Synthesis and Curing Study of 5–5 Ring-Fused Polyimide Based on Imidazole

Introduction. Aromatic polyimides are widely used in electronic applications because of low dielectric constants and outstanding thermal stability.[1,2] Recent research has aimed at investigating the effects of the structural changes in the polymer backbone upon the physical properties of the polyimides.[2-5] Structural variation in the backbone is needed, particularly in the linear aromatic polyimides, in order to control the physical properties such as the dielectric constant and glass transition temperature.

Recently, we have synthesized a new linear 5–5 ring-fused polyimide (**6**) which has a methyl substituent at the 1-position of the imidazole. Our materials have an unusually low hydrogen and high nitrogen content, allowing for lower flammability, oxidation resistance, and other unique properties.[6] The AA–B type monomer used to synthesize the new polyimide is 2-amino-1-methyl-4,5-imidazoledicarboxylic acid (**3**). Although this molecule is readily prepared by alkylating 2-amino-4,5-dicyanoimidazole (**1**), followed by hydrolysis, the polyimide cannot be prepared in the usual fashion. Normally, polyimides are prepared by a stepwise polymerization of a diamine and a dianhydride of a tetracarboxylic acid. The first step gives a polyamic acid which is then heated to a higher temperature to effect imidization. However, in our case this procedure leads to decarboxylation in the second step apparently due to the ring strain induced by fusion of two five-membered rings. For this reason we prepared various polyamic acid derivatives from **3** such as polyamic acid chloride using excess thionyl chloride at room temperature.

FT-IR spectroscopy was used to monitor the imidization process and the cleavage reaction of the imide bond. This paper discusses the synthesis and unique properties of the first example of 5–5 ring-fused polyimide containing imidazole.

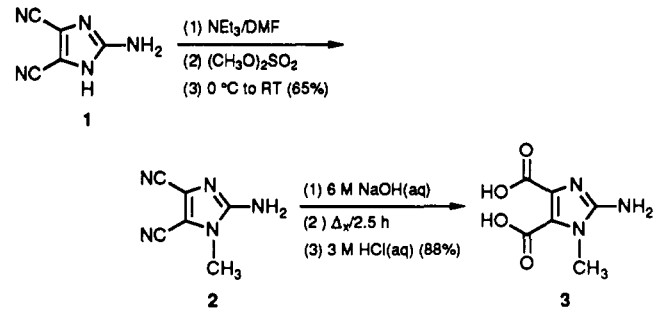
Experimental Section. All solvents were distilled by standard methods prior to use. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Proton nuclear magnetic resonance spectra were recorded on a Bruker AM-300 spectrometer. Nominal mass spectra were done on a Finnigan Model 4021 quadrupole mass spectrometer. Elemental analyses were done on a Perkin-Elmer 2400 CHN elemental analyzer or performed by Oneida Research Services Inc., Whitesboro, NY.

Monomer Preparation. 2-Amino-1-methyl-4,5-imidazoledicarboxylic acid was synthesized by hydrolysis of 2-amino-1-methyl-4,5-dicyanoimidazole (**2**) which was prepared according to the literature procedure[7-9] (Scheme I).

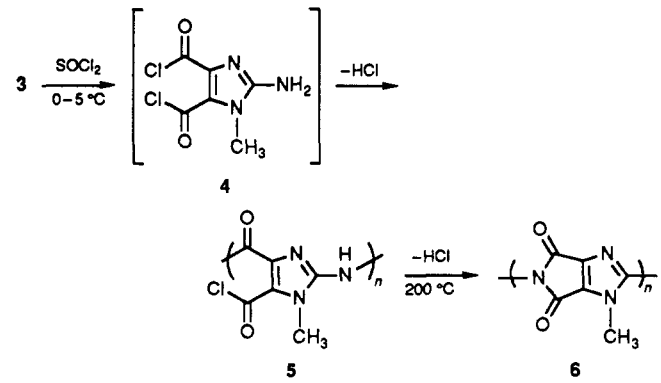
To a 100-mL flask was added **2** (2.72 g) and 6 N NaOH (40 mL). The mixture was refluxed for 2.5 h, then acidified with 3 N HCl (5 mL), and stirred for an additional 2 h at room temperature. The off-white solid was collected, washed with water, and recrystallized from water to give 3.0 g (88%) of **3**. Mp: 190–192 °C. IR (KBr): 3455 (m), 3264 (s), 3111 (s), 1680 (vs), 1582 (vs), 1549 (vs), 1381 (vs) cm^{-1}. MS (EI): m/z 185 (M^+), 141 (100%), 97. Anal. Calcd for $C_6H_7N_3O_4$: C, 38.92; H, 3.78; N, 22.70. Found: C, 38.46; H, 3.79; N, 22.69.

