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Thermal and optical characterization of polycyclohexylene cyclohexanedicarboxamides and polyphenyleneterephthalamides and their derivatives

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THERMAL AND OPTICAL CHARACTERIZATION OF
POLYCYCLOHEXYLENE CYCLOHEXANEDICARBOXAMIDES AND
POLYPHENYLENETEREPHTHALAMIDES AND THEIR DERIVATIVES

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
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BY
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The thermal and optical characterization of block copolyamides and their derivatives are described. Differential scanning calorimetry was employed to determine the glass transition temperatures, ($T_g$), and the melting temperatures, ($T_m$). Thermogravimetry was utilized to determine decomposition temperatures, ($T_d$), and polymer stability. The following polymers were used in both studies: poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide); poly(trans-1,4-cyclohexylene-cis,trans-1,4-cyclohexanedicarboxamide); poly(trans-1,2-cyclohexylene-trans-1,4-cyclohexanedicarboxamide); poly(1,4-phenyleneterephthalamide); poly[(2-methyl-1,3-phenylene)terephthalamide]; poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide; 1,4-phenyleneterephthalamide); poly(trans-1,4-cyclohexylene-cis,trans-1,4-cyclohexanedicarboxamide; 1,4-phenyleneterephthalamide); poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide; (2-methyl-1,3-phenylene)terephthalamide); poly[(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide: (2-methyl-1,3-phenylene)terephthalamide]
alamide); poly[trans-1,4-cyclohexylene-cis,trans-1,4-cyclohexanedicarboxamide:
(2-methyl-1,3-phenylene)terephthalamide]; poly [trans-1,2-cyclohexylene-trans-
1,4-cyclohexanedicarboxamide: 1,4-phenyleneterephthalamide]; and poly(2-
methyl-1,3-terephthalamide: 1,4-phenyleneterephthalamide).

Kinetic parameters were determined by the differential Freeman and
Carroll method for the following: poly(trans-1,4-cyclohexylene-trans-1,4-cyclo-
hexanedicarboxamide); poly [trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicar-
boxamide: (2-methyl-1,3-phenylene)terephthalamide]; poly(trans-1,4-cyclohexye-
lene-cis,trans-1,4-cyclohexanedicarboxamide); poly[trans-1,4-cyclohexylene-
cis,trans-1,4-cyclohexanedicarboxamide: (2-methyl-1,3-phenylene)terephthala-
mine]; poly(1,4-phenyleneterephthalamide); poly(trans-1,4-cyclohexylene-trans-
1,4-cyclohexanedicarboxamide: 1,4-phenyleneterephthalamide); poly [(2-methyl-
1,3-phenylene)terephthalamide: 1,4-phenyleneterephthalamide]; and poly(trans-
1,2-cyclohexylene-trans-1,4-cyclohexanedicarboxamide).

Preliminary examinations using polarizing microscopy were performed on
these polymers.
ACKNOWLEDGEMENTS

My greatest appreciation to my advisor, Dr. Kofi B. Bota, for his guidance and support in this research project. In addition, my sincere thanks to Dr. Malcolm Polk for his help when it was needed most. Special thanks to Mr. Fred Okoh for giving so generously of his time. I would like to acknowledge support from the Office of Naval Research (grant number NAG 113).
DEDICATION

To Mrs. Julia M. Robinson, my mother and friend, for her support, respect and love. And to my grandparents, Mr. and Mrs. Henry Montague, for their faith and guidance.
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INTRODUCTION

Analysis of various polymers has become an important area of research in recent years. Several different types of techniques can be utilized to accomplish this analysis, but only the following will be discussed; Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Optical Microscopy. Each of these techniques is individually important in polymer characterization, but combined give a more complete understanding of the polymer.

Modern thermal analysis has become a useful tool in the characterization of polymers in recent years. In the broadest sense, thermal analysis measures changes in physical or chemical properties as a function of temperature. Several instruments have been designed in recent years that produce qualitative and quantitative data. Used in this research was the DuPont 990 Thermal Analyzer with two module attachments; the differential scanning calorimeter and the thermogravimetric analyzer.

