Semi-Flexible Polyimide and Polyamide Systems

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SEMI-FLEXIBLE POLYIMIDE AND POLYAMIDE SYSTEMS

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Presented to
The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
of the Requirements for the Degree of
Master of Arts

by
John R. Evans
1984
This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Arts

Approved, 1984

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ABSTRACT

Macromolecular liquid-crystalline systems are technologically important to the fiber industry. Fibers spun from liquid-crystalline materials possess high-strength, low-weight properties, causing considerable excitement as to their potential industrial applications. Recent research has focused primarily on synthesizing thermotropic polymeric systems, since spinning fibers from anisotropic melts is exceedingly advantageous to conventional solution-spun techniques. Thus, polyimides and polyamides of the general structure

\[
\left[ \begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{O} \\
\end{array} \right]_n
\]

where \( x = \text{H}, \text{Br} \)

were prepared and examined for thermotropic liquid-crystallinity by Differential Scanning Calorimetry and hot-stage microscopy. These polymers were prepared with alternating rigid and flexible segments along the backbone. With the exception of the polyamide synthesized from sebacoyl chloride and sulfanilamide, all polymers possessed extremely stable crystalline states. In the case of the poly-pyromellitimides, crystalline stability was due to the strong intermolecular forces acting between the pyromellitic ring moieties. Placing a bromine substituent on the pyromellitic ring disrupted molecular symmetry, causing a decrease in crystalline melt transitions for these polyimides. Random copolymers from pyromellitic dianhydride and mixtures of aromatic diamines and aliphatic diamines produced polyimides with exceptionally high thermal stability. Random copolymers, from pyromellitic dianhydride and alkylene diamines of various lengths, produced polyimides with depressed crystalline melt temperatures, as compared to their respective homo-pyromellitimides. These macromolecular systems were further characterized by X-ray diffraction analyses, solubility, and viscosity measurements.
INTRODUCTION

Liquid-crystalline behavior was first recognized in 1888 by Reinitzer while examining the properties of cholesterol related compounds. Reinitzer discovered that heating samples of cholesteryl benzoate produced a separate intermediate phase between the crystal melt temperature and the isotropic liquid state. Further studies by Lehmann in 1890 showed similar behavior in ammonium oleate and p-azoxyphenetole. Lehmann called these unusual substances "Flüssige Kristalle", or liquid crystals.¹ The term seemed appropriate since heating these materials generated turbid melts which behaved similar to that of a solid and liquid.

Although these substances seemed to have some degree of fluidity during their anisotropic state, they still retained a great deal of orientational order. This order was exhibited by the appearance of birefringence when the liquid-crystalline phase was viewed between crossed polarizers.²

This anisotropic arrangement of molecules can assume three forms: smectic, cholesteric, and nematic. Smectic liquid crystals align in layers along a specific axis of direction. Cholesteric liquid crystals are also arranged in layers, but the direction of the orientational axis varies from layer to layer. Finally, in nematic liquid crystals, the molecules tend to align along a preferred axis but are not layered.³

Liquid crystallinity can be induced either by variances in temperature or by dissolving a substance in a particular solvent medium. If the mesophase occurs simply by heating or cooling, then the liquid crystal is referred to as thermotropic. Lyotropic liquid crystals, however, form anisotropic solutions at a specific or critical sample-solvent concentration.¹

Extensive studies on low molecular weight compounds such as p-azoxyanisole (PAA) and n-(p-methoxybenzylidene)-p'-butylaniline (MBBA) have provided valuable insight into the properties characteristic of liquid-crystalline materials.²

After examining these systems and other known liquid-crystalline systems, one can cite several common structural and physical features:

³

\[
\text{CH}_3\text{O} - \text{N} = \text{N} - \text{OCH}_3 \quad \text{PAA}
\]

\[
\text{CH}_3\text{O} - \text{C} = \text{N} - \text{C}_4\text{H}_9 - \text{n} \quad \text{MBBA}
\]
Intermolecular forces play an integral part in the formation and stability of the liquid-crystalline phase. After the breakdown of the crystal lattice, these forces act to maintain some measure of order and structure while permitting the fluidity associated with this state. These intermolecular forces (dipole-dipole and van der Waals interactions) can act more effectively if the molecules are typically elongated, linear rigid rods. Deviations from this structural conformation would hinder these attractive forces since they tend to act over a short range. Further, the rigid rod structural configuration facilitates molecular alignment and packing in the liquid-crystalline state.

The presence of aromatic moieties ideally enhances the thermal stability of the mesophase. Aromatics are fairly rigid, planar structures so they are commonly found in many liquid-crystalline compounds. Further, they are easily polarizable and thus increase the effect of attractive intermolecular forces.

Interest in liquid-crystalline materials has increased considerably in recent years due to potential industrial applications. Scientists have achieved remarkable success in incorporating low molecular weight liquid crystals in display devices such as calculators and watches. Because of their dielectric anisotropy, liquid crystals can be reoriented by applying a magnetic or electric field. Thus, fluctuations in the applied external field will cause the appropriate reorientation of the molecules in the mesophase.

Many properties inherent in low molecular weight liquid-crystalline systems are generally analogous to those found in macromolecular liquid-crystalline systems. Various biological polymeric systems have long been recognized to exhibit liquid-crystalline behavior. However, it was not until 1965 that Kwolek synthesized the first polymeric lyotropically liquid-crystalline compound of a non-biological nature. A mixture of poly (1,4-benzamide) in tetramethylurea/LiCl exhibited characteristics similar to known anisotropic polymer solutions. This was indeed a remarkable discovery, for Kwolek found that dry spinning the polymer solutions produced fibers of tremendous modulus and tenacity. Because the polymer chains are highly oriented in the liquid-crystalline state, dry spinning techniques produce fibers which retain this molecular orientation. Thus, for rigid, aromatic molecular structures such as poly (1,4-benzamide), one would expect that a high-strength fiber would subsequently result.
Further investigation into the propensity of aromatic polyamides ("aramids") to form liquid-crystalline solutions led to the discovery of Kevlar, Dupont's highly touted aramid fiber. Kevlar is poly (p-phenylene terephthalamide) spun from solutions of concentrated sulfuric acid. The amazing strength and durability of Kevlar fibers surpasses many conventional materials. Its high strength and low weight have caused considerable excitement as to its potential for commercial use.⁸

Although aramid fibers such as Kevlar were a major technological breakthrough for the fiber industry, the extreme processing techniques required to produce these materials has made them somewhat economically unattractive. However, Kevlar's success has sparked vigorous research into other potentially mesomorphic polymeric systems. Kevlar proved that liquid-crystalline compounds can produce high-strength, high-modulus fibers. The molecular structure of poly (p-phenylene terephthalamide) promotes this liquid-crystalline behavior and strength properties. However, polymeric systems with such rigidity along the chain backbone are typically highly crystalline materials. Intermolecular hydrogen bonding with the polyamides further enhances crystallinity.¹¹ Thus, thermal decomposition usually occurs before collapse of the crystal lattice and therefore the liquid-crystalline phase is not observed simply by heating. This poses an intriguing dilemma for industrial chemists. Rigid, rod-like moieties placed along the polymer backbone afford high-strength properties while necessitating harsh processing conditions in order to induce the liquid-crystalline state.

