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**POLYIMIDES WITH PENDANT ALKYL GROUPS**

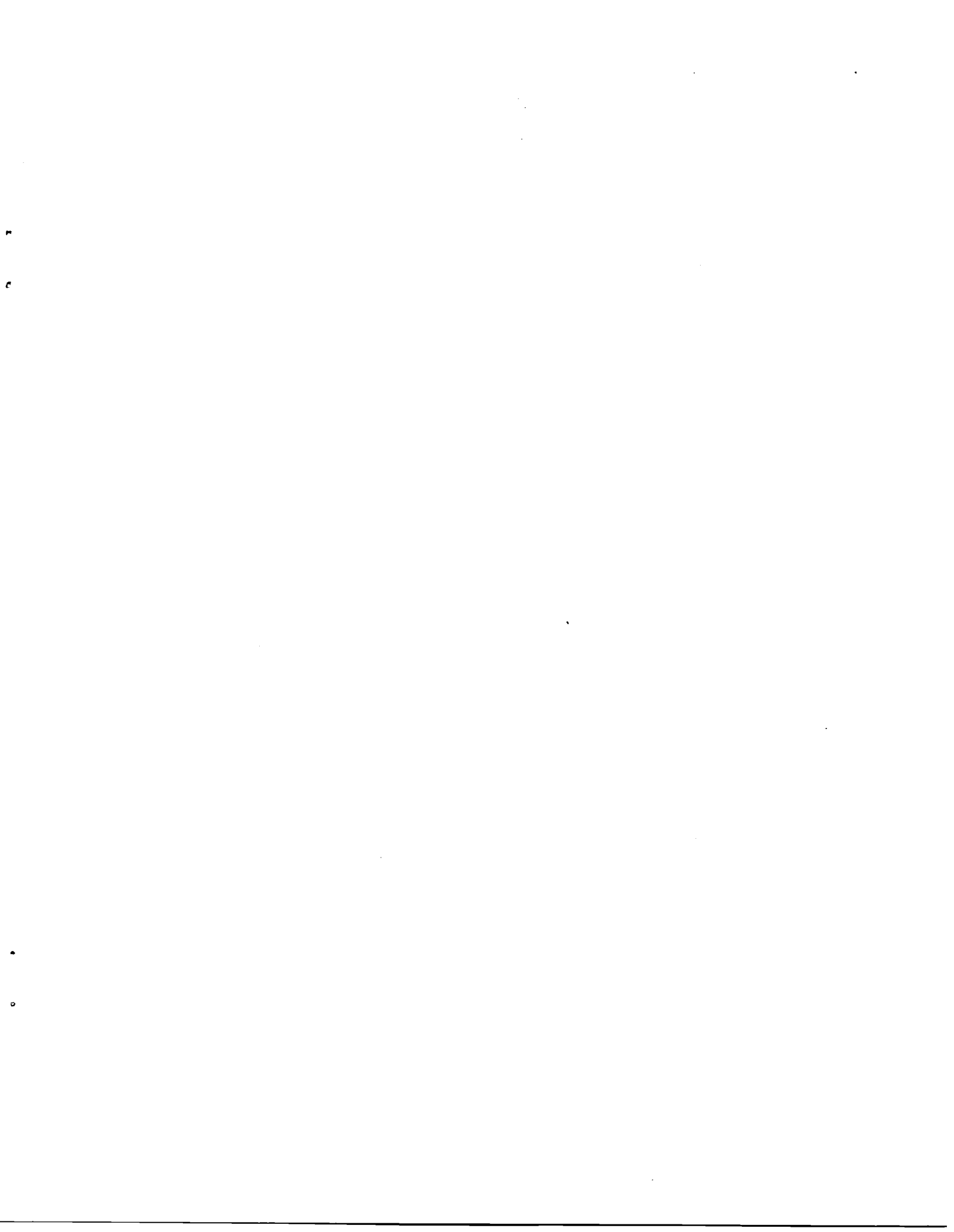
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## INTRODUCTION

Aromatic polyimides have potential for extended use in various aerospace applications provided they can be reliably processed into useful articles. However, inherent problems with solubility, high glass transition temperature ( $T_g$ ), and the evolution of volatiles during cure must be solved before this potential can be fully exploited. Several approaches have been taken to alleviate some of the difficulties associated with processability. Addition polyimides are being developed which are processed as oligomeric segments and then thermally cured through reactive end groups without the evolution of volatiles<sup>1-3</sup>. Stereoisomeric variations have been built into the polymer backbone and the effect on polymer properties determined<sup>4</sup>. Pendant phenyl groups were added to the polymer backbone in an effort to improve solubility<sup>5</sup>. Numerous other structure-property relationships have been explored.