The DSC technique records the energy necessary to establish a zero temperature difference between a substance and reference against time or temperature when subjected to identical conditions. These measurements provide both qualitative and quantitative data due to physical or chemical changes in the material. DSC is the measure of the thermal energy per unit time, \( \frac{dQ}{dt} \), transferred in or out of the sample as temperature is linearly changed. This differs from the classic DTA, differential thermal analysis, technique in that it does not measure the temperature difference between reference and sample. The advantages of DSC include increased improvements in precision with rapid
temperature control, in addition to being simple and well suited to the analysis of polymers.\(^4,5\)

Thermogravimetric analysis measures the continuous weight loss of a sample as a result of a programmed increase in temperature.\(^6\) The resultant data, the shape of the thermogram, is used to determine kinetic parameters such as: the activation energy (E), the pre-exponential factor (A), and the rate of reaction.\(^7-8\) TGA can be utilized in the study of thermal stability, the composition of plastics and composites, and polymer identification.\(^9\) The advantages of using TGA over other isothermal techniques include the following:\(^10\)

1. Considerably less data is required.
2. One sample may be used for the entire TGA process.
3. Continuous recording of weight loss versus temperature ensures that no features of the pyrolysis kinetics are overlooked.

This technique has as the one major disadvantage, its difficulty in maintaining precise temperature control.

Due to the numerous types of thermogravimetric balances, literature values have differed, usually in the thermograms or with respect to temperature reaction values. Studies of these discrepancies led to the following factors which affect the results of thermogravimetry.\(^3\)

1. Effects arising from the properties of the construction material used and the nature of the instrument.
   a. Reactions of sample and products with the apparatus.
   b. Sublimation and condensation of reaction products.
   c. Shape, material and size of the crucible.
II. Effects from construction and method of use.
   a. Heat transfer and heating rate.
   b. Recording rate of the curve.
   c. Composition of the atmosphere in the furnace.
   d. Nature of heating.
   e. Sensitivity of the balance.
   f. Method of temperature measurement.

III. Effects of the physical and chemical properties of the sample.
   a. Amount of sample.
   b. Particle size.
   c. Heat of reaction, and thermal conductivity of the sample.
   d. Nature of sample and type of changes that take place.

Polymer stability, which may be regarded as a polymer's resistance to physical and chemical change, has been difficult to accurately define. Inferring the thermal stability of polymers from their structures is not feasible due to the many factors influencing the polymer. The following factors affect the stability of a polymer.

1. bond strength
2. crosslinking
3. low molecular weight, volatile materials (impurities)

Molecular weight distribution and stereochemistry also influence polymer stability.

Many analytical methods have been used in the study of the kinetics of polymer degradation. Proposed methods for the estimation of kinetic
parameters from thermograms are based on the assumptions that thermal and diffusion barriers are minimal. Consider reactions of the single stage type

\[ aA_{(solid)} \rightarrow bB_{(solid)} + cC_{(gas)} \]

the rate of weight loss, \( k \), is given by the Arrhenius equation.\(^{14}\)

\[
k = \frac{dw}{dt} = A w^n e^{-E/RT} \tag{1}
\]

where

\( \frac{dw}{dt} = \) reaction rate (in mg/sec)

\( A = \) pre-exponential factor

\( w = \) weight of remaining sample

\( n = \) reaction order

\( E = \) activation energy

\( R = \) gas constant

\( T = \) temperature (K)

In logarithmic form equation (1) becomes

\[
Ink = \ln\left(\frac{dw}{dt}\right) = \ln A + n \ln w - \frac{E}{RT} \tag{2}
\]

Many methods, integral and differential, have been based on this equation for the determination of \( E \), \( A \) and \( n \). The Freeman and Carroll differential method is primarily used for the determination of the activation energy and the reaction order of simple reactions.\(^{15}\) This method requires only small amounts of data and the kinetics can be studied over the entire temperature range, although determination of slopes is difficult for steep regions of the thermogram.
Equation (2) is separated into two equations in this differential method, where

\[ \log\left(\frac{dw}{dt}\right)_1 = \log A - \frac{E}{2.3R(1/T)}_1 + n\log w_1 \] (3a)

and

\[ \log\left(\frac{dw}{dt}\right)_2 = \log A - \frac{E}{2.3R(1/T)}_2 + n\log w_2 \] (3b)

3a and 3b are at different temperatures. When equation (3a) is subtracted from (3b) the difference equation is obtained;

\[ \Delta \log\left(\frac{dw}{dt}\right) = n\Delta \log w - \frac{E}{2.3R}\Delta (1/T) \] (4)

The use of equation (4) in the determination of kinetic parameters is straightforward. One parameter, usually \( \Delta (1/T) \) due to ease in reading, must be kept constant for proper calculations. From a plot of \( \Delta \log\left(\frac{dw}{dt}\right) \) versus \( \Delta \log w \), the reaction order, \( n \), can be determined from the slope and the energy of activation from the intercept at \( \Delta \log w = 0 \).
EXPERIMENTAL

Apparatus and Procedures

The DuPont 990 Thermal Analyzer with DSC and TGA plug-in modules were the instruments used for all of the analyses.