In 1975 Roviello and Sirigu¹² found that polyesters with the following structure exhibited thermotropic liquid-crystalline behavior:

\[
\left[-\text{OOC(CH}_2\text{)}_x\text{-COO}\text{C(CH}_3\text{)}_2\text{ = N-N = C(CH}_3\text{)}_2\right]_n
\]

Methylene spacer groups inserted between the rigid units within the polymeric structure provide the flexibility necessary so that liquid crystallinity can be observed upon heating. As the length of the methylene segment increases, the nematic-isotropic transitions recorded for this polyester steadily decrease. This is due to the additional flexibility along the polymer backbone. The polymer has less mesogenic character since the \(-\text{CH}_2\) groups possess a high degree of rotational freedom.¹³

Thermotropic polymeric behavior has extreme technological importance. Spinning fibers from anisotropic melts is exceedingly advantageous to conventional solution-spun techniques. Less processing is involved as well as
milder processing conditions. This translates into reduced production expenditures for the manufacturer.\textsuperscript{1}

Thermotropic polyesters with alternating rigid and flexible segments have been extensively studied.\textsuperscript{14-16} High-strength, high-modulus fibers have been spun from anisotropic melts of liquid-crystalline polyesters.\textsuperscript{1} Our investigation concerned the synthesis and characterization of other macromolecular systems incorporating flexible methylene spacer groups along the polymer backbone. We investigated these systems for thermotropic liquid-crystalline behavior and subsequent potential as a fiber. We have primarily focused our attention on the polyimides and initial research was conducted on polypyromellitimides with the following structure:

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N-} \\
\text{O} \\
\text{C} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{C} \\
\text{N-(CH}_2)_x- \\
\end{array}
\]

Polyimide systems have been utilized extensively on spacecraft and airplanes because of their many desirable physical properties: thermal and oxidative stability, radiation resistance, hydrolytic stability,\textsuperscript{17} high glass-transition temperatures, resistance to solvent attack, and minimal weight loss due to thermal degradation.\textsuperscript{18}

Many of the attractive features inherent in polyimide systems are especially important when considering possible mesogenic behavior. If fibers can be spun from anisotropic melts of polyimide systems, many exceptional characteristics would be imparted to the substance.

No case of liquid crystallinity has yet been reported for the polyimides. However, polyimide systems such as the polypyromellitimides possess many features characteristic of mesogenic compounds. The pyromellitimide ring system is rigid, planar, and highly polarizable. Further, polymerization with primary diamines produce linear polymer chains with large length-to-breadth ratios. Rigid, rod-like segments (such as the pyromellitic moiety) situated along the polymer backbone promote the formation of the nematic liquid-crystalline state.

In 1955 Edwards and Robinson\textsuperscript{19} discovered that polyimides from pyromellitic acid and alkylene diamines possessed many desirable properties necessary for injection molding of shaped articles. Toughness, thermal and oxidative stability, suitable melt viscosity, and tractability were some of their outstanding characteristics. However, the possibility of mesogenic behavior for these polypyromellitimides was probably not explored. Thus, because of the structural and physical properties aforementioned, we decided that the
polypyrromellitimides were worthy of our attention; and, since the chemistry involved in the preparation of polypyrromellitimides had been fully documented (see figures 1 and 2), this system seemed ideal for initial study.
EXPERIMENTAL

I. Synthesis of Polyesters Derived from 4,4'-Dihydroxy-\(\alpha,\omega\) -Diphenoxyalkanes and Terephthalic Acid

**Monomer Preparation**

4,4'-Dihydroxy-\(\alpha,\omega\) -Diphenoxyalkanes

\[
\begin{align*}
\text{HO} & - \text{O} - (\text{CH}_2)_x \text{O} - \text{OH} \\
\text{where } x &= 8,9
\end{align*}
\]

The 4,4'-dihydroxy-\(\alpha,\omega\) -diphenoxyalkanes were prepared as described by Griffin and Havens:\textsuperscript{15}

\[
.50 \text{ HO} - \text{OH} + .05 \text{ Br} - (\text{CH}_2)_x \text{Br} \xrightarrow{\Delta} \text{KOH}
\]

4,4'-dihydroxy-\(\alpha,\omega\) -diphenoxoctane \(\text{mp } 151^\circ - 153^\circ \text{C}\)
(Literature\textsuperscript{21} mp 152° - 153°C)

4,4'-dihydroxy-\(\alpha,\omega\) -diphenoxynonane \(\text{mp } 114^\circ - 116^\circ \text{C}\)
(No reported melting point)

**Terephthaloyl Chloride**

\[
\text{Cl} - \text{C} - \text{O} \quad \text{O} - \text{C} - \text{Cl}
\]

The terephthaloyl chloride was obtained commercially and purified by sublimation, in vacuo.\textsuperscript{22}
Polymerization

The polyesters were prepared as described by Jin et al.23

Polyester from 4,4'-dihydroxy-\(\alpha,\omega\)-diphenoxyoctane and Terephthalic Acid

The 4,4'-dihydroxy-\(\alpha,\omega\)-diphenoxyoctane (0.00175 mole) was added, with stirring, to s-tetra-chloroethane (50 ml) and pyridine (10 ml) in a 500 ml three-necked round bottom flask. The terephthaloyl chloride (0.00175 mole), dissolved in 50 ml s-tetra-chloroethane, was added slowly (5 minutes) to the diphenol solution under an atmosphere of nitrogen. The mixture was stirred under nitrogen for 22.5 hours. Acetone (300 ml) was then added producing a fibrous, white precipitate of the polyester. The solution was filtered with suction, and the precipitate washed with acetone-deionized water-acetone. The polymer was then dried, in vacuo, at approximately 60 °C. The \((\text{CH}_2)_8\) polyester appeared as a white solid with the following thermal (DSC) characteristics:

\[
\begin{align*}
\text{EXO} & = 197 \, ^\circ\text{C} \\
T_m & = 234 \, ^\circ\text{C} \\
T_c & = 287 \, ^\circ\text{C}
\end{align*}
\]

Polyester from 4,4'-dihydroxy-\(\alpha,\omega\)-diphenoxynonane and Terephthalic Acid

The 4,4'-dihydroxy-\(\alpha,\omega\)-diphenoxynonane (0.005 mole) was added, with stirring, to s-tetra-chloroethane (50 ml) and pyridine (10 ml) in a 500 ml three-necked round bottom flask. The terephthaloyl chloride (0.005 mole), dissolved in 50 ml s-tetra-chloroethane, was added slowly (5 minutes) to the diphenol solution under an atmosphere of nitrogen. The mixture was stirred under nitrogen for 21.5 hours. Acetone (300 ml) was then added producing a fibrous, white precipitate of the polyester. The solution was filtered with suction, and the precipitate washed with acetone-deionized water-acetone. The polymer was then dried, in vacuo, at approximately 60 °C. The \((\text{CH}_2)_9\) polyester appeared as a white solid with the following thermal (DSC) characteristics: \(T_m = 348 \, ^\circ\text{C}\)
II. Synthesis of Polypyromellitimides from Pyromellitic Dianhydride and $\alpha,\omega$-Diaminoalkanes

Monomer Preparation

The pyromellitic dianhydride (PMDA) and $\alpha,\omega$-diaminoalkanes were obtained commercially and used without further purification.