The objective of the present research was to investigate the effect on selected properties when alkyl groups of various lengths were attached pendant to the polyimide backbone. The eight variations studied are shown in Figure 1. The polyimide with no pendant group was included as a control. Although the data obtained

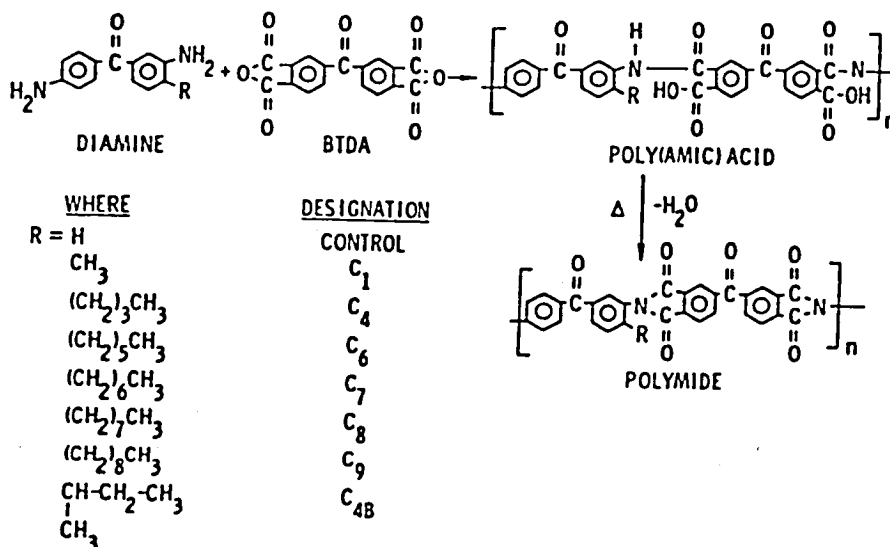


Figure 1. Polyimide synthetic scheme.

in this study was somewhat limited by the amount of sample available, fundamental information was gained on how particular variations in molecular structure affected such properties as  $T_g$ , thermal stability, and toughness.

## EXPERIMENTAL

### Characterization

Analytical chromatographic separations were obtained on a Waters Associates ALC/GPC-244 HPLC. Analyses were performed at 254 nm on either a Waters  $\mu$ Porasil or  $C_{18}$  -  $\mu$ Bondapak column (3.9 mm id x 30 cm). Preparative separations were obtained on a Waters Prep LC/System 500 using a Prep PAK-500/Silica column and a refractive index detector. Gel permeation chromatography was performed on a  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$  Å  $\mu$ Styragel column bank. The mobile phase for all separations was prepared from chromatographic grade methylene chloride, methanol, 1-propanol, water, or N,N'-dimethylacetamide (DMAc). Poly(amic) acid inherent viscosities ( $\eta_{inh}$ ) were measured at 0.5% concentration in DMAc at 35°C with a Cannon-Ubbelohde viscometer.

Thermal analyses were performed on a DuPont Model 990 Thermal Analyzer in combination with a standard differential scanning calorimetry (DSC) cell. Thermomechanical analyses (TMA) were performed on films in combination with a DuPont Model 940 Thermomechanical Analyzer. Torsional Braid Analyses (TBA) were performed using an in-house system<sup>6</sup> on glass braids impregnated with a 5% poly(amic) acid solution in DMAc and cured in vacuum at 100°C, 200°C, and 275°C for one hour each. Thermogravimetric analyses (TGA) were obtained on approximately 2 mg film samples with a Perkin-Elmer TGS-2 instrument in 15 cm<sup>3</sup>/min flowing air.

Infrared spectra of monomers were obtained on KBr pellets with a Perkin-Elmer Model 297 Spectrophotometer. Spectra of polymeric films were recorded on a Nicolet 3600A FTIR System. Elemental analyses of monomers, shown in Table I, were performed by Galbraith Laboratories, Knoxville, Tennessee.

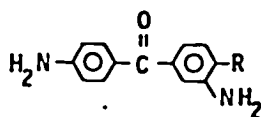
Mechanical properties were measured on an Instron Tensile Tester at a crosshead speed of 0.2 in/min and a gauge length of 3.0 in. Five one-inch wide and nominally one-mil thick film specimens were tested for each sample.

