Studies of the Formation of Polyisoinimides and Their Imidization in Solution State

Young Jun Kim†, Jee Seok Kim, and Kil-Yeong Choi*

Department of Textile Engineering, Sung Kyun Kwan University, Suwon 440-746, Korea
*Advanced Material Division, Korea Research Institute of Chemical Technology, Taejon, Korea

Received August 17, 2001; Accepted September 21, 2001

Abstract: The phthalic anhydride (PA) end-capped polyamic acid was prepared by reacting 4,4'-oxydianiline (4,4'-ODA) with 4,4'-oxydiphtalhydric anhydride (ODPA) and phthelic anhydride (PA) as an end-capper in N-methylpyrroolidine (NMP). Subsequently, the end-capped polyamic acid was cyclo-dehydrated using 1,3-dicyclohexylcarbodiimide (DCC) as a dehydrating agent to form corresponding polyisoinimide. Syntheses of polyisoiimides at five different temperatures of -20 °C, 0 °C, 15 °C, 30 °C and 50 °C were investigated by employing FTIR spectroscopy. The reaction temperature in polyisoinimide synthesis was observed to have a profound effect on the content of polyisoinimide. Thus, the % polyisoinimide increased with decreasing reaction temperature as a result of the fact that polyisoinimide is a kinetically controlled product. The kinetics of thermal imidization of polyisoinimide in solution state was also studied. The thermal imidization of polyisoinimide was well described by the first order kinetics with the activation energy of 76 KJ/mol and the frequency factor of 4.0×10^7 sec⁻¹.

Keywords: polyisoinimide, kinetics, imidization, solution state, kinetically controlled product

Introduction

Aromatic polyimide is one of the most important classes of high-performance polymers. Excellent electrical, thermal, and high temperature mechanical properties make these polymers suitable for applications as high temperature insulators and dielectrics, adhesives and matrices for high performance composites [1-3]. Since most of them show insolubility, infusibility, and thus, poor processability, they are generally processed from the more soluble corresponding polyamic acid precursor form in a high boiling solvent, such as N-methyl-2-pyrroolidone (NMP). Conversion of polyamic acids to polyimides, however, leads to generation of water, which in turn causes the formation of voids or pin holes in the laminates and in the adhesive joints. In an effort to eliminate these drawbacks, polyisoinimides, which can be converted to polyimides without the formation of water, have been utilized as precursors for polyimides [4-7].

Polyisoinimides can be synthesized via cyclodehydration of polyamic acids with suitable dehydrating agents such as 1,3-dicyclohexylcarbodiimide (DCC) [8] and trifluoroacetic anhydride in combination with basic catalysts [9]. However, the fundamental chemistry of polyisoinimide formation is not fully understood primarily due to the complexity of the isoinimide chemistry. Furthermore, little kinetic information on thermal imidization of polyisoinimides is available in the literature, even though it is essential to the optimization and control of the processing of these important materials. In the following paper, we will describe the results of our study on the homogeneous formation of polyisoinimides and their imidization kinetics in solution state.

Experimental

Materials

High-purity 4,4'-oxydianiline (4,4'-ODA) and 4,4'-oxydiphtalhydric anhydride (ODPA) from Chrisskev Co. were vacuum dried before use. Dehydrating agent, dicylclohexylcarbodiimide (DCC), was purchased from
Aldrich and used without further purification. Phthalic anhydride (PA) purchased from Aldrich was purified by sublimation. The solvent, N-methylpyrrolidone (NMP), was distilled from phosphorus pentoxide.

**Polyisoimide Syntheses**

Polyisoimides were synthesized via cyclodehydration of polyamic acids with dehydrating agent 1,3-dicyclohexylcarbodiimide as shown in Figure 1. The number average molecular weights (Mn) of polyamic acids were controlled to theoretical number average molecular weight of 40000 g/mol using Carothers equation. As reported previously [4], end capping the amine groups of polyamic acids is critically important for preventing gelation during the dehydrocyclization step in polyisoimide synthesis. One typical example of polyamic acid synthesis is as follows: 11.7641 g (58.7550 mmol) of 4,4'-ODA was dissolved in 149 g of dry NMP in a reaction flask equipped with a mechanical stirrer, nitrogen inlet, and a drying tube. After the diamine was dissolved, 0.2220 g (1.4991 mmol) of phthalic anhydride was added to the stirring solution of the diamine and was allowed to react with diamine for several minutes. Next, 17.9928 g of ODPA (58.0001 mmol) was added as solid incrementally to the diamine solution such that the previous addition had dissolved before more dianhydride was added and the reaction was allowed to proceed for an additional 15 h at room temperature under nitrogen atmosphere. To the prepared polyamic acid solution, 25.6778 g (124.4502 mmol) of dicyclohexylcarbodiimide was added with stirring and the reaction mixture was stirred for 8 h at 0 °C. The formed solid dicyclohexyl urea was filtered off and the collected polyisoimide solution was poured into a large excess amount of isopropanol. The precipitated polyisoimide was filtered off and dried in vacuum at 60 °C for 24 h and 150 °C for 12 h.