Polymerization. Reaction was carried out at room temperature using excess thionyl chloride in the presence of pyridine by the synthesis route depicted in Scheme II.

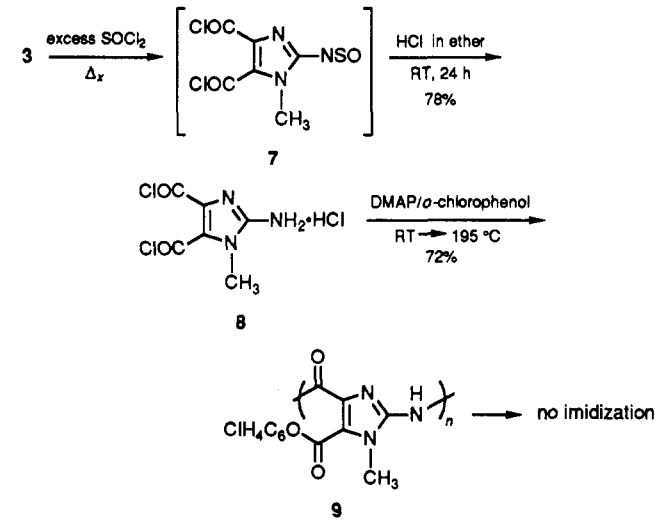
Scheme I



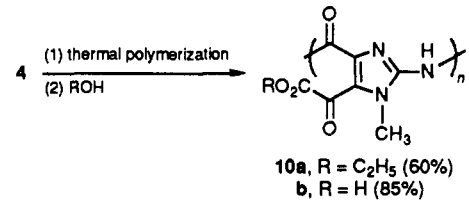
Scheme II



Scheme III



Scheme IV



10a, R = C_2H_5 (60%)
b, R = H (85%)

A 25-mL three-neck flask, equipped with a nitrogen inlet, was charged with 5 mL of thionyl chloride and 0.15 mL of pyridine (1.86 mmol). To this mixture of 0 °C is added 0.10 g of 2-amino-1-methyl-4,5-imidazoledicarboxylic acid. The reaction was stirred at 0–5 °C for 1 h. This solution was filtered under nitrogen into a 25-mL Schlenk flask, and excess thionyl chloride was removed under vacuum. The remaining viscous material was coated onto the surface of the flask and gradually heated to 200 °C under nitrogen for 2 h. The reaction was cooled, and a brown polyimide

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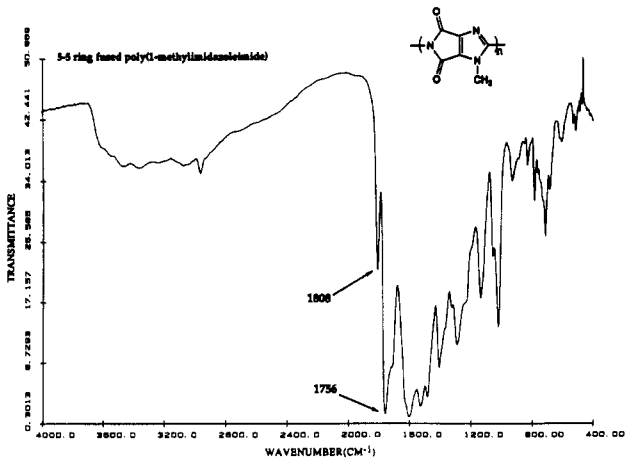

Figure 1. Infrared spectrum of the polyimide.