### Monomers

The monomer 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) was obtained from commercial sources and vacuum sublimed prior to use.

Table I.

## ELEMENTAL ANALYSIS OF DIAMINE MONOMERS



EMPERICAL FORMULA	PENDANT GROUP	%C		%H		%N	
		CALC.	FOUND	CALC.	FOUND	CALC.	FOUND
C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O	H	73.57	73.44	5.70	5.71	13.20	13.01
C <sub>17</sub> H <sub>20</sub> N <sub>2</sub> O	C <sub>4</sub>	76.09	75.92	7.51	7.61	10.44	10.39
C <sub>17</sub> H <sub>20</sub> N <sub>2</sub> O	C <sub>4B</sub>	76.09	76.24	7.51	7.64	10.44	10.60
C <sub>19</sub> H <sub>24</sub> N <sub>2</sub> O	C <sub>6</sub>	76.99	77.07	8.16	8.21	9.45	9.51
C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O	C <sub>7</sub>	77.38	77.54	8.44	8.22	9.02	9.00
C <sub>21</sub> H <sub>28</sub> N <sub>2</sub> O	C <sub>8</sub>	77.74	77.87	8.70	8.83	8.63	8.64
C <sub>22</sub> H <sub>30</sub> N <sub>2</sub> O	C <sub>9</sub>	78.05	78.24	8.95	9.00	8.28	8.29

Diamines were obtained from several sources. The *m,p'*-diaminobenzophenone (control) was synthesized by a previously reported method<sup>4</sup> and purified by recrystallization from benzene, toluene, and finally benzene. The *p*-methyl-*m,p'*-diaminobenzophenone monomer (C<sub>1</sub>) was synthesized by the scheme shown in Figure 2. This synthetic scheme was typical for all diamines included in the study. The acid chloride I was reacted via a Friedel-Crafts acylation with toluene and the resulting compound II nitrated in mixed nitric and sulfuric acids. The dinitro compound III was reduced by catalytic hydrogenation at 50 psi with a 5% platinum on carbon catalyst yielding 35-40% of compound IV. The remaining product formed appeared to be a hydrate. Compound IV was purified by preparative liquid chromatography after unsuccessful recrystallization attempts. The *p*-sec-butyl-*m,p'*-diaminobenzophenone (C<sub>4B</sub>) was prepared on a grant<sup>7</sup> with the Mississippi University for Women, Dr. J. Richard Pratt, Principle Investigator. It was purified by recrystallizing twice from benzene/cyclohexane. Five diamines were prepared on a grant<sup>8</sup> with the University of Southern Mississippi, Dr. Shelby F. Thames, Principle Investigator. Butyl (C<sub>4</sub>) and nonyl (C<sub>9</sub>) monomers were polymer grade as received while the other three (C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>) were purified by preparative liquid chromatography.

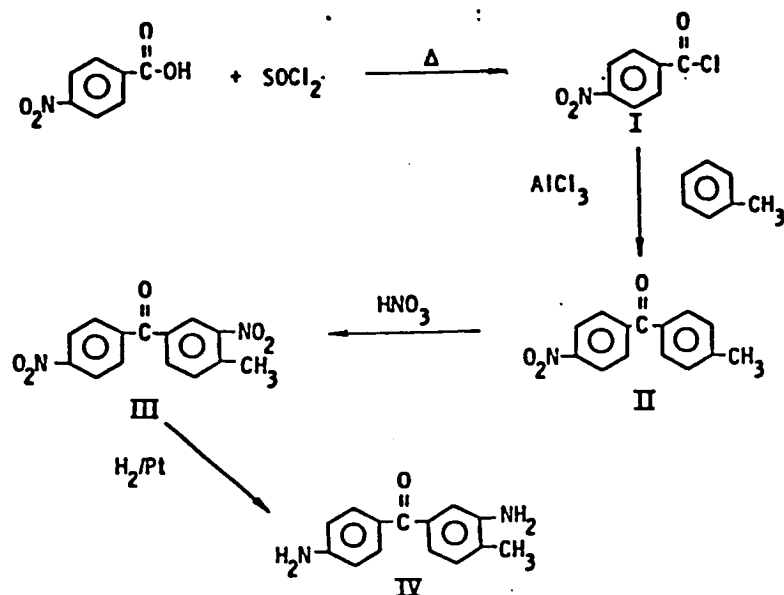


Figure 2. Synthetic scheme for C<sub>1</sub> diamine (R=CH<sub>3</sub>).

