Synthesis and characterization of poly(ime-sulfonamides)

Eric J. Kuckhoff
Synthesis and Characterization of Poly(Imide-Sulfonamides)

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THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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Objective

The objective of this research project was to synthesize and characterize eight novel copoly(imide-sulfonamides) 1, 2, where R was 4,4'-oxydianiline, 4,4'-methylene dianiline, 4,4'-diamino diphenyl sulfone, and 1,12 diaminododecane, respectively.

![Chemical Structure 1](image1)

1

![Chemical Structure 2](image2)

2

1a, 2a where R = –O–O–

1b, 2b where R = –O–CH₂–

1c, 2c where R = –O–SO₂–

1d, 2d where R = –(CH₂)₁₂–

After synthesis, these eight polymers were characterized by dilute solution viscosity, infrared spectroscopy, thermal gravimetric analysis, and differential scanning calorimetry.

Prepared polamic acids of copoly(imide-sulfonamides) were cast on glass plates and thermally cured to give films which would be evaluated for reverse osmosis and hyperfiltration.
INTRODUCTION

High molecular weight molecules, known as polymers are formed by linking together large numbers of smaller, simpler chemical units called monomers. The joining of monomers occurred in a very specific and particular fashion to achieve a high molecular weight compound. It is this high molecular weight that accounts for a polymer's properties. These properties may be modified by introducing aromatic or aliphatic linkages in the monomers.

The mechanism for the type of polymerization used in this project was step-growth. Step-growth polymers are formed by an intermolecular condensation of functional groups usually involving the loss or elimination of a small molecule. Characteristically in a step-growth polymerization: (a) any two molecular species can react; (b) monomers react early in the reaction such that less than one percent monomer remains at a degree of polymerization of 10; (c) polymer molecular weight slowly increases during the reaction; (d) long reaction times are necessary to achieve high molecular weight; and (e) all molecular species are present at any point in the polymerization.

The type of product formed was determined by the functional groups present. Bifunctional monomers, such as dianhydride and diamines gave linear polymers. This is seen in the following poly-condensation.

\[ H_2N-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\text{NH}_2 + \quad \overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}} \quad \rightarrow \quad [\overset{\text{N}}{\text{N}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}]_\eta \]
The rate of these reactions are dependent upon the reactivity of the functional groups and the concentration of these functionalities. As molecular weight rises, there will be some dilution inherent to polymerization resulting in a slight decrease in rate. To maximize and ensure a successful polymerization, a reasonable concentration must be established. There must be exact equivalence of functional groups and the absence of any side reactions. High reaction conversion and high monomer purity are necessary to guarantee a high molecular weight polymerization.

These reactions were carried out using solution polymerization. Solution polymerization involved the addition of the monomers to a solvent, where the reactants dissolved and reacted. This technique was preferred due to the ready control of heat. Heat is easily removed by placing the vessel in an ice bath or allowing reflux to occur. The solution was also directly useable. The only major difficulty was in the removal of all trapped solvent from the polymer. The removal of solvent was difficult, almost to the point of being impractical. In some instances the heat needed to remove the solvent would destroy the polymer.

Once the polymer was synthesized it was characterized. The analysis and testing of a polymer was necessary to determine its usefulness. Infrared spectroscopy was a valuable method to determine whether or not the condensation had occurred. By observing the disappearance of one functionality and the appearance of another, it was determined whether or not the desired product was formed.

Differential scanning calorimetry (DSC), a thermal technique, had an important bearing upon the perceived success of the synthesized
polymers. With a reference and a sample placed on the instrument the temperature was raised in a predetermined fashion. While heating progressed, an average temperature circuit compared the temperature difference between the samples. The circuit also proportioned power to maintain equal temperature between the samples. When there was a thermal transition the power was adjusted, and this difference was recorded. This technique revealed two very important physical properties of the polymer. The glass transition temperature (Tg) is the temperature at which the polymer changes from a hard crystalline substance, resembling an inorganic glass, to a rubbery amorphous compound. This is shown on the DSC curve as the point where the curve rose sharply. As heating progressed, the polymer chains began moving over one another followed by crystallization. This is shown by a sharp drop in the specific heat diagram. This is followed by actual melting (Tm°C) of the crystals. The specific heat curve of poly(ethylene terephthalate) is illustrated on the following page.

