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Characterization of the One Step Polymide Synthesis

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13. ABSTRACT *(Maximum 200 words)*

The one step high temperature reaction of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 1,5-naphthyl diamine (DAN) in *m*-cresol was investigated using UV-Visible, fluorescence, and Infrared spectroscopy. Results have shown that UV-Visible can be used to monitor the wavelength shift from the diamine to the polyamic acid to the poylimide. Deconvolution of the spectra at various reaction times revealed the composition of amic acid and imide, which were also in good agreement with the Infrared analysis. Fluorescence spectroscopy utilized the fluorescence nature of the diamine to probe the reactivity of the species during the reaction. Early complexation of the diamine was evidenced by the absence of fluorescence emission due to DAN, which then appeared later in time to a maximum of 9.4%. Upon further reaction, DAN is consumed completely, as evidenced by the gradual decline in emission. Investigation of this reaction in NMP with only 10% *m*-cresol at lower temperatures revealed that the apparent rate constants of amic acid formation was actually slower than the controls, 100% NMP as determined by Infrared. However, these laced systems did induce imidization at the lower temperatures.

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Characterization of the One Step Polyimide Synthesis

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Introduction

High temperature heterocyclic polymers, in particular polyimides are based on the reaction of dianhydrides with diamines. Common methods of synthesizing these materials are thermal and chemical imidization. A simple one step thermal method, consisting of a high boiling solvent such as *m*-cresol can be used to aid in the imidization process, bypassing the isolation of the polyamic acid. To take advantage of this process, it is necessary to examine the kinetics and mechanisms of these reactions.

There have been numerous studies reported for the imidization process from the precursor polyamic acid to the polyimide in a variety of solvents[1-5]. However, there have been only few reports on the one step process[6,7].

The objectives of this research were to delineate possible mechanism and the kinetics from the reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 1,5-naphthyl diamine (DAN) in *m*-cresol and to estimate the composition of various components which occur throughout the reaction. Model compounds were used to elucidate the compositions at various times. The reaction was monitored using UV-Visible, fluorescence, and Fourier Transform Infrared (FT-IR) spectroscopy. The conclusions from this study provide a basis for understanding the imidization chemistry in acidic solvents. From this understanding, the optimum processing conditions for the synthesis of polyimides can be made

Experimental

The polymerization was carried out using a stoichiometric mixture of BTDA and DAN in *m*-cresol to yield a 1 wt% reaction solution, under an argon atmosphere, at 210°C. Aliquots were taken at various time intervals and diluted into NMP for UV-Vis and fluorescence analyses via Perkin-Elmer Lambda 6 and Perkin-Elmer MPF66 spectrometers, respectively. Reaction aliquots were analyzed by Infrared using a Mattson Cygnus 100 spectrometer with a resolution of 4 cm^{-1}.

Analogous solutions were made using NMP as the reaction solvent, either with or without the addition of 10% *m*-cresol to the system at temperatures of 25, 30, and 45°C. Aliquots were also taken and analyzed by UV-Vis and fluorescence. Infrared studies were accomplished with a liquid cell sample holder equipped with a temperature controller for in situ analyses of the reaction.

Results and Discussion

Figure 1 represents the overall blue shift of the reaction analyzed during the reaction process. We can see that as the reaction progresses, the absorbing peaks shifts to shorter wavelengths due to an electron withdrawing effect on the amino group of the DAN species. As the reaction proceeds, imide formation would lead to the fartheat blue shift, or shortest wavelength due to the high content of carbonyl linkages, causing an extensive electron withdrawing effect. The amic acid formation is seen at 15 mins as confirmed by deconvolution of the peak by using model compound, diamic acid made from trimellitic anhydride and DAN After the reaction was complete, the spectrum taken revealed a composition of 90% imide as compared by deconvolution and independently confirmed by the FT IR analysis At the later stages of the reaction, the percentage of imide as determined by UV deconvolution and by Infrared seemed to be in good agreement as seen in Table 1 In the fluorescence analysis, the species that was monitored was DAN since all other species, especially BTDA have no appreciable fluorescence. The fluorescence emission spectra exhibits spectral changes early in the reaction An increase and then a decrease in fluorescence intensity of the DAN species was evident Thus indicates that the diamine species is complexed initially and upon reaction time, is freed or dissociated to show fluorescence intensity. At about 15 mins, the intensity reached a maximum of 9.4% DAN species present Later in the reaction, the fluorescence emission from DAN was no longer observed, indicating that the DAN has reacted.