The 990 Thermal Analyzer, in Fig. 1, has two independent and complete functions. It controls the plug-in thermal analysis modules and it also records the results of their analyses. The two functional units are a temperature programmer-controller, which records the temperature of the sample under analysis, and an X-Y-Y' recorder. Sample property variance, energy absorption or release, weight or dimensional change is recorded on the Y or Y' axis; whereas the sample temperature is recorded on the x axis. Figure 2 is a block diagram of the basic Thermal Analysis (TA) system.

Thermogravimetric System

The DuPont 951 Thermogravimetric Analyzer, shown in Fig. 3, measures the weight and rate of change of weight of the material continuously either as a function of increasing temperature or at a preselected temperature over a period of time. The horizontal design of this module permits other analytical instruments such as the Gas Chromatograph and Mass Spectrometer to be interfaced with the 951 TGA.

The Thermogravimetric Analyzer has three units (see Fig. 4); the Furnace Assembly, the Balance Assembly, and the Cabinet Assembly. The Cabinet Assembly contains the balance operating controls and associated electronic
Fig. 1. 990 Thermal Analyzer.

Fig. 2. Block diagram of a thermal analysis system.
Fig. 3. 951 Thermogravimetric analyzer.

Fig. 4. Thermogravimetric analyzer diagram.
circuits. The Balance Assembly, which is mounted on support rods, has an envelope on each end. The large glass envelope encloses the control end while the other envelope encloses the furnace end of the balance. The Furnace Assembly is a 500 watt external furnace of low thermal mass; therefore, rapid heating and cooling is possible over a temperature range of room temperature to 1200° C. The furnace can be heated at a continuously variable rate of 0.5 to 30° C/min.

The transducer in the 951 Analyzer is a photo-sensitive null detector, which is positioned on one end of the balance. This transducer is composed of a pair of diodes which are arranged in a series. The pivot point of the balance is a taut-band torque motor and the other end of the balance is a quartz rod from which the sample is suspended within a quartz glass envelope.

Sample sizes of 1 mg to 300 mg can be accommodated by the 951 Thermo-gravimetric Analyzer with a sensitivity of 0.3% of full scale. Initial sample weights of 2 to 15 mg were used in this study. Samples were weighed and suspended on the balance and heated at a programmed rate of 10°/min in a nitrogen atmosphere. As the sample weight decreases during programmed heating the balance rotates. The flag is moved so that unequal amounts of light fall on each diode. The resultant e.m.f. is amplified and used as the input for the vertical Y-axis recorder for direct weight percent readout. Sample temperature or time is monitored by the X-axis recorder. All data were recorded on corrected TGA charts from DuPont. The data obtained were used in evaluation of the kinetics of decomposition.

Differential Scanning Calorimetry System

The DuPont 910 Differential Scanning Calorimeter, shown in Fig. 5, may be used for all calorimetric determinations. This system measures both the tempera-
Fig. 5. 910 Differential scanning calorimeter.
ture and the heat changes associated with transitions in materials. Both qualitative and quantitative data on physical and chemical changes in the material involving either endothermic or exothermic processes may be measured. The temperature range of this instrument is $-180$ to $750^\circ$ C.

The measuring cell, in Fig. 6, within the calorimeter has two symmetrical platforms. The sample and reference platforms are heated individually. This is because the heater adjusts continuously in response to thermal effects in the sample. The resistance thermometers and the heating unit in the platform base are the primary temperature control unit for this system. A zero temperature difference between the two platforms is maintained by a secondary temperature control unit by means of a heating current. The amount of heat measured is that necessary to maintain a null temperature difference and is plotted as a function of time or temperature.