#### Polymers and Film Preparation

Polymers were synthesized by solution polymerization in DMAC distilled over calcium hydride and stored under nitrogen. Polymerizations were run for 24 hr at 25°C and 15% solids content in a dry serum bottle equipped with a rubber stopper and a magnetic stirring bar. No attempts were made to increase viscosity other than by monomer purification. Solutions were stored at approximately -10°C until use.

Poly(amic) acid solutions were spread on glass plates using a doctor blade set at 15 mil. Films were dried overnight in a flowing-air dry box at 25°C. Each film was then cured in vacuum for one hour each at 100°C, 200°C, and 280°C. Three other films were cured in air for one hour each at 100°C, 200°C, and 300°C. Resultant films were approximately 1-mil thick.

## RESULTS AND DISCUSSION

The primary concern in the polymer synthesis was whether sufficiently high molecular weight polymer could be obtained to cast films. Therefore, high purity monomers were essential to eliminate the possibility of impurities limiting polymer molecular weight. Since the pendant groups were adjacent to the amine reactive site, steric hindrance was also considered a potential problem. The C<sub>4B</sub> (branched) diamine was included to further investigate this area of concern.

Recrystallization was the first method employed to purify the diamine monomers. If this was unsuccessful, vacuum sublimation was utilized. Monomers that were still unacceptable were further purified by preparative liquid chromatography. Monomers were subjected to both normal and reverse phase chromatography to test for purity. Figure 3 is an example of normal phase chromatography on the C<sub>6</sub> diamine, as received and after purification by preparative chromatography. Infrared spectra were consistent with the corresponding structures and were essentially identical except for increasing absorption with increasing alkyl group length from 2930 cm<sup>-1</sup> to 2850 cm<sup>-1</sup>.

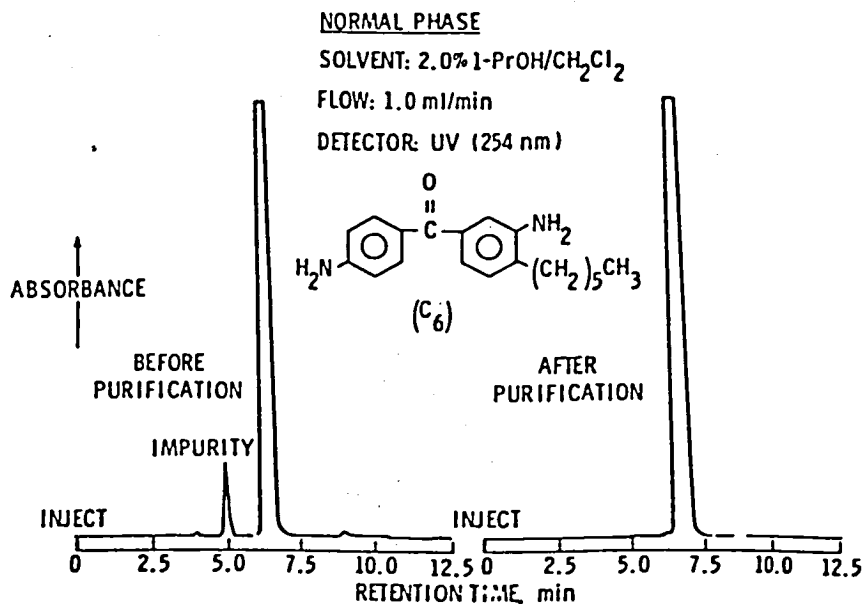


Figure 3. High pressure liquid chromatography of C<sub>6</sub> diamine before and after purification.

After obtaining the purest monomers possible, polymerizations were run on approximately one gram of each monomer. Although the control diamine was the only monomer less than 99% pure, it produced the highest viscosity polymer. The C<sub>4B</sub> diamine produced polymer with inherent viscosity ( $\eta_{inh}$ ) of 0.19 dl/g and the C<sub>1</sub> diamine produced polymer of only 0.31 dl/g viscosity. The C<sub>4B</sub> polymer was possibly limited by steric hinderence. This did not apply to the C<sub>1</sub> polymer. The latter polymerization was repeated with the same results. Neither of these two polymers could be included in much of the testing since they would not form flexible films. However, one polymerization of the C<sub>9</sub> diamine which resulted in polymer with  $\eta_{inh} = 0.28$  dl/g did form a usable film. Figure 4 shows gel permeation chromatograms of the poly(amic) acids along with corresponding  $\eta_{inh}$ . As expected, a decrease in elution time with increasing  $\eta_{inh}$  is observed.