![PMDA Structure](image)

$\text{H}_2\text{N-}(\text{CH}_2)_x\text{-NH}_2$
where $x = 8,9,10,12$
$\alpha,\omega$-Diaminoalkanes

Polymerization

The polypyromellitimides were prepared as described by Tang,$^{24}$ and Edwards and Robinson.$^{19}$

Polypyromellitimides from Pyromellitic Dianhydride and $\alpha,\omega$-Diaminoalkanes

Stoichiometric amounts (0.005 - 0.015 moles) of the PMDA and $\alpha,\omega$-diaminoalkane were used. The diamine was added, with stirring, to 30 ml deionized water in a 100 ml round bottom flask equipped with a glass cannula. The PMDA was mixed with 30 ml of 95% ethanol in a 100 ml erlenmeyer flask. Both solutions were then immersed in a water bath and warmed to approximately 70°C. When the monomers had completely dissolved, the PMDA solution was combined with the diamine in the round bottom flask. The temperature of the water bath was increased (85°C - 90°C), and the mixture was refluxed for 20 minutes under an atmosphere of nitrogen. The hot solution was then poured into a beaker and allowed to cool slowly. The diamine salt precipitated as white,
powdery crystals. Further crystallization ensued after cooling in a refrigerator (5°C) overnight. The crystals were collected on a buchner funnel and washed with a 50/50 ethanol-water mixture. The diamine salt was then recrystallized from a solution of 30 ml ethanol and 30 ml deionized water and subsequently allowed to air dry.

The salt crystals were finely ground using a mortar and pestle. The powder was then placed in a glass tube and heated, in vacuo, to 110° - 138°C for approximately 30 minutes. The temperature was slowly raised, and polymerization was completed after heating to 250° - 300°C for 10 to 20 minutes. The polypyrromellitimides appeared as granular, white solids with the following thermal (DSC) characteristics:

\[-(\text{CH}_2)_8-\quad T_m = 383°C\]
\[-(\text{CH}_2)_9-\quad T_m > 350°C \text{ (observed visually)}\]
\[-(\text{CH}_2)_{10}-\quad T_m = 323°C\]
\[-(\text{CH}_2)_{12}-\quad T_m = 305°C\]

III. Synthesis of Polybromopyromellitimides from Bromopyromellitic Acid and \(\alpha,\omega\)-Diaminoalkanes

**Monomer Preparation**

**Bromodurene**

\[\text{H}_3\text{C} \quad \text{Br} \quad \text{CH}_3\]
\[\text{H}_3\text{C} \quad \text{CH}_3\]

Bromodurene was prepared as described by Smith and Moyle\textsuperscript{25}

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{CH}_3 \\
\text{H}_3\text{C} \quad \text{CH}_3
\end{array} + \text{Br}_2 \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{Br} \quad \text{CH}_3 \\
\text{H}_3\text{C} \quad \text{CH}_3
\end{array} + \begin{array}{c}
\text{H}_3\text{C} \quad \text{Br} \\
\text{H}_3\text{C} \quad \text{CH}_3
\end{array}
\]

Monobromodurene + Dibromodurene \[\rightarrow\text{Steam} \rightarrow \text{Distillation}\]
Bromodurene ------------------------ mp 57 °C
(Literature\textsuperscript{25} mp 60.5 °C)
(See figure 3 for NMR analysis)

Bromopyromellitic Acid

Bromopyromellitic acid was prepared similarly to that described by Mills\textsuperscript{26}.

In a 2000 ml three-necked round bottom flask, bromodurene (0.0469 mole) was dissolved in 100 ml of a 1.5 N potassium hydroxide solution. The mixture was heated with stirring to approximately 85\textdegree - 95 °C. Potassium permanganate (296 ml of a 5% solution) was then added in 4 equal portions at 1 hour intervals. The stirred solution was maintained at a temperature of 85\textdegree - 95 °C for 48 hours. The mixture was then allowed to cool and methanol added to remove any remaining permanganate. The mixture was filtered and the filtrate concentrated. Acetic acid was then carefully added to the hot filtrate until slightly acidic. A boiling solution of BaCl\textsubscript{2}-2H\textsubscript{2}O (0.1876 mole) in 245 ml water was added producing a white precipitate of barium bromopyromellitate. The precipitate was collected on a sintered-glass buchner funnel and washed with water. The crystals were dried in an oven at approximately 80 °C.

The barium bromopyromellitate (26.4 g) was added to 365 ml of a 3 N HCl solution and the stirred mixture brought to a boil. Hot sulfuric acid (125 ml of a 3 N solution) was then added and a white precipitate of BaSO\textsubscript{4} resulted. The mixture was quickly filtered and the filtrate allowed to cool slowly. The bromopyromellitic acid gradually precipitated as fine, white crystals. Further crystallization ensued after cooling in a refrigerator overnight. The precipitate was collected on a sintered-glass buchner funnel, washed with ethanol, and air dried (Yield, 35.76%).

Bromopyromellitic acid ------------------------ Decomposition without melting \approx 260 °C

(Literature\textsuperscript{27}, Decomposition without melting 240\textdegree - 265 °C)
**α,ω-Diaminoalkanes**

The α,ω-diaminoalkanes were obtained commercially and used without further purification.

\[
\text{H}_2\text{N-}(\text{CH}_2)_x\text{-NH}_2
\]

where \( x = 8,9,10,12 \)

**Polymerization**

**Polybromopyromellitimides from Bromopyromellitic Acid and α,ω-Diaminoalkanes**

\[
\begin{array}{c}
\text{O} \\
\text{Br} \\
\text{O} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{N} \\
\end{array} \\
\begin{array}{c}
-(\text{CH}_2)_x\text{-N} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{O} \\
\end{array} \\
\text{n}
\]

Polymerization of the polybromopyromellitimides proceeded as described for the polypyrromellitimides (see pp. 8-9). The polymers appeared as orange solids with the following thermal (DSC) characteristics:

- \(-(\text{CH}_2)_8\)”
  - EXO 158 °C
  - ENDO 320 °C
- \(-(\text{CH}_2)_9\)”
  - EXO 158 °C
  - ENDO 263 °C
  - ENDO 286 °C
- \(-(\text{CH}_2)_{10}\)”
  - EXO 99 °C
  - ENDO 238 °C
  - ENDO 291 °C
- \(-(\text{CH}_2)_{12}\)”
  - EXO 99 °C
  - ENDO 238 °C
  - ENDO 305 °C

**IV. Synthesis of Random Copolymers via the Diamine Salt**

**Monomer Preparation**

**Diamine Salts**

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{C} \text{-OC}_2\text{H}_5 \\
\end{array} \\
\begin{array}{c}
\text{H}_5\text{C}_2\text{O} \text{-O}^-
\end{array} \\
\begin{array}{c}
\text{NH}_3 \text{-}(\text{CH}_2)_8\text{-NH}_3^+
\end{array}
\]

Pyromellitic Octamethylene Diamine Salt
Dissolving bromopyromellitic acid or pyromellitic dianhydride in ethanol results in the formation of the respective diacid diester. Mixing this species with alkylene diamines produces the 1:1 organic salt (see p. 8-9 for synthesis procedures).