The instrument was temperature calibrated with indium ($mp$ 156.6 C). Samples were measured at a rate of $20^\circ$/min at sensitivities of 5-50 mV/cm. Sample sizes of 5 to 10 mg were encapsulated in platinum pans which were hermetically sealed for proper thermal contact. An empty platinum pan was used as a reference in contrast to the classical DTA technique.

**Optical Microscopy**

Saturated solutions of aliphatic and aromatic polymers and their block copolymers were prepared by dissolving the samples in concentrated $H_2SO_4$. A thin layer of the solutions was placed on a microslide and viewed in polarized light at magnifications of 100X - 400X. The Aus Jena Amplival Pol. D. photomicroscope was used in this study.
Fig. 6. DSC cell cross-section.
Materials

The polymer samples used are aliphatic and aromatic polymers and their corresponding block copolymers. All the polymers used in this study were prepared by James Grainger in the research organization of the Department of Chemistry at Atlanta University.
RESULTS AND DISCUSSION

Glass Transition and Melting Temperatures

Differential Scanning Calorimetry was used to determine the glass transition (T_g) and melting (T_m) temperatures. This method detects the T_g and T_m of polymers when a specific heat change is involved.

The glass transition temperature is a narrow temperature range, above which the polymer is rubbery and below which it is glassy. This temperature is a property of the polymer. Below this temperature only vibrational and positional motion of atoms is possible; when the glass transition temperature is reached sufficient energy for segmental and translational motion is supplied.

The glass transition is a second order thermodynamic function. A thermodynamic property such as specific volume or heat capacity exhibits a discontinuity with temperature at the glass transition. Not all polymers have this property.

Factors which influence the glass transition temperature are chain length, chain stiffness, branching, polarity, and attractive forces between molecules. Stiff chain polymers with rigid backbones and bulky side groups have a high T_g. This loss of flexibility results in a reduction in molecular motion unless heated to high temperatures. The glass transition temperature is one of the most significant parameters in the evaluation of a polymer's properties, therefore, it gives an indication of a polymer's usefulness.

Melting is a first order transition in which solid and liquid phases are in equilibrium. Polymers exhibit a melting endotherm over a broad temperature
range due to amorphous regions and a limited degree of crystallinity. All polymers have some amorphous material, therefore, not all have a crystalline melting point.

All of the samples studied in this research were extended chain polyamides which do not melt before decomposition. In addition, no glass transition temperature values were identified for any of the samples due to the structure, chain regularity, high crystallinity or impurities in the various polymers. The DSC thermograms of a number of polymer systems are shown in Figs. 7-9. The polymers are identified in Table 1.

Polymer Stability and Decomposition

The thermal stability in polymers may be expressed by a comparison of the heat resistance of different polymer structures. The decomposition temperature, \( T_d \), is the temperature where thermal or thermochemical degradation occurs. For most linear polymers the \( T_g \) and \( T_m \) values are lower than the decomposition temperature. The reverse occurs in crosslinked or rigid molecules.

The maximum peak of the derivative curve is the decomposition temperature minus 10° C. This subtraction is due to the design of the instrument. Table 1 contains a list of polymers and their decomposition values. Polyamides have a high degree of hydrogen bonding which increases the decomposition temperature. Aromatic polyamides have a higher \( T_d \) than their corresponding aliphatic polyamides. The benzene rings increase their thermal stability. The block copolyamides can have two peaks or one peak in which case the results are additive. \( T_g \) thermograms are shown in Figs. 10-15.
Fig. 7. DSC thermograms of a. ALI-1, b. ALI-2, and c. ALI-3.
Fig. 8. DSC thermograms of a. BLC-3, b. BLC-4, c. BLC-5 and d. BLC-6.
Fig. 8. Continued.
Fig. 9. DSC thermograms of a. ARO-1, b. ARO-2, c. BLC-1 (30), and d. BLC-1(43).
Fig. 9. Continued.
Table 1. Decomposition Temperatures ($T_d$) of Aromatic and Aliphatic Polyamides and Block Copolyamides.