**Thermal Imidization of Polyisoimides**

For kinetic study, the polyisoimide solutions were thermally imidized at constant temperatures of 70 °C, 80 °C, 100 °C, 120 °C, and 130 °C, respectively. The reaction temperature was precisely controlled (±1 °C) using a temperature controller. While the imidization proceeded, reaction samples were withdrawn into sample vials using disposable pipets at defined time intervals and quenched using a dry ice/acetone bath. In order to obtain partially imidized isoimide/imide powder samples, the quenched samples were precipitated into a large excess amount of methanol and dried in vacuum at 25 °C for 24 h for further characterization.

**Fourier Transform Spectroscopy (FTIR)**

Perkin Elmer Spectrum-2000 FTIR spectrometer was used for obtaining spectra of polyisoimide, polyisoimide/imide and polyimide powder (KBr) samples. Analytical bands were those ones centered around 1778 cm⁻¹, 1800 cm⁻¹ and 1500 cm⁻¹ that are assignable to imide carbonyl stretch, isoimide carbonyl stretch, and aromatic double bond stretch, respectively. Even though the isoimide band at 1800 cm⁻¹ was overlapped, in small degree, with the imide carbonyl band at 1778 cm⁻¹, they were resolved into two constituent peaks via the deconvolution process using PE Spectrum V3.02.01 software for obtaining more accurate data.

**Results and Discussion**

**Studies of Polyisoimide Formation Reactions**

The cyclodehydration of polyamic acids can be easily achieved at ambient temperature as shown in Figure 2. It is known, however, that the mechanism of the cyclodehydration is quite complex and the outcome of the reaction could be very different depending on the type of dehydrating agents, monomer components of polyamic acids, reaction temperature, and other factors [9-12]. In our study, the effect of temperature on the dehydration of polyamic acids based upon 4,4'-ODA/ODPA were investigated using dicyclohexylcarbodi-
Figure 2. Polyimide formation and isoiomide/imide isomerization.

Imide as a dehydrating agent.

FTIR spectroscopy was utilized to study polyisoiomide formation reactions. Figure 3 shows the FTIR spectra of polyimide (a) and polyisoiomide (b), respectively. The absorption band centered at 1800 cm⁻¹ is assignable to the carbonyl stretch and that at 905 cm⁻¹ is assignable to the isoiomide ring vibration. For completely imidized sample, characteristic imide carbonyl stretches are shown at 1778 cm⁻¹ and 1724 cm⁻¹. Figure 4 shows the FTIR spectra of the 4,4'-ODA/ODPA polyisoiomide systems synthesized at different temperatures of 20 °C, 0 °C, 15 °C, 30 °C, and 50 °C. These spectra clearly show that the absorbance of the isoiomide peak at 1800 cm⁻¹ increases in intensity with decreasing reaction temperature. The content of polyisoiomide in a given polyimide/polyisoiomide sample can be determined from FTIR spectra. Since 100% pure polyisoiomide sample was not available, the % polyimide was first determined to calculate back the % isoiomide by comparing the intensity of 1778 imide peak of the sample to that of a completely imidized polyimide reference sample that can be considered to be pure polyimide. The content of polyimide in a given sample can be related to the ratio of the area of the imide band at 1778 cm⁻¹ to that of completely imidized sample (in this study, polyamic acid was completely imidized by the well established solution imidization technique [14]). The ratio should, of course, be normalized by dividing its area by that of reference band at 1500 cm⁻¹, whose absorption should be constant throughout the reaction, in order to eliminate the effect of sample thickness (path length in Beer's law). Thus, the content of polyisoiomide in a given sample is given by the following equation.

\[
\text{\% polyisoiomide} = 100 - \left( \frac{A_{1778(\text{sample})}}{A_{1778(\text{reference})}} \right) \left( \frac{A_{1500(\text{sample})}}{A_{1500(\text{reference})}} \right) \tag{1}
\]

where \( A_{1778(\text{sample})} \) and \( A_{1778(\text{reference})} \) are the absorbance at 1778 cm⁻¹ of a sample and a reference that can be considered as a pure polyimide, respectively; \( A_{1500(\text{sample})} \) and \( A_{1500(\text{reference})} \) are the absorbance at 1500 cm⁻¹ of a sample and a reference, respectively. Using equation (1), the contents of polyisoiomides synthesized at five different temperatures were determined and are shown in Figure 5. The % polyimide increases with decreasing reaction temperature, which is consistent with the earlier experimental results observed for the low molecular weight compounds [15]. It also suggests that polyisoiomide is a kinetically controlled product and polyimide is a thermodynamically controlled product. Namely, at low reaction temperature, thermal energy is not sufficient enough to overcome the activation energy required the formation of polyimide.