**Polymerization**

**Random Copolymer from Pyromellitic Octamethylene Diamine Salt and Pyromellitic Dodecamethylene Diamine Salt**

A 50/50 molar mixture of pyromellitic octamethylene diamine salt and pyromellitic dodecamethylene diamine salt was mixed in a mortar and ground to a fine powder. The salts were then imidized thermally, in vacuo (see pp. 8-9). A homogeneous random copolymerization product was not obtained. Differential Scanning Calorimetry indicated two distinct polymer melts due to the respective \((\text{CH}_2)_8\) and \((\text{CH}_2)_{12}\) homo-polypyromellitimides.
Random Copolymer from Bromopyromellitic Octamethylene Diamine Salt and Pyromellitic Dodecamethylene Diamine Salt

\[
\begin{array}{c}
\text{Br} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{N} \text{-(CH}_2\text{)}_g \text{-N} \text{-(CH}_2\text{)}_12 \text{-N} \\
\text{O} \\
\text{O}
\end{array}
\]

A 50/50 molar mixture of bromopyromellitic octamethylene diamine salt and pyromellitic dodecamethylene diamine salt was mixed in a mortar and ground to a fine powder. The salts were then imidized thermally, in vacuo (see pp. 8-9). Again, a homogeneous random copolymerization product was not obtained.

V. Synthesis of Random Copolymers via the Polyamide-acid

**Monomer Preparation**

The pyromellitic dianhydride, p-phenylene diamine, 1,5-diaminonaphthalene, and \(\alpha,\omega\)-diaminoalkanes were obtained commercially and used without further purification. The bromopyromellitic acid was prepared as previously noted (see p. 10).

\[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{N} \text{H}_2
\end{array}
\]

p-Phenylenediamine

\[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{N} \text{H}_2
\end{array}
\]

1,5-Diaminonaphthalene

**Polymerization**

Polyimides from the polyamide-acid were synthesized as described by Edwards,\textsuperscript{28} Edwards and Endrey,\textsuperscript{29} and St. Clair and Progar.\textsuperscript{30}
Random Copolymer from Bromopyromellitic Acid; PMDA; 1,8-Diaminooctane; and, 1,12-Diaminododecane

The 1,8-diaminooctane (0.001 mole) and 1,12-diaminododecane (0.001 mole) were added, with stirring, to 10 ml N,N-dimethylformamide. Gentle warming was necessary to induce complete dissolution of the diamines. The mixture was cooled in an ice-water bath to approximately 15 °C. The bromopyromellitic acid (0.001 mole) and PMDA (0.001 mole) were then added in four equal portions at 1 minute intervals. The solution was stirred (24 hours) until a substantial increase in viscosity had been attained.

The viscous gel was spread on a glass plate and dried in an oven (70 °C) for approximately 3 hours. The resulting cloudy film was removed with a razor blade and imidized, in vacuo, at a temperature of 250 °C - 300 °C for 10 minutes.

The polymer appeared as an orange solid. Differential Scanning Calorimetry indicated no endothermal transitions at temperatures below 400 °C.

Random Copolymer from PMDA; 1,8-Diaminooctane; and, 1,12-Diaminododecane

The 1,8-diaminooctane (0.0073 mole) and 1,12-diaminododecane (0.0073 mole) were dissolved by warming and agitation in 28 ml N,N-dimethylformamide. The mixture was cooled to 15 °C in an ice-water bath and the PMDA (0.01468 mole) added in four equal portions at 1 minute intervals. After 48 hours the mixture appeared highly viscous. The polyamide-acid was spread on a glass plate and dried in an oven (79 °C) for approximately 1 hour.

Imidization was effected by placing the glass plate in a 2:2:1 solution of benzene: pyridine: acetic anhydride overnight. The resulting cloudy, gel-like solution was heated to drive off the solvents present.

The polymer appeared as an off-white solid and melted (DSC) at
approximately 276°C.

Imidization was also carried out thermally. The dried polyamide-acid film was heated, in vacuo, to 250° - 300°C for 20 minutes.

Random Copolymer from PMDA; 1,10-Diaminodecane; and, p-Phenylene Diamine

The p-phenylene diamine (0.0065 mole) and 1,10-diaminodecane (0.0065 mole) were dissolved in 30 ml N,N-dimethylformamide (agitation and slight warming necessary). The solution was then cooled in an ice-water bath to approximately 15°C. The PMDA (0.01304 mole) was then added in four equal portions at 1 minute intervals. An increase in viscosity was noted after stirring the mixture overnight. A thin film of the viscous solution was spread on a glass plate and dried at 70°C for 2.5 hours. The yellowish-brown film was then removed with a razor blade and imidized, in vacuo, at 250° - 300°C for approximately 20 minutes.

The polymer possessed exceptionally high thermal stability. No melting endotherm was revealed by DSC analysis below 350°C.

Random Copolymer from PMDA; 1,10-Diaminodecane; and, 1,5-Diaminonaphthalene

The 1,5-diaminonaphthalene (0.004 mole) and 1,10-diaminodecane (0.004 mole) were dissolved in 25 ml N,N-dimethylformamide (agitation and slight warming necessary). The solution was then cooled in an ice-water bath to approximately 15°C. The PMDA (0.008 mole) was added in four equal portions at 1 minute intervals. The solution was then stirred overnight. A thin film of the resulting viscous mixture was spread on a glass plate and dried at 70°C for 2.5 hours. The film was removed with a razor blade and imidized, in vacuo, at 250°-
300 °C for approximately 15 minutes.

The polymer appeared as a brown solid and possessed extremely high thermal stability. No melting point was observed with the DSC below 350 °C.

VI. Synthesis of Polyimides from Bis-(4-amino-phenoxy)alkanes and Pyromellitic Dianhydride

Monomer Preparation

Bis-(4-Nitro-Phenoxy) Alkanes

\[
\begin{align*}
\text{O}_2\text{N} &- \bigcirc - \text{O-} - (\text{CH}_2)_{x} - \text{O-} - \bigcirc - \text{NO}_2 \\
\text{where} \ x & = 10
\end{align*}
\]

The bis-(4-nitro-phenoxy) decane was prepared similarly to that described by Partridge and Short,\textsuperscript{31} Cope,\textsuperscript{32} and Ashley et al.\textsuperscript{33}

In a 250 ml round bottom flask, the p-nitrophenol (0.030 mole) and sodium hydroxide (0.030 mole) were dissolved in 100 ml of 95% ethanol. The 1,10-dibromodecane (0.015 mole) was then added and the mixture heated to reflux for approximately 42 hours. A yellow precipitate of the bis-(4-nitro-phenoxy)-decane resulted upon cooling to room temperature. The crystals were collected on a buchner funnel and washed thoroughly with ethanol and water to remove all traces of sodium bromide. The product appeared as an off-white, powdery solid.