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<tr>
<th>Polymer</th>
<th>Code Name</th>
<th>$T_d$ (°C)</th>
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<tbody>
<tr>
<td>Poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide)</td>
<td>ALI-1</td>
<td>480</td>
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<tr>
<td>Poly(trans-1,4-cyclohexylene-cis,trans-1,4-cyclohexanedicarboxamide)</td>
<td>ALI-2</td>
<td>485</td>
</tr>
<tr>
<td>Poly(trans-1,2-cyclohexylene-trans-1,4-cyclohexanedicarboxamide)</td>
<td>ALI-3</td>
<td>425</td>
</tr>
<tr>
<td>Poly(1,4-phenyleneterephthalamide)</td>
<td>ARO-1</td>
<td>535</td>
</tr>
<tr>
<td>Poly[(2-methyl-1,3-phenylene)terephthalamide ]</td>
<td>ARO-2</td>
<td>435</td>
</tr>
<tr>
<td>Poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide: 1,4-phenyleneterephthalamide)</td>
<td>BLC-1</td>
<td>565</td>
</tr>
<tr>
<td>Poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide: 1,4-phenyleneterephthalamide)</td>
<td>BLC-1</td>
<td>515, 550</td>
</tr>
<tr>
<td>Poly(trans-1,4-cyclohexylene-cis,trans-1,4-cyclohexanedicarboxamide: 1,4-phenyleneterephthalamide)</td>
<td>BLC-2</td>
<td>440</td>
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Table 1. Continued.

<table>
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<th>Polymer</th>
<th>Code Name</th>
<th>$T_d$ ($^\circ$C)</th>
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<tr>
<td>Poly [trans-1,4-cyclohexylene-trans-1,4-cyclohexane-dicarboxamide:</td>
<td>BLC-3</td>
<td>555</td>
</tr>
<tr>
<td>(2-methyl-1,3-phenylene)terephthalamide]</td>
<td></td>
<td></td>
</tr>
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<td>Poly [trans-1,4-cyclohexylene-cis,trans-1,4-cyclohexane-dicarboxamide:</td>
<td>BLC-4</td>
<td>490</td>
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<td>(2-methyl-1,3-phenylene)terephthalamide]</td>
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<td></td>
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<td>Poly (trans-1,2-cyclohexylene-trans-1,4-cyclohexane-dicarboxamide:</td>
<td>BLC-5</td>
<td>425, 535</td>
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<tr>
<td>1,4-phenyleneterephthalamide)</td>
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<td></td>
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<tr>
<td>Poly[(2-methyl-1,3-phenylene)terephthalamide:</td>
<td>BLC-6</td>
<td>555</td>
</tr>
<tr>
<td>1,4-phenyleneterephthalamide ]</td>
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Fig. 10. TGA thermograms of a. ALI-1 and b. ALI-2.
Fig. 11. TGA thermograms of a. ALI-3 and b. ARO-1.
Fig. 12. TGA thermograms of a. BLC-1(30) and b. BLC-1(43).
Fig. 13. TGA thermograms of a. BLC-2 and BLC-3.
Fig. 14. TGA thermograms of a. BLC-4 and b. BLC-5.
Fig. 15. TGA thermograms of a. ARO-2 and b. BLC-6.
Kinetics

Determination of the decomposition temperature is necessary for the characterization of these polymers. Freeman and Carroll's differential method is used to determine the kinetic parameters for the polymer comparisons. This expression,

$$\frac{dw}{dt} = A w^n e^{-E/RT}$$

is the parent form for all calculations. Graphs of $w$ and $dw/dt$ at constant $\Delta (1/T)$ were plotted (see Figs. 16 and 17). Parameters $n$, $A$ and $E$ were determined by plotting $\Delta \log dw/dt$ versus $\Delta \log w$ at constant $\Delta(1/T)$ and the use of equation 4. The activation energy, $E$, is found from the intercept at $\Delta \log w = 0$ and the order of reaction, $n$, from the slope. The third parameter, the pre-exponential factor, $A$, is calculated by substitution of values into equation 2. Due to the steepness of the thermograms much scatter in the data points was present. Plots of $\Delta \log dw/dt$ versus $\Delta \log w$ for several polymers are presented in Figs. 18-21.

The TGA thermograms of the polymer samples all have the same type of downward slope at the beginning of the heating process, instead of the expected horizontal pathway until sample decomposition. This result can be attributed to atmospheric water that the samples picked up during transferring processes. This problem is correctable by heating the sample to approximately $150^\circ$ C, a temperature above the b.p. of water; then cooling the instrument and starting the process as usual to completion.