To alleviate the fast kinetics occurring at high temperatures, and to observe the effect of a weak acid, low temperature studies were performed on reactions in which 10% m-cresol was added. Infrared studies revealed polyamic acid formation for the reaction of BTDA and DAN at temperatures such as 25, 30, and 45°C. In addition, imide formation was also evident as indicated by the characteristic C-N absorption at ~1345 cm^{-1} as seen in Figure 2. Controlled experiments in 100% NMP, exhibited amic acid formation, but no imide. These doped experiments seemed to inhibit the rate of BTDA disappearance as compared to the controls as shown in Figure 3. This would suggest some interaction of the acid with either the diamine or the dianhydride. This was evidenced by the salt formation detected for the amine with the *m*-cresol. The weak acid contains a proton which is able to donate to the amine group. This type of complexation would inhibit the reaction with the anhydride, since a nucleophile is necessary to attack the anhydride carbonyl. It is speculated that once the polyamic acid is formed, the weak acid is able to aid in the imidization step. This is a possible explanation for the imide formation seen in IR at such low temperatures. Using classical second order kinetics, the rate constants for the amidation step can be determined. For the reactions containing *m*-cresol, kinetic expressions for a consecutive reaction consisting of a second order reaction followed by a first order behavior was used. Table 2 summarizes these results and illustrates the apparent rate constants (k_1) for the formation of polyamic acid to increase with temperature and to be slower in the *m*-cresol doped cases. UV-Vis spectroscopy confirmed reaction conversion as seen by blue shifts from the reactant component, DAN (λs' at 340 & 350nm). Fluorescence studies revealed a gradual depletion of the DAN species as the reaction time was increased.

Summary

It has been shown that the one step high temperature reaction is complex and reveals many interesting features with the use of *m*-cresol as the reaction solvent. The results have shown that UV-Visible spectroscopy can be used to monitor the wavelength shift from the diamine to the polyamic acid to the polyimide Compositional analysis by Infrared for later stages in the reaction showed good agreement with the UV deconvolution. The conversion of the diamine was also monitored by fluorescence which revealed an initial complexation of the diamine indicative of the absence of fluorescence intensity. Upon reaction time, free diamine was detected to a maximum of 9.4%. This technique shows the sensitivity of detecting diamine in the reaction vessel.

Due to the complexity of this system, it is necessary to determine the nature of the acid, *m*-cresol with respect to the reactants At low temperatures using an in situ method, FT-IR revealed that when 10% *m*-cresol was added to the reaction in NMP, the rate of anhydride disappearance was slower than without *m*-cresol It has also been shown by IR analysis that imide formation and salt formation were occurring even at low temperatures UV Vis analysis of analogous reactions showed blue shifts and double peak maxima as the reaction progressed, supporting the trends observed by IR studies.

Overall, these spectroscopic techniques have so far provided new insight to the understanding of this complex system.