Bis-(4-nitro-phenoxy)decane -------------- mp 81 ° - 83 °C
(No reported melting point)

Bis-(4-Amino-Phenoxy) Alkanes

\[
\begin{align*}
\text{H}_2\text{N} &- \bigcirc - \text{O-} - (\text{CH}_2)_{x} - \text{O-} - \bigcirc - \text{NH}_2 \\
\text{where} \ x & = 10
\end{align*}
\]

The bis-(4-amino-phenoxy)decane was prepared similarly to that described by Chau, Muramatsu, and Iwakura.\textsuperscript{34}

Concentrated hydrochloric acid (30 ml) and anhydrous ethanol (100 ml)
were added to 25 g. of stannous chloride dihydrate (SnCl$_2$ * 2H$_2$O) in a 250 ml round bottom flask. The bis-(4-nitro-phenoxy)decane (0.0086 mole) was then added and the solution heated to reflux for approximately 2 hours. The solution was allowed to cool slowly resulting in the precipitation of the white, crystalline diamine salt. The mixture was further cooled in an ice bath and subsequently filtered with suction. The crystals were then washed with ethanol and air dried.

Sodium carbonate (90 ml of a 10% solution) was added to the diamine salt dissolved in 150 ml water. The yellowish precipitate was collected on a buchner funnel, washed with water, and allowed to air dry.

The impure product was recrystallized from 100 ml of 95% ethanol and 10 ml water. The bis-(4-amino-phenoxy)decane appeared as a iridescent, powdery white solid.

Bis-(4-amino-phenoxy)decane ------------------------ mp 116° - 118 °C
(No reported melting point)
(See figure 4 for IR analysis)

POLYMERIZATION

Polyimide from Bis-(4-Amino-Phenoxy)Decane and Pyromellitic Dianhydride

Polymerization proceeded as described by Chau et al.$^{34}$

The bis-(4-amino-phenoxy)decane (0.001 mole) was dissolved in 10 ml N,N-dimethylacetamide with stirring. The PMDA (0.001 mole) was added in four equal portions at 1 minute intervals. The solution was then stirred at room temperature overnight. A thin film of the mixture was spread on a glass plate and dried in an oven at 70 °C for 2 hours. The resulting yellow film was removed with a razor blade and imidized, in vacuo, at 220 °C for one hour.

The polymer appeared as a yellow solid with high thermal stability. No melting endotherm was recorded with the DSC below 350 °C.
VII. Synthesis of Polyamides

Monomer Preparation

The terephthaloyl chloride, sulfanilamide, sebacoyl chloride, and \( \omega \)-diaminoalkanes were obtained commercially and used without further purification.

\[
\begin{align*}
&\text{H}_2\text{N-} \quad \text{O} \\
&\quad \text{O} \\
&\quad \text{S} - \text{N} - \text{NH}_2
\end{align*}
\]

Sulfanilamide

\[
\begin{align*}
&\text{Cl} - \text{C} - (\text{CH}_2)_8 - \text{C} - \text{Cl}
\end{align*}
\]

Sebacoyl Chloride

Polymerization

Polymerization proceeded as described by Griffin and Havens,\(^{15}\) and Blumstein et al: \(^{16}\)

Polyamide from Terephthaloyl Chloride; Sulfanilamide; and, \(1,8\)-Diaminoctane

\[
\begin{align*}
\left[ \begin{array}{c}
\text{H} \\
\text{O} \\
\text{O} \\
\text{N-} \\
\text{C-} \\
\text{C-N} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{S} - \text{N} - \text{C} - \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{N-} \\
\text{C-} \\
\text{C-N} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{S} - \text{N} - \text{C} - \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{N-} \\
\text{C-} \\
\text{C-N} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{S} - \text{N} - \text{C} - \\
\text{O} \\
\text{H} \end{array} \right]_n
\end{align*}
\]

In a 250 ml round bottom flask, sodium hydroxide (0.0165 mole) and benzyltriethylammonium chloride (1.01 g) were dissolved in 100 ml water. The sulfanilamide (0.001 mole) and \(1,8\)-diaminoctane (0.004 mole) were added to the mixture with stirring. The terephthaloyl chloride (0.005 mole), dissolved in 50 ml methylene chloride, was then added resulting in a white precipitate of the polymer. The solution was stirred vigorously for 10 minutes. The precipitate was collected on a buchner funnel, washed thoroughly with water and acetone, and air dried.
The polymer appeared as a powdery, white solid with the following thermal (DSC) characteristics:

\[
\begin{align*}
\text{ENDO } & 328^\circ C & \text{ENDO } & 335^\circ C \\
\text{Polyamide from Terephthaloyl Chloride; Sulfanilamide; and, } & 1,12\text{-Diaminododecane} & \\
\end{align*}
\]

In a 230 ml round bottom flask, sodium hydroxide (0.0156 mole) and benzyltriethylammonium chloride (1.0 g) were dissolved in 100 ml water. The sulfanilamide (0.0005 mole) and 1,12-diaminododecane (0.0045 mole) were added to the mixture with stirring. The terephthaloyl chloride (0.0050 mole), dissolved in 50 ml methylene chloride, was then added resulting in a white precipitate of the polymer. The solution was stirred vigorously for 10 minutes. The precipitate was collected on a buchner funnel, washed thoroughly with water and acetone, and air dried.

The polymer appeared as a powdery, white solid with the following thermal (DSC) characteristics:

\[
\begin{align*}
\text{ENDO } & 282^\circ C & \text{ENDO } & 292^\circ C \\
\text{Polyamide from Sebacoyl Chloride and Sulfanilamide} & \\
\end{align*}
\]

In a 250 ml round bottom flask, sodium hydroxide (0.0136 mole) and benzyltriethylammonium chloride (1.02 g) were dissolved in 110 ml water. The sulfanilamide (0.0038 mole) was added to the mixture with stirring. The sebacoyl chloride (0.0038 mole), dissolved in 50 ml chloroform, was then added resulting in a clear, gel-like precipitate of the polymer. The solution was stirred for 15 minutes and subsequently mixed with 150 ml methanol. The fibrous polymer was isolated and air dried.

The polymer appeared as a white solid with the following thermal (DSC) characteristics:

\[
\begin{align*}
\text{ENDO } & 105^\circ C & \text{ENDO } & 117^\circ C \\
\end{align*}
\]
## VIII. List of Reagents

<table>
<thead>
<tr>
<th>REAGENT</th>
<th>SUPPLIER</th>
<th>PURITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Anhydride</td>
<td>Aldrich</td>
<td>99+%</td>
</tr>
<tr>
<td>Barium Chloride Dihydrate</td>
<td>Fisher</td>
<td>99%</td>
</tr>
<tr>
<td>Benzyltriethylammonium Chloride</td>
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</tr>
<tr>
<td>Bromine</td>
<td>Fisher</td>
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<tr>
<td>Chloroform</td>
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<tr>
<td>1,10-Diaminodecane</td>
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<td>1,12-Diaminododecane</td>
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<td>1,5-Diaminonaphthalene</td>
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</tr>
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<td>---</td>
</tr>
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<td>Burdick &amp; Jackson</td>
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<td>NASA</td>
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<td>Purity</td>
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<td>Methylene Chloride</td>
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<td>p-Nitrophenol</td>
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<tr>
<td>Terephthaloyl Chloride</td>
<td>Aldrich</td>
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</tr>
</tbody>
</table>
IX. Characterization

Differential Scanning Calorimetry

Polymers synthesized during the present research were examined thermally with a Perkin-Elmer DSC-2 differential scanning calorimeter (see figures 5-18). Samples were analyzed under an atmosphere of nitrogen at variable heating rates. Sample size varied from approximately 3 to 7 mg. An empty aluminum DSC pan was used as the reference material. The instrument was calibrated with an indium standard prior to use.