Characterization of the polymers in the cured imide form included infrared analysis on film samples which exhibited the same trend as the monomers, increased absorption in the 2930 cm<sup>-1</sup> - 2850 cm<sup>-1</sup> region as the pendant groups increased in length. This data also confirmed that imidization had taken place during cure by the appearance of characteristic imide absorptions at 1780 cm<sup>-1</sup>, 1730 cm<sup>-1</sup>, 1380 cm<sup>-1</sup>. and 720 cm<sup>-1</sup>. No significant difference in the IR spectra for air cured and vacuum cured films of the same polymer was noted.

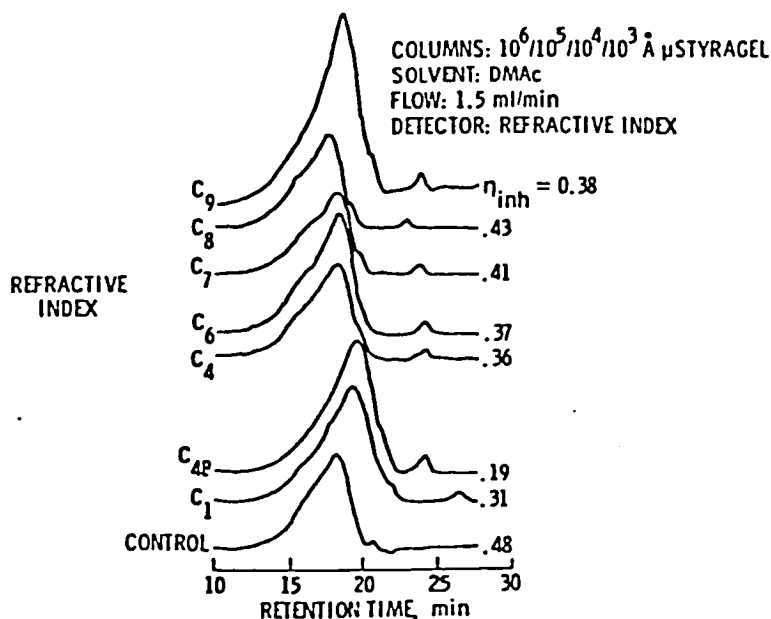


Figure 4. Gel permeation chromatography of poly(amic) acid solutions.



One objective of this project was to study the effect the variation in diamine structure had on polymer  $T_g$ . Therefore,  $T_g$  was measured by several techniques. Torsional braid analyses data are summarized in Figure 5. The damping peak maximum and the corresponding loss of rigidity are indicative of polymer  $T_g$ . Vacuum cured polyimides showed a decrease in  $T_g$  as the alkyl group increased in length. For the  $C_9$  polyimide, a decrease of approximately  $60^\circ\text{C}$  from that of the control ( $T_g = 274^\circ\text{C}$ ) was noted. Further evidence for the decrease in  $T_g$  is shown in Figure 6 by DSC thermograms of vacuum cured films. Figure 7 gives the same trends by thermomechanical analysis. The opposite trend in  $T_g$  was observed for air cured samples. Although the effect of air cure was not as dramatic, a  $20^\circ\text{C}$  increase in  $T_g$  for the  $C_9$  polyimide over the control was noted. This data is summarized in Figure 8. An increase in  $T_g$  is probably indicative of air induced crosslinking. Apparently, the longer pendant group polyimides crosslinked to a greater extent than the shorter pendant chain polymers. This data suggests the possibility of varying the  $T_g$  of a polyimide over a wide temperature range by varying the length of an alkyl group pendant to the backbone and by choice of cure atmosphere.