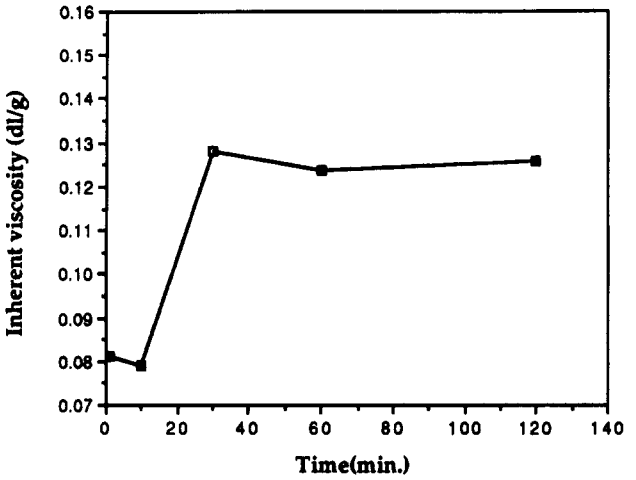

Figure 2. Effect of reaction time on the inherent viscosity at room temperature.

film was removed from the sides of the flask. A total of 0.07 g of the desired polymer (84%) was recovered. IR (film): 3065, 2978, 2940, 1808, 1756, 1601, 1524, 1485, 1405, 1327 cm^{-1} (Figure 1). UV cut-off (20 μm): 418 nm. The film was hydrolyzed in deionized water at room temperature to the corresponding polyamic acid to permit viscosity studies. η_{inh} = 1.52 dL/g at 30 °C for a 0.5 g/dL polymer solution in concentrated CH_3HSO_3. IR (film): 3335, 3118, 3089, 1710, 1558, 1361, 1262, 1038 cm^{-1}. UV cut-off (10 μm): 417 nm. ^1H NMR (DMSO-d_6): δ 3.7 (br, 3 H, s). Anal. Calcd for $C_6H_5N_3O_3$: C, 43.12; H, 2.98; N, 25.14. Found: C, 43.11; H, 2.52; N, 26.49.

Results and Discussion. Our first approach to synthesizing polyimide was to prepare a reactive polyamic ester as a precursor. Polyamic *o*-chlorophenol ester was synthesized from the monomer, 2-amino-1-methyl-4,5-imidazoledicarbonyl chloride hydrochloride, using *o*-chlorophenol as a solvent. The compound was prepared from 3 via 1-methyl-2-(sulfinylamino)-4,5-imidazoledicarbonyl chloride (7), without isolation, by modifying the synthetic method reported by Kwolek et al.[10] The polymer structure as a polyamic *o*-chlorophenol ester was supported by IR, ^1H NMR, and elemental analysis. However, the curing study with **9** at high temperature did not show any evidence of imidization (Scheme III).

Other polyamic acid derivatives such as ethyl ester and acid chloride were synthesized. The preparation of the polyamic acid derivatives was carried out by reacting 3 with excess thionyl chloride and pyridine at low temperature. The low temperature was used to avoid the side

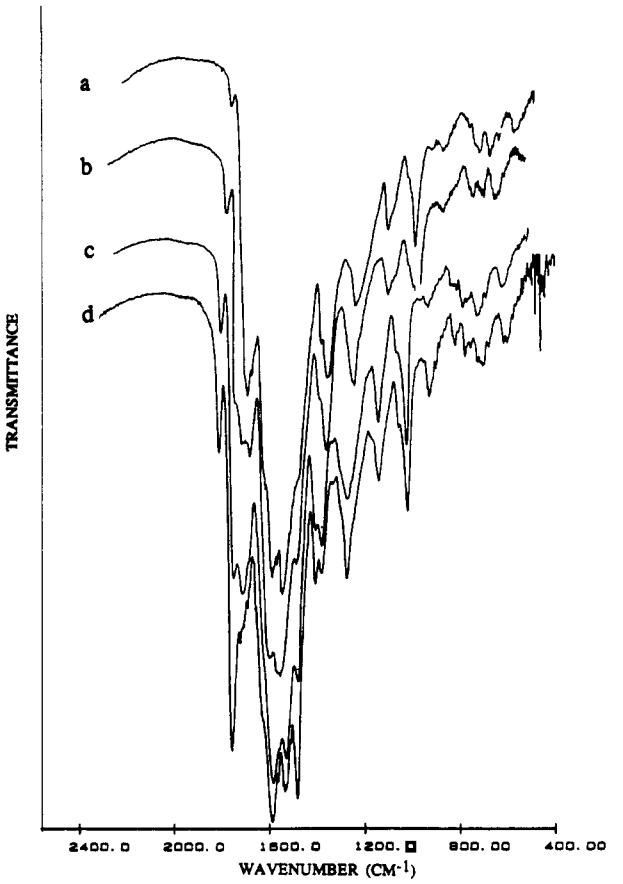

Figure 3. Changes in infrared spectra as a function of the reaction time at room temperature: (a) 10 min, (b) 30 min, (c) 1 h, (d) 2 h.