Optical Properties

All polymers were examined visually with a Leitz hot-stage cross-polarizing microscope at a 82X power magnification.

X-ray Diffraction Analysis

X-ray diffraction was conducted on a Diano XRD-6 at the NASA Langely Research Center in Hampton, Virginia (see figures 19-21). The polybromopyromellitimides were examined in a glass sample holder with nickel-filtered CuKα radiation (λ = 1.54178 Å).

Solubility

Solubility studies were conducted on the \((\text{CH}_2)_2\) bromopyromellitimide polymer, since it possesses the longest aliphatic chain and it has the lowest melting temperature of the homopolymers. It was felt that dissolution of this polymer would occur more readily than the other homologues. However, the \((\text{CH}_2)_2\) polymer was insoluble in most common organic solvents (dimethylsulfoxide, dimethylformamide, dimethylacetamide, 2-methoxyethyl ether) and only slightly soluble in concentrated sulfuric acid and m-cresol. Complete dissolution of the polymer was obtained in m-cresol after agitating a 0.5% polymer-cresol mixture in an oven at 205 °C for approximately 48 hours.

Solubility studies of the random copolymers were conducted on the polypyromellitimide from PMDA and \((\text{CH}_2)_8\) and \((\text{CH}_2)_2\) alkylene diamines (see p. 14). Solubility (0.5%) in m-cresol was obtained after warming on a hot-plate.

Viscosity

The inherent viscosity \((\eta_{inh})\) of the random copolymer from PMDA and \((\text{CH}_2)_8\) and \((\text{CH}_2)_2\) alkylene diamines was obtained using an Ubbelohde
viscometer. Viscosity measurements were determined at 25.3°C with a polymer concentration (w/v) of 0.4% in m-cresol. The polymer was dissolved in the m-cresol on a hot-plate, filtered, and added to the viscometer in a constant temperature bath. The inherent viscosity for the random copolymer was calculated to be 0.86 dl g⁻¹, indicating a high average molecular weight.

RESULTS AND DISCUSSION

The polymeric systems prepared during this research were characterized primarily by Differential Scanning Calorimetry (DSC) and polarizing microscopy. At present, DSC and optical analyses are the best techniques available for quick and accurate determination of liquid-crystalline materials.⁵

By DSC analysis, the thermal properties of a substance are recorded. Thus, phase changes associated with the transition of an enantiomorph from its crystalline to mesomorphic state and subsequently from the mesomorphic to isotropic state is determined. Further, the presence of polymesomorphism is also apparent after using this technique.

The polarizing microscope can also detect the presence of liquid crystallinity. Birefringence in fluids is strongly indicative of a mesomorphic phase. In the ordered molecular arrangement of the liquid-crystalline state, a mesomorph possesses an orientational axis. Thus, polarized light passing through the liquid crystal experiences two indices of refraction, i.e. from the ray vibrating normal to the orientational axis (n₀) and from the ray vibrating parallel to the axis (nₑ). The difference between nₑ and n₀ is termed birefringence.³⁶-³⁸ Since birefringence can be observed from the crystalline morphology of the solid state, it is important to note the presence of fluidity when identifying the anisotropic phase. As the mesomorph melts to the isotropic state, birefringence is no longer observed.

The polymers synthesized here were carefully prepared from their respective monomers using stoichiometric 1:1 mole ratios. Great care was taken to optimize polymerization conditions, such as reaction temperature, time, and purity of reagents. After polymerization, the samples were analyzed with a Perkin-Elmer DSC-2 differential scanning calorimeter and a Leitz hot-stage cross-polarizing microscope in order to identify possible thermotropic liquid-crystalline behavior.

Polypyromellitimides from Pyromellitic Dianhydride and α,ω-Diaminoalkanes

Pyromellitimides from pyromellitic dianhydride and alkylene diamines (see pp. 8-9) were examined first in our search for a liquid-crystalline polymeric system. Nonamethylene, decamethylene, and dodecamethylene
Polyesters Derived from 4,4′-Dihydroxy-α,ω-Diphenoxalkanes and Terephthalic Acid

Since thermotropic polymers are not commercially available, liquid-crystalline polyesters were prepared to serve as model compounds for our studies. Polyesters with eight and nine methylene spacer groups were synthesized (see pp. 6-7).

Differential Scanning Calorimetry (see figure 5) revealed two broad endotherms for the (CH$_2$)$_8$ polyester. The endotherms appeared approximately 53 °C apart with peak maximums at 234 °C and 287 °C. An exotherm was also recorded at 197 °C, perhaps indicating an ordering below the crystallization temperature. The initial endotherm (234 °C) results from melting of the solid, crystalline state to the nematotic state. The second endotherm (287 °C) thus marks the transition of the nematic to the amorphous isotropic state.

When viewed on the Leitz hot-stage cross-polarizing microscope, the (CH$_2$)$_8$ polyester appeared birefringent between the above determined melt transitions. Furthermore, the polymer exhibited a slight degree of fluidity during this interval.

Differential Scanning Calorimetry (see figure 6) and microscopy showed no indication of mesomorphic behavior for the (CH$_2$)$_9$ polyester. The cause of this deviation from expected literature results is not readily apparent.

Polybromopyromellitimides from Bromopyromellitic Acid and α,ω-Diaminoalkanes

A study of thermotropic polyesters has shown that crystalline melting temperatures were substantially depressed by placing lateral substituents on the...
rigid sections within these polymers. Moreover, the stability of the crystalline state was disrupted without significantly altering the mesogenic character of these polyesters. As previously noted, polypyrromellitimides from PMDA and alkylene diamines possess a highly crystalline morphology. Thus, in an attempt to destabilize the crystalline state, a bromine substituent was placed on the pyromellitic ring structure. Polybromopyrromellitimides were prepared with methylene spacer groups of various lengths (see p. 11).

Through X-ray diffraction analysis, the bromopyrromellitimides were classified as semi-crystalline polymers (see figures 19-21). Apparently, monobromination of the pyromellitic moiety partially destabilized polymer crystallinity. Although crystalline melt temperatures for the bromopyrromellitimides were depressed as compared to their respective non-brominated counterparts, these values still remained relatively high (238° - 320 °C). A comparison of bromo to non-bromo transitions (DSC) is shown in figure 22.