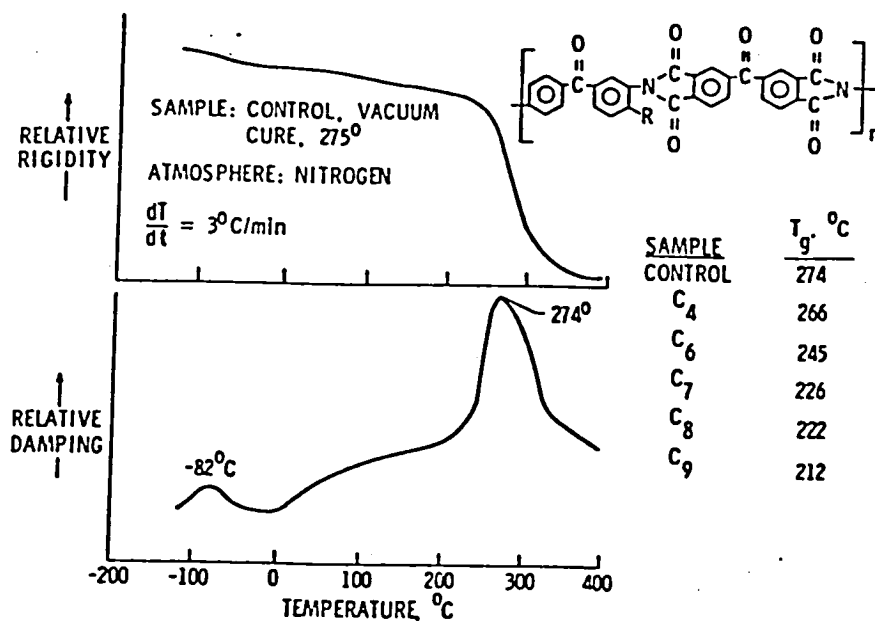


Figure 5. Polyimide  $T_g$  by torsional braid analysis.

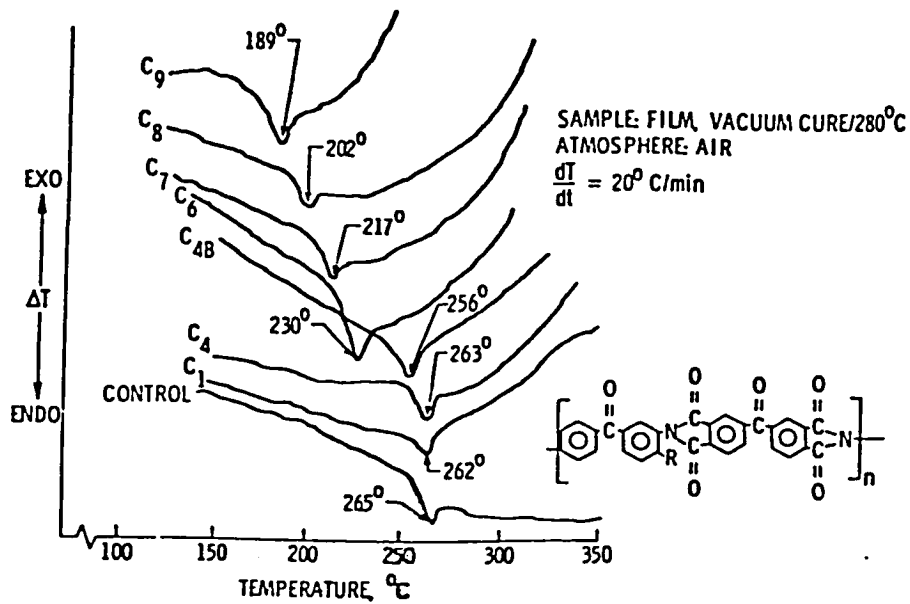


Figure 6. Differential scanning calorimetry of polyimide films.