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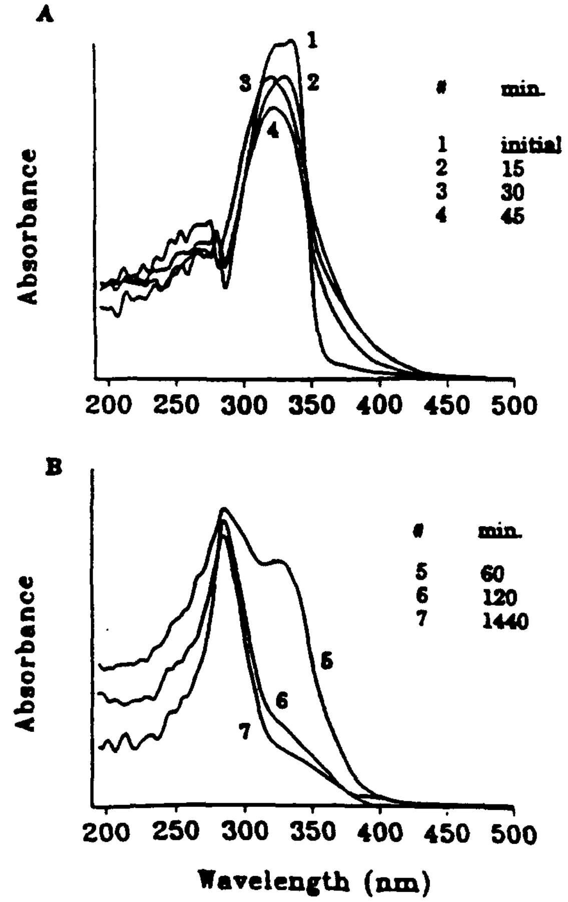

Figure 1 UV-Visible spectral changes for the reaction of DAN and BTDA at 210°C in *m*-cresol.

Table 1 Percentage of imide as determined by UV deconvolution and by Infrared for the reaction at 210°C in *m*-cresol

Time (min)	UV deconvolution	Infrared
60	40	33
90	80	84
120	90	84
1440	90	85
1500	90	95

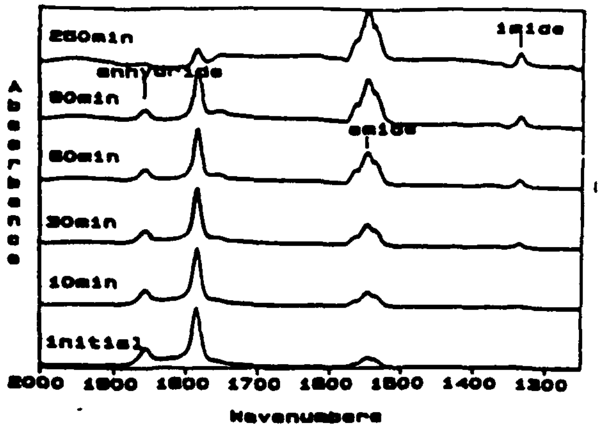

Figure 2 FT-IR spectra of amide and imide formation for the reactionof BTDA & DAN in NMP with 10% *m*-cresol at 25°C.

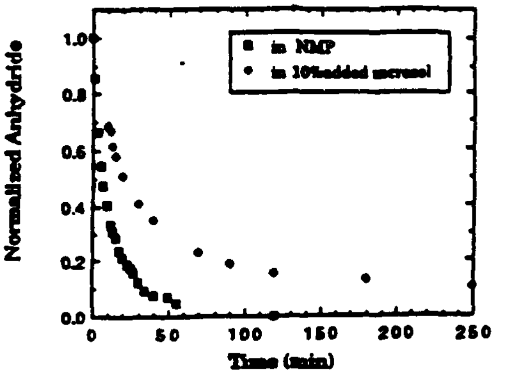

Figure 3 Anhydride disappearance as a function of reaction time of BTDA & DAN at 25°C with or without *m*-cresol added.

Table 2 Apparent rate constants for the imidization reaction under various conditions.

	25°C	30°C	45°C
In NMP			
$K_1(M^{-1}min^{-1})$	5	5	16
Ea(Kcal/mole)	12		
In NMP w/ 10% *m*-cresol			
$K_1(M^{-1}min^{-1})$	0.9	1	4
Ea(Kcal/mole)	14		
$K_2\ (min^{-1})x10^{-3}$	6	29	28

K_1: for the formation of polyamic acid
K_2: for the formation of imide
Ea: activation energy