The polybromooctamethylenepyrromellitimide and polybromodecamethylenepyrromellitimide showed no evidence of mesomorphism when examined optically and with the DSC (see figures 7 and 9). However, the bromo (CH₂)₉ and (CH₂)₁₂ polyimides initially showed indications of possible mesogenic behavior. Multiple endotherms were recorded for these polymers by DSC analysis (see figures 8 and 10). Endotherms for the (CH₂)₉ polymer occurred at approximately 263 °C and 286 °C. The (CH₂)₁₂ polymer showed endothermal transitions at approximately 238 °C and 305 °C.

Further examination of these polymer samples with the Leitz hot-stage cross-polarizing microscope failed to verify the existence of a stable liquid-crystalline state. Birefringence was not observed for the (CH₂)₁₂ bromo polymer between its endothermal transition temperatures. Furthermore, significant decomposition occurred after heating the (CH₂)₁₂ sample to 300 °C and above under the microscope. Although the bromo (CH₂)₉ polyimide did appear birefringent between 263° - 286 °C, the sample showed no fluidity during this interval.

Griffin and Havens,¹⁵ as well as other researchers,⁴²-⁴³ believe that multiple endotherms observed in polymeric materials are caused by the melting of two crystalline forms which vary only by the size and perfection of their crystallite structure. During the course of a DSC scan, the polymer is able to melt and recrystallize. As these crystallites grow and the crystal lattice increases in perfection, the resulting structure becomes more stable and thus melts at higher temperatures. Holdsworth and Turner-Jones⁴² state that this melting-recrystallization process continues gradually throughout the heating cycle, and thus, is not observable in DSC baseline fluctuations. With higher heating rates, however, the polymer chains have less time for recrystallization and therefore only one endothermal peak is subsequently observed.
The multiple endothermic transitions recorded for the \((\text{CH}_2)_9\) bromopyromellitimide apparently results from the melting of two crystalline forms of the type described above. At higher heating rates the endothermic doublet observed for this polymer disappears and only one melting transition is recorded. However, the second endotherm recorded for the \((\text{CH}_2)_{12}\) polymer most likely results from oxidative degradation. Initial DSC scans for this polymer show multiple endothermic transitions; but, on subsequent DSC scans of the same \((\text{CH}_2)_{12}\) sample, no endothermal transitions were observed. Thus, the \((\text{CH}_2)_{12}\) polymer must degrade rapidly at temperatures above 300 °C, and therefore, subsequent DSC scans would show an absence of melting transitions due to the degraded state of the sample.

**Random Copolymers via the Diamine Salt**

Random copolymers were also prepared in an effort to reduce the stability of the pyromellitimide crystalline state. A 50:50 molar mixture of pyromellitic octamethylene diamine salt and pyromellitic dodecamethylene diamine salt was imidized in order to produce a copolymer with alkylene spacer groups of varying lengths along the polypyromellitimide backbone (see p. 12). Further, a 50:50 molar mixture of bromopyromellitic octamethylene diamine salt and pyromellitic dodecamethylene diamine salt was imidized in order to produce a copolymer where the rigid sections vary as well as the length of the methylene segments (see p. 13).

Thermally imidizing the solid salt mixtures failed to produce a homogeneous copolymerization product, as evidenced with the DSC (see figures 11 and 12). Endothermic transitions were recorded at temperatures previously noted for the respective homo-polypyromellitimides.

**Random Copolymers via the Polyamide-acid**

Solution polymerizations via the polyamide-acid successfully produced copolymers in which the various rigid and flexible segments apparently alternated randomly along the polymer backbone.

The random copolymer from bromopyromellitic acid, PMDA, 1,8-diaminoctane, and 1,12-diaminododecane showed an absence of an endothermal melt transition when analyzed by the DSC below 400 °C (see figure 13). Further, no melting was observed visually under the Leitz hot-stage microscope. The polymer did appear to "soften" at approximately 220 °C, but no further change was recorded until 320 °C, where substantial oxidative degradation occurred. This suggests that the sample possessed little or no crystallinity. It may be that 220 °C is the glass transition temperature of this material.
The random copolymer from PMDA, 1,8-diaminooctane, and 1,12-diaminododecane melted at approximately 276°C (see figure 14). The melt transition observed for this polymer was below each of the transitions recorded for its parent homo-polypyromellitimides. As previously stated, the (CH$_2$)$_8$ pyromellitimide melted at 383°C while the (CH$_2$)$_{12}$ pyromellitimide showed a $T_m$ at 305°C. Obviously, polymer crystallinity had been disrupted to some extent; however, no evidence of mesomorphism was detected.

The crystalline phase of the polypyromellitimides from aromatic and alkylene diamines (see p. 15) possessed exceptionally high thermal stability. No endothermal melt transitions were recorded by DSC analysis below 350°C. Similar behavior was observed visually with the Leitz hot-stage microscope. Lengthening the rigid sections in these polypyromellitimides apparently increased the effect of attractive intermolecular forces which further stabilized the crystalline state.

**Polyimides from Bis-(4-amino-phenoxy)alkanes and Pyromellitic Dianhydride**

The (CH$_2$)$_{10}$ polyimide was prepared (see p. 17) and examined for mesomorphic behavior. Again, this polypyromellitimide possessed high thermal stability. Optical and DSC analyses failed to reveal a melting transition below 350°C.

**Polyamides**

The polyamides from terephthaloyl chloride, sulfanilam ide, and eight and twelve alkylene diamines (see pp. 18-19) were obtained through interfacial polymerizations in water and methylene chloride. Both homologues exhibited multiple endothermal transitions when analyzed by DSC (see figures 15 and 16). These transitions occurred at 328°C and 335°C for the x=8 polyamide, and at 282°C and 292°C for the x=12 polymer. Since birefringence with fluidity was not observed between the above transition temperatures, the multiple endotherms were apparently due to crystal-crystal transitions and not mesomorphism.

The polyamide from sebacoyl chloride and sulfanilamide (see p. 19) also showed two endothermal transitions with the DSC (see figure 17). These transitions occurred at 105°C and 117°C. Again, these transitions were caused by the melting of two crystalline forms. This polyamide was obtained through an interfacial polymerization in water and chloroform.

**Two-Component Systems: Polymer Mixtures with 4,4'-Azoxydianisole**

Mixtures of 4,4'-azoxydianisole and the random copolymer from PMDA, 1,8-diaminooctane, and 1,12-diaminododecane (see p. 14) were prepared at
polymer concentrations (w/w) of 9.54%, 19.78%, and 38.78%.

The 4,4'-azoxydianisole is a mesogenic low-molecular weight compound. Its liquid-crystalline mesophase occurs between 118°C - 135°C. This compound was selected as a solvent for the aforementioned polyimide to test for a lyotropically induced liquid-crystalline state. Ideally, the rigid, rod-like structure of the anisole molecules would facilitate orientation of the polymer chains.

All three samples behaved similarly upon heating in an oil bath. At approximately 118°C the 4,4'-azoxydianisole melted to its liquid-crystalline state and at 130°C the isotropic state was obtained. No further change in the samples was observed until approximately 190°C - 205°C where the polymer appeared to melt forming a homogeneous, viscous polymer solution. Cooling the mixtures to room temperature and subsequently reheating to 200°C produced identical results. No evidence of mesogenic behavior was observed for the polymer mixtures.