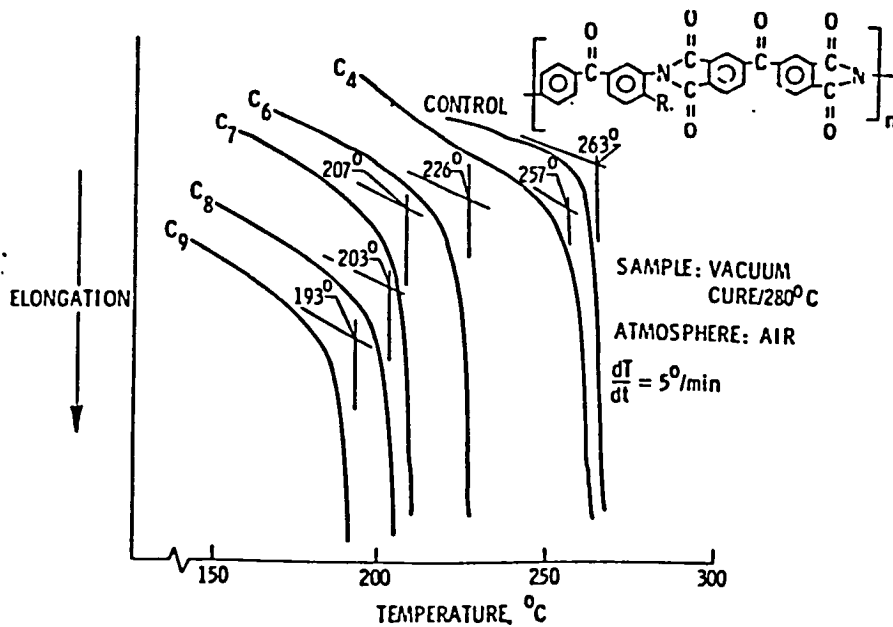


Figure 7. Thermomechanical analyses of vacuum cured polyimide films.

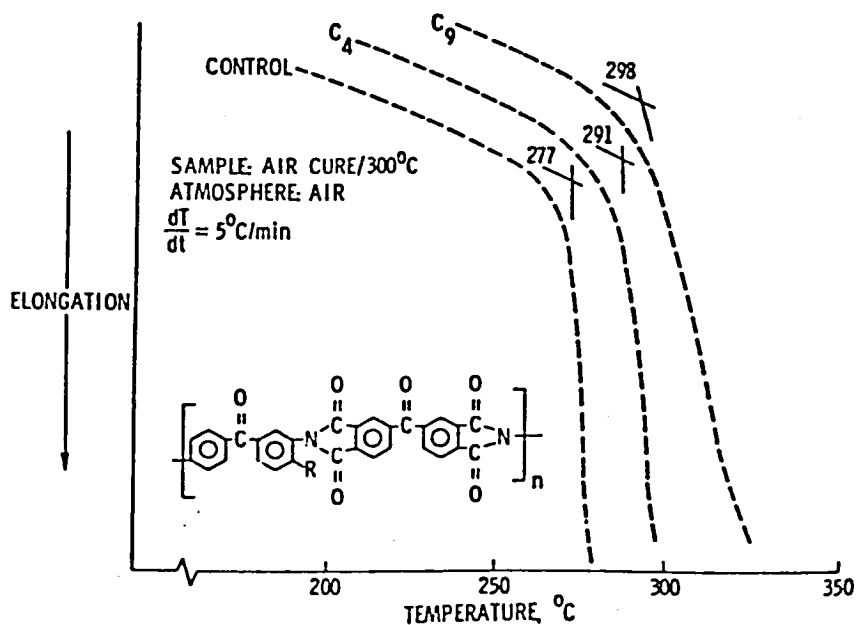


Figure 8. Thermomechanical analyses of air cured polyimide films.

Thermogravimetric analyses were run to determine the effect of structural variations on thermal stability. Figure 9 shows TGA curves for the control and C<sub>9</sub> polyimides. No noticeable weight loss is observed below 300°C for any of the polymers. Above 300°C, the C<sub>9</sub> polyimide was the least thermally stable and the control the most stable. The polymers with intermediate alkyl group length fell in order between these two extremes. Air cured films exhibited slightly better thermal stability than corresponding vacuum cured films. Depending on the potential application, the detrimental decrease in thermal stability with increasing alkyl group length may be offset by a corresponding beneficial lowering in T<sub>g</sub>. Also, processing in vacuum but post curing in air could result in an increase in T<sub>g</sub> of about 100°C.

Vacuum cured films were also subjected to tensile testing. The resultant data are presented in Table 2. Inherent viscosity is included to give an indication of polymer quality and relative molecular weight. The toughness index, the ratio of sample stress-strain curve area to control stress-strain curve area, gives an indication of film toughness. No improvement in toughness was observed by this index. One trend apparent from the table is the relationship between film properties and  $\eta_{inh}$ . If all polymers had the same approximate molecular weight as the control, an increase in toughness might have been observed.