Thermogravimetric analysis (TGA) is another useful thermal technique used to characterize a polymer. A very sensitive balance is used to monitor weight loss as a function of heating. This helped to assess thermal stability decomposition temperature and extent of cure. An example of thermogravimetric analysis is shown on the following page.3

Inherent or logarithmic solution viscosity was utilized to determine the extent of polymerization and molecular weight. Measurements were made by measuring the efflux time (t) of a specified concentration (c) of polymer solution relative to the solvent time (t0). Measurements
are made in capillary viscometers such as the Ostwald-Fenske or Ubelode. These parameters were used in the following equation to give the inherent viscosity.

\[ \eta_{inh} = \frac{\ln(t/t_0)}{C} \]
Figure 2. Thermogram of Polyvinyl chloride (PVC), poly methyl methacrylate (PMMA), High density poly ethylene (HDPE), polytetrafluoroethylene (PTFE), and polyimide (PI).

An increased inherent viscosity indicates a greater molecular weight. These previously mentioned points were all used in the preparation and characterization of the copoly(imide-sulfonamides). To better understand the project, it was necessary to study the individual parts of the polymer in a historical sense.

POLYIMIDES

Polyimides are polymers containing the imide linkage as part of the repeat monomer unit. The first known synthesis of a high molecular weight polyimide was reported in 1908. The self condensation of 4-aminophthalic anhydride gave, shown below.

\[
\text{Imide} + \text{H}_2\text{N-Phal} \rightarrow \text{Imide dimer} + \gamma \text{H}_2\text{O}
\]
A general preparation scheme for aromatic and various aliphatic polyimides was reported\(^5\) by W. M. Edwards and A. L. Endrey in 1959 and 1963 respectively. The scheme used by the authors involved reacting a diamine and dianhydride, in solution and at room temperature, to form a soluble polyamic acid 5. The soluble polyamic acid was dehydrated either chemically or thermally to form polyimide 6.

\[
\text{AR} + \text{H}_2\text{N-R-NH}_2 \rightarrow \begin{array}{c}
\text{HOOC} \\
\text{HNOC}
\end{array} \text{CONH-R} \begin{array}{c}
\text{COOH} \\
\text{COOH}
\end{array}
\]

Where AR = aromatic

\[ R = \text{either aromatic or aliphatic group.} \]

High molecular weight polymers were achieved in such reactions by the use of extremely pure monomer, exact equivalence of functional groups, absence of side reactions, and high reaction conversion. Rigorous exclusion of moisture and the maintainance of low temperature was mandatory. Reaction temperature must be maintained below 50\(^\circ\)C in order to prevent premature polyimide formation, which would release water and cause the hydrolysis of existing poly-amic acids. High temperature also increases the chance of a trans-amidation\(^6\) by the diamine with the solvent, N,N'-dimethyl acetanide, occurring.

\[
\text{H}_3\text{C-C-CH}_3 + \text{H}_2\text{N-R-NH}_2 \rightarrow \text{H}_2\text{N-R-N} \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]
The preparation scheme devised by W. M. Edwards and A. L. Endrey was used to create a large number of polyimides. The following tables illustrate the variety of diamines and dianhydrides that have been utilized in the preparation of polyimides.
Table 1. Assorted diamines used to form polyimides