Differential Scanning Calorimetry further substantiated the visual observations. Figure 18 shows the DSC heating scan for the 38.78% polymer mixture. Heating the sample produced two endothermic peaks occurring at 113°C and 129°C. These peaks denote the transition of the 4,4'-azoxydianisole to its liquid-crystalline and isotropic states, respectively. A broad endotherm was observed between 177°C and 216°C where the polymer dissolved.
CONCLUSION

The various macromolecular systems examined showed no evidence of thermotropic liquid-crystalline behavior. The polypyromellitimides possessed extremely stable crystalline states. We attribute this to the strong intermolecular forces acting between the pyromellitic ring moieties. The flexibility along the polymer backbone afforded by the aliphatic spacer groups was insufficient to substantially disrupt crystalline stability. Thus, mesomorphism was not observed.

The bromopyromellitimides destabilized pyromellitimide crystallinity to some extent. Placing the bromine substituent on the pyromellitic ring disrupted molecular symmetry, thus hindering crystallization. However, the crystalline melt transitions for these polymers were still relatively high (>200 °C).

Random copolymerizations, from PMDA and alkylene diamines of various lengths, produced polyimides with depressed crystalline melt temperatures; but again, mesogenic behavior was not observed. These copolymers were obtained via the polyamide-acid in solutions of DMF or DMAc. Polymerizations of this type produced copolymers in which the various rigid and flexible segments apparently alternated randomly along the polymer backbone.

Random copolymers from PMDA and mixtures of aromatic and aliphatic diamines produced polyimides with exceptionally high thermal stability. These polymers failed to show a melting transition below 350 °C.

The three polyamides synthesized also failed to exhibit mesomorphism. The polyamide prepared from sebacoyl chloride and sulfanilamide did, however, melt at a relatively moderate temperature (105 °C). In this case, the length of the mesogenic moiety (rigid rodlike segment) was substantially shortened. Thus, the polymer chains possessed enough flexibility so that a gradual collapse of the crystal lattice to the anisotropic phase did not occur.

Multiple endothermal transitions were recorded for several of the polyimide and polyamide systems. However, these transitions were not representative of mesomorphism. The multiple endotherms most likely were caused by the melting of two crystalline forms that varied only by the size and perfection of their crystallite structure.
REFERENCES

FIGURE 1

POLYPYROMELLITIMIDES FROM DIAMINE SALT INTERMEDIATES

\[ \text{Diamine Salt Intermediate} \]

\[ \text{Diamine Salt} \xrightarrow{\Delta} \text{Polypyrromellitimides} \]
FIGURE 2

POLYPYROMELITIMIDES PREPARED FROM THE POLYAMIDE-ACID\(^{(20)}\)

where R=an aliphatic or aromatic moiety
FIGURE 3

NMR ANALYSIS OF BROMODURENE.

Br
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]
\[ \text{H}_3\text{C} \]
\[ \text{H}_3\text{C} \]
Bromodurene

CHCl₃

ppm (δ)
FIGURE 4

INFRARED ANALYSIS

Sample: Bis-(4-Amino-Phenoxy) Decane

Wavenumber (cm⁻¹)

3500 3000 2500 1700 1600 1400 1200 800
FIGURE 5
DIFFERENTIAL SCANNING CALORIMETRY.

Perkin-Elmer
DSC-2

POLYMER: \[
\begin{array}{c}
\text{C-} \\
\text{O-} \\
\text{O-} \\
\text{O-(CH}_2\text{)}_8\text{-O-} \\
\end{array}
\]

Heating Rate: 20 deg/min
FIGURE 6
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

Temperature (°C)

POLYMER: $\left[ \begin{array} {ccc} \text{C} & -\text{C-O-} & \text{O}-(\text{CH}_2)_n\text{-O-} \end{array} \right]_n$

Heating Rate: 80 deg/min
FIGURE 7
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

Temperature (°C)

POLYMER:

Heating Rate: 40 deg/min

ENDO

ΔE

EXO

200 250 300 350
FIGURE 8
DIFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

ENDO

\[ \Delta E \]

EXO

Temperature (°C)

POLYMER:

\[ -\left(\text{CH}_2\right)_9\text{N} - \]

Heating Rate: 20 deg/min
FIGURE 9
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

ENDO

EXO

Temperature (°C)

POLYMER:

Heating Rate: 20 deg/min
FIGURE 10
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

ENDO

EXO

ΔE

Temperature (°C)

POLYMER:

Heating Rate: 20 deg/min
FIGURE 11
Differential Scanning Calorimetry

Endo

Exo

Perkin-Elmer
DSC-2

Temperature (°C)

Polymor: \[ -(CH_2)_8 -N \]

Heating Rate: 20 deg/min

(Polymer prepared via the diamine salt)
FIGURE 12
Differential Scanning Calorimetry

Perkin-Elmer DSC-2

Temperature (°C)

280 330

Heating Rate: 20 deg/min

(Polymer prepared via the diamine salt)
FIGURE 13
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

Temperature (°C)

POLYMER: \[
\begin{pmatrix}
- \text{(CH}_2\text{)}_8 \text{N} \\
\text{Br}
\end{pmatrix} \\
\begin{pmatrix}
\text{N-} \text{(CH}_2\text{)}_{12} \text{N} \\
\text{N-}
\end{pmatrix}
\]

Heating Rate: 20 deg/min

(Polymer prepared via the polyamide-acid)
FIGURE 14
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

ENDO

\[ \Delta E \]

EXO

Temperature (°C)

200 250 300 350 400

POLYMER: \([-(CH_2)_8-N-C\leftarrow-C\leftarrow-C\leftarrow-N-(CH_2)_{12}-N-C\leftarrow-C\leftarrow-C\leftarrow-N-]^n\]

Heating Rate: 20 deg/min

(Polymer prepared via the polyamide-acid; imidized thermally.)
FIGURE 15
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

Temperature (°C)

POLYMER:

Heating Rate: 20 deg/min
FIGURE 16
DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer
DSC-2

Temperature (°C)

POLYMER:

Heating Rate: 20 deg/min
FIGURE 17
DIFFERENTIAL SCANNING CALORIMETRY

Temperature (°C)

POLYMER:

Heating Rate: 20 deg/min
DSC heating scan for 4,4'-azoxydianisole, copolymer mixture (38.78%). Heating Rate: 20 deg/min
Sample: Poly (bromo-octamethylenepegomellitimide)
Figure 20

X-ray diffraction analysis

Sample: Poly(bromo-decamethyleneBMI)

\[ d = 17.0 \text{ Å} \]
FIGURE 21
X-RAY DIFFRACTION ANALYSIS

Sample: Poly (bromo-dodecamethylene pymellitimide)
FIGURE 22
MELT TRANSITIONS (DSC) FOR BROMO AND NON-BROMO PYROMELLITIMIDES

- Polypyromellitimides
- Polybromopyromellitimides

Number of methylene groups

Temperature, °C
VITA

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