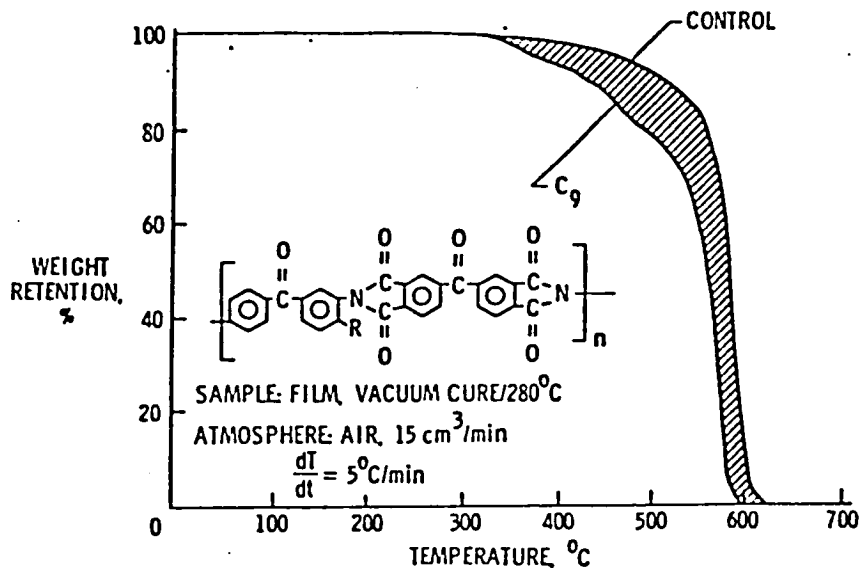


Figure 9. Thermogravimetric analyses of vacuum cured polyimide films.

Table 2.

MECHANICAL PROPERTIES OF VACUUM CURED POLYIMIDE FILMS<sup>(a)</sup>

SAMPLE	$\eta_{inh}^{(b)}$ dl/g	TENSILE <sup>(c)</sup> STRENGTH, MPa	ELONGATION, % <sup>(c)</sup>	TOUGHNESS <sup>(d)</sup> INDEX
CONTROL	.48	106.9	4.55	1.00
C <sub>1</sub>	.31	(e)	(e)	(e)
C <sub>4</sub> <sup>(f)</sup>	.36	71.6	3.39	0.44
C <sub>4B</sub>	.19	(e)	(e)	(e)
C <sub>6</sub>	.37	86.3	4.33	0.75
C <sub>7</sub>	.41	85.8	4.96	0.93
C <sub>8</sub>	.43	87.2	5.22	0.95
C <sub>9</sub>	.38	82.9	4.90	0.82

(a) CURED AT 280°C

(b) 0.5% SOLIDS IN DMAc AT 35°C

(c) AVERAGE OF FIVE SPECIMENS

(d) RATIO OF AREA UNDER STRESS-STRAIN CURVES

(e) WOULD NOT FORM FILM

(f) POOR QUALITY FILM

## CONCLUSIONS

An investigation was conducted to determine the affect on polyimide properties when alkyl groups are attached pendant to the polymer backbone. A control polymer with no pendant groups and seven different polymers with pendant groups ranging in length from one carbon to nine carbons were included in this study. The polymers were characterized in both the poly(amic) acid and polyimide stages.

The data obtained in this study proves the feasibility of varying  $T_g$  over a wide temperature range by attaching alkyl groups pendant to the polyimide backbone. A 70°C decrease was observed for the vacuum cured C<sub>9</sub> polyimide compared to the control as measured by TMA. Also, an increase in  $T_g$ , indicative of crosslinking, was observed for air cured films as the alkyl group increased in length. However, the incorporation of pendant alkyl groups in the polymer chain led to a slight sacrifice in thermal stability as measured by TGA. Mechanical property data indicated no improvement in film toughness with increasing pendant alkyl group length.

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16. Abstract  <p>An investigation was conducted to determine the effect on selected polyimide properties when pendant alkyl groups were attached to the polymer backbone. A series of polymers were prepared using benzophenone tetracarboxylic acid dianhydride (BTDA) and seven different p-alkyl-m,p'-diaminobenzophenone monomers. The alkyl groups varied in length from C<sub>1</sub> (methyl) to C<sub>9</sub> (nonyl). The polyimide prepared from BTDA and m,p'-diaminobenzophenone was included as a control.</p> <p>All polymers were characterized by various chromatographic, spectroscopic, thermal, and mechanical techniques. Increasing the length of the pendant alkyl group resulted in a systematic decrease in glass transition temperature (T<sub>g</sub>) for vacuum cured films. A 70°C decrease in T<sub>g</sub> to 193°C was observed for the nonyl polymer compared to the T<sub>g</sub> for the control. A corresponding systematic increase in T<sub>g</sub>, indicative of crosslinking, was observed for air cured films. Thermogravimetric analysis revealed a slight sacrifice in thermal stability with increasing alkyl length. No improvement in film toughness was observed.</p>					
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