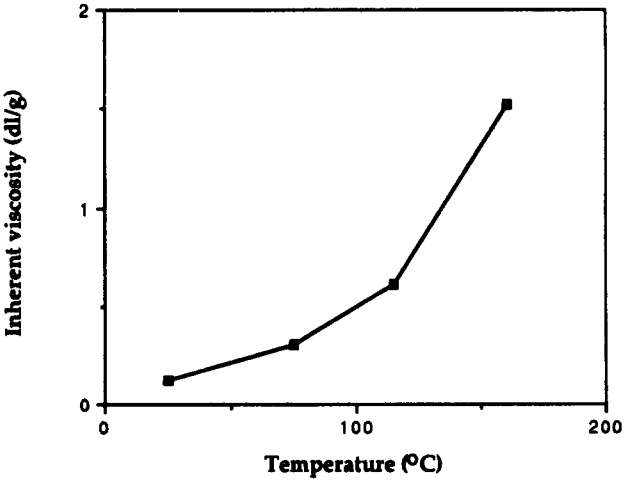

Figure 4. Effect of polymerization temperature on the inherent viscosity.

reaction of the amine group at the 2-position of imidazole with thionyl chloride. After filtering the insolubles and removing the excess thionyl chloride, the remaining material was heated to 120 °C under nitrogen and poured into water or anhydrous ethanol to give the polyamic acid (85%) or polyamic ethyl ester (60%), respectively (Scheme IV). These polymeric materials were characterized by IR, ^1H NMR, and elemental analysis. Thermal imidization attempts of these polymers were unsuccessful. Thermal decomposition occurred in the case of the polyamic ethyl ester, as mentioned before, decarboxylation was observed with the polyamic acid.

Infrared spectroscopy has proven to be a useful technique for following the degree of imidization of polyim-

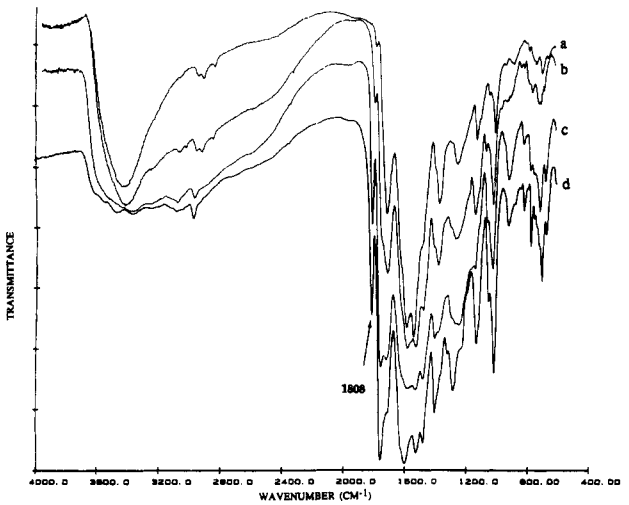

Figure 5. Changes in infrared spectra as a function of polymerization temperature: (a) 25 °C, (b) 75 °C, (c) 120 °C, (d) 180 °C.