Table 2 lists kinetic parameters for eight samples: ALI-1, ALI-2, ALI-3, ARO-1, BLC-1, BLC-3, BLC-4 and BLC-6. All the aliphatic polyamides have their
Fig. 16. Graph of $w$ vs. $1/T$ for ALI-2.
Fig. 17. Graph of $dw/dt$ vs. $1/T$ for ALI-2.
Fig. 18. Graph of $\Delta \log dw/dt$ vs. $\Delta \log w$ for ALI-1.
Fig. 19. Graph of $\Delta \log dw/dt$ vs. $\Delta \log w$ for ALI-3.
Fig. 20. Graph of $\Delta \log \frac{dw}{dt}$ vs. $\Delta \log w$ for BLC-3.
Fig. 21. Graph of $\Delta \log \frac{dw}{dt}$ vs. $\Delta \log w$ for BLC-6.
Table 2. Kinetic Parameters.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Code</th>
<th>Order of Rxn(n)</th>
<th>Activation Energy (E) (kJ mol(^{-1}))</th>
<th>Pre-exponential factor (A) (min(^{-1}))</th>
<th>(\frac{1}{T}) (K(^{-1})X10(^{-2}))</th>
<th>(T_d) (°C)</th>
<th>(\eta_{inh})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide)</td>
<td>ALI-1</td>
<td>1.02</td>
<td>63</td>
<td>2.41 X 10(^4)</td>
<td>0.005</td>
<td>480</td>
<td>0.76</td>
</tr>
<tr>
<td>Poly [trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide: (2-methyl-1,3-phenylene)terephthalamide]</td>
<td>BLC-3</td>
<td>3.81</td>
<td>46</td>
<td>3.19 X 10(^{-4})</td>
<td>0.003</td>
<td>555</td>
<td>0.40</td>
</tr>
<tr>
<td>Poly(trans-1,4-cyclohexene-cis,trans-1,4-cyclohexanedicarboxamide)</td>
<td>ALI-2</td>
<td>1.33</td>
<td>56</td>
<td>1.05 X 10(^3)</td>
<td>0.005</td>
<td>485</td>
<td>0.64</td>
</tr>
<tr>
<td>Poly[trans-1,4-cyclohexene-cis,trans-1,4-cyclohexanedicarboxamide: (2-methyl-1,3-phenylene)terephthalamide]</td>
<td>BLC-4</td>
<td>0.947</td>
<td>27</td>
<td>6.97 X 10(^1)</td>
<td>0.005</td>
<td>490</td>
<td>0.57</td>
</tr>
<tr>
<td>Polymer</td>
<td>Code</td>
<td>Order of Rxn(n)</td>
<td>Activation Energy (E) (kJ mol(^{-1}))</td>
<td>Pre-exponential factor (A) (min(^{-1}))</td>
<td>1/T (K(^{-1})X10(^{-2}))</td>
<td>T(_d) (°C)</td>
<td>(\eta_{inh})</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td>----------------</td>
<td>-----------------------------------------</td>
<td>--------------------------------------------</td>
<td>--------------------------------</td>
<td>--------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Poly(1,4-phenylene-terephthalamide)</td>
<td>ARO-1</td>
<td>0.877</td>
<td>18</td>
<td>2.41 X 10(^1)</td>
<td>0.003</td>
<td>535</td>
<td>0.36</td>
</tr>
<tr>
<td>Poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedicarboxamide: 1,4-phenylene-terephthalamide)</td>
<td>BLC-1</td>
<td>0.900</td>
<td>33</td>
<td>3.95 X 10(^2)</td>
<td>0.003</td>
<td>515</td>
<td>0.78</td>
</tr>
<tr>
<td>Poly(2-methyl-1,3-phenylene)terephthalamide: 1,4-phenyleneterephthalamide)</td>
<td>BLC-6</td>
<td>2.73</td>
<td>63</td>
<td>1.65 X 10(^0)</td>
<td>0.005</td>
<td>555</td>
<td>0.91</td>
</tr>
<tr>
<td>Poly(trans-1,2-cyclohexylene-trans-1,4-cyclohexanedicarboxamide)</td>
<td>ALI-3</td>
<td>0.736</td>
<td>30</td>
<td>7.06 X 10(^2)</td>
<td>0.005</td>
<td>425</td>
<td>0.14</td>
</tr>
</tbody>
</table>
parameters listed. They are very similar in structure with these exceptions: ALI-2 has a cis-trans junction and ALI-3 has its nitrogen groups adjacent. The cis and trans forms have similar decomposition temperatures, whereas ALI-3's is much lower as shown in Table 1. All three samples show a reaction order of approximately unity. The largest dissimilarity in these samples is the inherent viscosity, ALI-1 and ALI-2 have values of 0.756 and 0.64 respectively, but the value for ALI-3 is 0.136. The activation energies and pre-exponential factors decrease with decreasing inherent viscosity values. This difference supports the proposed molecular weight differences in these samples. The aromatic polyamide, ARO-1, has a reaction order of 1. The activation energy, pre-exponential factor and inherent viscosity values are low, but this polymer is very stable as can be seen by its symmetry and decomposition temperature. The block copolymers BLC-1, BLC-3, BLC-4 and BLC-6 are all synthesized in homogeneous polymerization systems. Two samples, BLC-4 and BLC-1, have reaction orders of unity, whereas the other two block copolymers have values of about three. BLC-1 has an aliphatic and aromatic block, whereas BLC-6 is completely aromatic. Both have good stability as shown by their decomposition temperatures and inherent viscosities. There is an inverse type relationship between their activation energies and pre-exponential factors which can be explained due to the difference in their reaction orders. BLC-3 and BLC-4 have the same general structure but BLC-4 has a cis junction which makes it less stable. This stability difference is a factor in the kinetic parameter values. BLC-3 has a reaction order of unity whereas BLC-4 has a value of over three. The inherent viscosity and pre-exponential factor of BLC-4 are higher than BLC-3, but the activation energy and the decomposition temperature of BLC-3 are larger than the values of BLC-4.
The most influential factor seems to be the reaction order, which affects the other kinetic parameters.

