight loss was observed at 325 °C under nitrogen or 311 °C in air. A corresponding polyurethane, made from 1,4-butanediol and a 2 to 1 ratio of MDI and PAPI 580 polymeric MDI, exhibited a significant weight loss at a temperature that was more than 50 °C lower. In other words, the polyamide has better thermal stability than the corresponding polyurethane.

The glass transition temperature (T_g) of the polyamide prepared from **6** and a 2 to 1 ratio of MDI and PAPI 580 polymeric MDI was 131 °C. In comparison, the glass transition temperatures of the corresponding polyurethane and polyurea polymers (prepared from a 2 to 1 ratio of MDI and PAPI 580 polymeric MDI with 1,4-butanediol or 1,4-butanediamine) were 115 and 124 °C, respectively. Table I shows that the glass transition temperatures of the polyamides can be controlled by varying the ratio of MDI and PAPI 580 polymeric MDI. Cross-link density decreases as the ratio of PAPI 580/MDI decreases, and therefore T_g decreases.

Mechanical properties of thermoset polyamides made from a 2:1 mixture of MDI and PAPI 580 polymeric MDI with 1,1′-(1,4-butanediyl)bis(imidazole), 1,1′-(1,6-hexanediyl)bis(imidazole), and 1,1′-(oxydi-2,1-ethanediyl)bis(imidazole) are shown in Table II. The properties of diglycidyl ether of Bisphenol A (DGEBA) cured with 4,4′-methylenedianiline (MDA) are included for comparison purposes.[13] The flexural properties and tensile modulus were comparable to those of DGEBA cured with MDA. Tensile strength was lower. The degree of toughness as measured by Izod impact testing was remarkable for thermoset polymers.

IV. Conclusion

1,1′-(α,ω-Alkanediyl)bis(imidazole) compounds undergo addition reactions with aromatic isocyanates to form polyamides. No volatiles are produced in these reactions which make the reactions suitable for thermoset polymer applications—the first such thermoset polyamide polymers ever reported. The polymers have good thermal stability and mechanical properties. The high degree of toughness is exceptional for thermoset polymers. In contrast, a phenylenediimidazole did not result in a high conversion to a polyamide when it was reacted with isocyanates.

Acknowledgment. I thank Dr. Giles Dillingham and Mr. Wendell Meyer of The Dow Chemical Co. for obtaining the attenuated total reflectance IR and helpful discussion, respectively.

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(10) Literature mp 102–104 °C reported in ref 11. Literature mp 104–106 °C reported in: Pinkerton, F. H.; Thames, S. F. *J. Heterocycl. Chem.* **1972**, *9*, 67.

(11) Papadopoulos, E. P. *J. Org. Chem.* **1977**, *42*, 3925–3929.

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Registry No. **1**, 35342-94-0; **6**, 69506-86-1; A (copolymer), 134443-65-5; B (copolymer), 134443-66-6; C (copolymer), 137494-71-4; (**6**)(PAPI580) (copolymer), 134443-69-9; (**6**)(MDI) (copolymer), 137494-73-6; (PAPI580)(1,1′-(1,4-butanediyl)bis(benzimidazole)) (copolymer), 137494-74-7; phenyl isocyanate, 103-71-9; 1-methylimidazole, 616-47-7; imidazole, 288-32-4; 1,4-dichlorobutane, 110-56-5; 1,1′-(1,2-phenylene)bis(imidazole), 137494-64-5; *o*-dibromobenzene, 583-53-9; 1,1′-(1,4-butanediyl)bis(benzimidazole), 39677-03-7; 1,4-diiodobutane, 628-21-7; benzimidazole, 51-17-2.