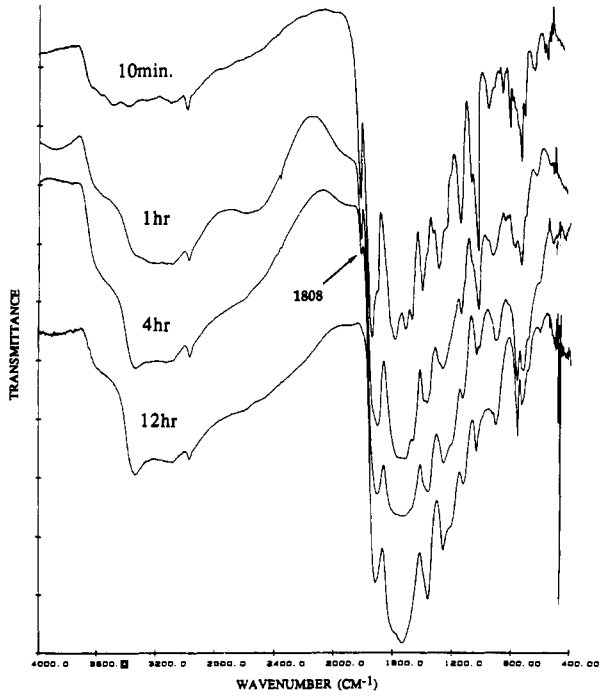

Figure 6. Changes in infrared spectra during hydrolysis at room temperature.

ides.[10] The samples were prepared at room temperature with different reaction times. As shown in Figures 2 and 3, the imidization reaction begins at low temperature and the intensity of the carbonyl stretching peaks at 1808 (antisym) and 1756 (sym) cm^{-1} increases with time. Although the degree of imidization increased continuously, the inherent viscosities of the corresponding polyamic acids reached a maximum after 30 min of reaction. This fact suggests that the molecular weight growth depends on reaction temperature, while intramolecular cyclization of the molecules does not. Figures 4 and 5 show the correlation between the intensity of the carbonyl stretching peak at 1808 cm^{-1} and the molecular weight of the partially imidized polyamic acid as a function of curing temperature. As shown in these figures, molecular weight and the peak intensity of the imide band increased with temperature simultaneously. The highest η_{inh} value, 1.52 dL/g, was obtained from the sample reacted at 180 °C.

Polyimides normally show a relatively low stability toward alkali, acidic aqueous media, and superheated

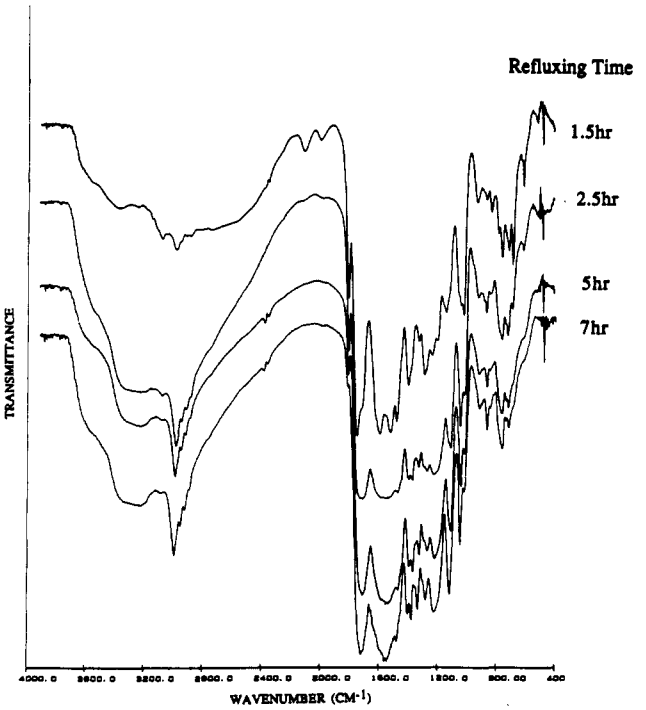

Figure 7. Changes in infrared spectra during ethanolysis at refluxing temperature.

steam.[11] Under these conditions, the carbonyl group in the imide ring is the primary site of hydrolysis. The infrared study of hydrolysis of the polyimide prepared in our laboratory shows that the hydrolysis rate of the imide bond in deionized water is unusually fast possibly due to the implicit strain in fused five-membered rings. The infrared spectrum of hydrolyzed polyimide film does not contain the characteristic imide bands. Hydrolysis of the imide bond was complete in 12 h at room temperature as shown in Figure 6 while ethanolysis was complete in several hours under reflux (Figure 7). The film obtained after hydrolysis was more brittle than the original. This fact implicates hydrolysis of the amide backbone in polyamic acid as well as cleavage of the imide ring.

The polyimide film, upon immersion in 1 N NaOH at 25 °C, swelled and changed color in several hours but retained enough strength to remain as a film. The resultant film was moderately soluble in water but was insoluble in DMF and other polar organic solvents.

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