**Optical Microscopy**

Preliminary work on these samples for the determination of crystallinity was done. Further study of these polymers using polarizing microscopy is recommended for more structural insight.

**Calculation of E and A**

A sample calculation of E and A (see Fig. 18) is shown below:

\[
(1/T) = 0.005 \times 10^{-2}
\]

From equation (4),

\[-E/2.3R \times (1/T) = \text{intercept}\]
\[-E/(2.3 \times 8.314\text{JK}^{-1}\text{mol}^{-1}) \times (0.005 \times 10^{-2}) = \text{intercept}\]
\[-(0.005 \times 10^{-2})E/(19.1222\text{JK}^{-1}\text{mol}^{-1}) = -0.1659772\]
\[-(0.005 \times 10^{-2})E = -3.1738402\text{JK}^{-1}\text{mol}^{-1}\]
\[E = -(3.1738492\text{JK}^{-1}\text{mol}^{-1})/(-0.005 \times 10^{-2}) = 6.3477 \times 10^{4}\text{JK}^{-1}\text{mol}^{-1}\]

The value of A can be calculated from equation (2),

\[\ln 103 = \ln A + 1.02 \ln 98 - (63477\text{JK}^{-1}\text{mol}^{-1}/8.314\text{JK}^{-1}\text{mol}^{-1} \times 753\text{K})\]
\[4.63 = \ln A + 4.67 - 10.14\]
\[4.63 = \ln A - 5.46\]
\[\ln A = 10.09\]
\[A = 2.41 \times 10^{4}\text{min}^{-1}\]
other $E$ and $A$ values were calculated in the same manner. For the calculation of the $A$ values $dw/dt$, $w$ and $T$ were at the decomposition temperature.
CONCLUSION

The Freeman and Carroll method is best suited for the study of kinetics of simple reactions. Such reactions are essentially of first order kinetics. Other integral and differential methods give more accurate results for complex degradation reactions with higher orders of reaction. The kinetic parameters reported in Table 2 represent the best results obtainable using the Freeman and Carroll method. All the polymer samples with reaction order other than unity in Table 2 may not have been truly characterized by the method employed in this investigation. This limitations of the Freeman and Carroll method could be averted by a more comparative study. For purposes of further study, it will be necessary to use other integral and differential methods to characterize these polymers. Therefore, a conclusion could not be made for the true magnitude of all the kinetic parameters tabulated in Table 2.

Suffice to say that on the basis of the accuracy of the Freeman and Carroll method and other physical and chemical properties of the polymers studied; that an objective kinetic characterization has been achieved for the useful assessment of the stability and end use of these polymers.
REFERENCES


2. "Determination of Purity by Differential Scanning Calorimetry", Thermal Analysis Newsletter, No. 5, Perkin-Elmer Corporation, Norwalk, CT.