Kinetic Studies of Thermal Solution Imidization of Polyisoiomides

In order to obtain kinetic parameters the polyisoiomide/imide powder samples obtained at different temperatures were analyzed by FTIR spectroscopy. The extent of imidization at any time can be related to the ratio of the area of the isoiomide band at 1800 cm⁻¹ to its initial area.
Figure 5. The effect of reaction temperature on the formation of polyisimide.

as follows:

\[ p(t) = 1 - \frac{A_{1800}(t)}{A_{1800}(0)} / \frac{A_{1500}(t)}{A_{1500}(0)} \]  

(2)

where \( A_{1800}(t) \) and \( A_{1800}(0) \) are the absorbance at 1800 cm\(^{-1}\) at time \( t \) and zero, respectively; \( A_{1500}(t) \) and \( A_{1500}(0) \) are the absorbance at 1500 cm\(^{-1}\) at time \( t \) and zero, respectively; and \( p(t) \) is the extent of imidization at time \( t \).

Figure 6 and Figure 7 show FTIR spectra of 4,4'-ODA/ODPA poly(isimide/imide) at different imidization stages at 70 °C and 120 °C, respectively. As imidization proceeded, the characteristic isimide peak at 1800 cm\(^{-1}\) decreased in intensity and the imide peak at 1778 cm\(^{-1}\) increased in intensity. As can be seen in Figure 6, the rate of imidization at 70 °C was so slow that only 44% of polyimide was converted to polyimide even after 1290 min (21.5 h). On the other hand, the rate of imidization at 120 °C was so fast that high extent of imidization of 97% was achieved after 330 min (Figure 7).

One of the most conspicuous features of solution imidization of polyisimides is that imidization does proceed at such relatively low temperature as 70 °C. In our previous work studied by differential scanning calorimetry [16], it was demonstrated that thermal imidization of polyimide based upon 4,4'-ODA/ODPA in solid state does not occur below 250 °C possibly due to the restricted chain mobility in solid state.

Since isimide/imide isomerization is an intramolecular reaction, it is quite reasonable to analyze the obtained kinetic data using the following first order kinetic equation.

\[ -\ln(1 - p(t)) = kt \]  

(3)

where \( p(t) \) is the degree of imidization, \( k \) is a rate constant, and \( t \) is the reaction time. The kinetic plot of \( -\ln(1 - p(t)) = kt \) vs. reaction time \( t \) for the 4,4'-

Figure 6. FTIR spectra of 4,4'-ODA/ODPA poly(isimide/imide) at different imidization stages at 70 °C: (a) 0 min; (b) 20 min; (c) 50 min; (d) 60 min; (e) 150 min; (f) 330 min; (g) 630 min; (h) 810 min; (i) 1050 min; (j) 1290 min.

Figure 7. FTIR spectra of 4,4'-ODA/ODPA poly(isimide/imide) at different imidization stages at 120 °C: (a) 0 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 60 min; (g) 90 min; (h) 150 min; (i) 210 min; (j) 330 min.

ODA/ODPA polyimide system is shown in Figure 8. The good linearity shown in the kinetic plot suggests that the kinetics of solution imidization of polyimide could be described by the first-order kinetics. The rate constants determined from the slope of the kinetic plot are summarized in Table 1. The temperature dependence of the rate constant can be expressed by the Arrhenius relation (Eq. 4), which employs frequency factor and activation energy.

\[ k = A \exp\left(\frac{-E_a}{RT}\right) \]  

(4)

where \( A \) is the frequency factor, \( E_a \) the activation energy and \( R \) is the gas constant. Using the obtained rate constants, the Arrhenius plot was generated as shown in
Figure 8. The kinetic plot of $-\ln(1-p(t)) = kt$ vs. reaction time ($t$) for the 4,4'-ODA/ODPA polyimide system.

Table 1. The Rate Constants Derived from First Order Kinetics for 4,4'-ODA/ODPA Polyimide System.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>70</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k(T) \times 10^4$ (sec$^{-1}$)</td>
<td>0.9</td>
<td>2.5</td>
<td>9.6</td>
<td>29.9</td>
<td>55.4</td>
</tr>
</tbody>
</table>

Figure 9. Arrhenius plot of the first order kinetic data for the 4,4'-ODA/ODPA polyimide system.

Figure 9. From the slope and intercept of the plot in Figure 9, the activation energy and the frequency factor were determined to be 76 KJ/mol and $4.0 \times 10^5$ sec$^{-1}$, respectively.

Conclusions

In conclusion, studies of the formation of polyisomidies based upon 4,4'-oxydianiline and 4,4'-oxydiphenallic anhydride and their Thermal Imidization kinetics were performed by FTIR spectroscopy. The content of polyiso-

References