<table>
<thead>
<tr>
<th>Diamines</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>m-phenylenediamine</strong></td>
<td><img src="image1" alt="" /></td>
</tr>
<tr>
<td><strong>p-phenylenediamine</strong></td>
<td><img src="image2" alt="" /></td>
</tr>
<tr>
<td><strong>4,4'-diaminodiphenylpropane</strong></td>
<td><img src="image3" alt="" /></td>
</tr>
<tr>
<td><strong>4,4'-diaminodiphenylmethane</strong></td>
<td><img src="image4" alt="" /></td>
</tr>
<tr>
<td><strong>benzidine</strong></td>
<td><img src="image5" alt="" /></td>
</tr>
<tr>
<td><strong>4,4'-diaminodiphenyl sulfide</strong></td>
<td><img src="image6" alt="" /></td>
</tr>
<tr>
<td><strong>4,4'-diaminodiphenyl sulfone</strong></td>
<td><img src="image7" alt="" /></td>
</tr>
<tr>
<td><strong>4,4'-diaminodiphenyl ether</strong></td>
<td><img src="image8" alt="" /></td>
</tr>
<tr>
<td><strong>1,5-diaminonaphthalene</strong></td>
<td><img src="image9" alt="" /></td>
</tr>
<tr>
<td><strong>3,3'-dimethylbenzidine</strong></td>
<td><img src="image10" alt="" /></td>
</tr>
<tr>
<td><strong>3,3'-dimethoxybenzidine</strong></td>
<td><img src="image11" alt="" /></td>
</tr>
<tr>
<td><strong>2,4-bis(β-amino-τ-butyl)toluene</strong></td>
<td><img src="image12" alt="" /></td>
</tr>
<tr>
<td><strong>bis(p-β-amino-τ-butylphenyl) ether</strong></td>
<td><img src="image13" alt="" /></td>
</tr>
<tr>
<td><strong>bis(p-β-methyl-δ-aminopentyl)benzene</strong></td>
<td><img src="image14" alt="" /></td>
</tr>
<tr>
<td><strong>4-isopropyl-m-phenylenediamine</strong></td>
<td><img src="image15" alt="" /></td>
</tr>
<tr>
<td><strong>1,2-bis(3-aminoproxy)ethane</strong></td>
<td><img src="image16" alt="" /></td>
</tr>
</tbody>
</table>
Table 1 (continued):

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-xylene diamine</td>
<td><img src="image" alt="m-xylene diamine" /></td>
</tr>
<tr>
<td>p-xylene diamine</td>
<td><img src="image" alt="p-xylene diamine" /></td>
</tr>
<tr>
<td>bis(4-aminocyclohexyl)methane</td>
<td><img src="image" alt="bis(4-aminocyclohexyl)methane" /></td>
</tr>
<tr>
<td>piperazine</td>
<td><img src="image" alt="piperazine" /></td>
</tr>
<tr>
<td>decamethylenediamine</td>
<td><img src="image" alt="decamethylenediamine" /></td>
</tr>
<tr>
<td>3-methylheptamethylenediamine</td>
<td><img src="image" alt="3-methylheptamethylenediamine" /></td>
</tr>
<tr>
<td>4,4-dimethylheptamethylenediamine</td>
<td><img src="image" alt="4,4-dimethylheptamethylenediamine" /></td>
</tr>
<tr>
<td>2,11-dodecanediamine</td>
<td><img src="image" alt="2,11-dodecanediamine" /></td>
</tr>
<tr>
<td>2,2-dimethylpropylenediamine</td>
<td><img src="image" alt="2,2-dimethylpropylenediamine" /></td>
</tr>
<tr>
<td>octamethylenediamine</td>
<td><img src="image" alt="octamethylenediamine" /></td>
</tr>
<tr>
<td>3-methoxyhexamethylenediamine</td>
<td><img src="image" alt="3-methoxyhexamethylenediamine" /></td>
</tr>
<tr>
<td>2,5-dimethylhexamethylenediamine</td>
<td><img src="image" alt="2,5-dimethylhexamethylenediamine" /></td>
</tr>
<tr>
<td>2,5-dimethylheptamethylenediamine</td>
<td><img src="image" alt="2,5-dimethylheptamethylenediamine" /></td>
</tr>
<tr>
<td>3-methylheptamethylenediamine</td>
<td><img src="image" alt="3-methylheptamethylenediamine" /></td>
</tr>
<tr>
<td>5-methylnonamethylenediamine</td>
<td><img src="image" alt="5-methylnonamethylenediamine" /></td>
</tr>
<tr>
<td>1,4-cyclohexanediamine</td>
<td><img src="image" alt="1,4-cyclohexanediamine" /></td>
</tr>
<tr>
<td>1,12-octadecanediene</td>
<td><img src="image" alt="1,12-octadecanediene" /></td>
</tr>
<tr>
<td>bis(3-aminopropyl) sulfide</td>
<td><img src="image" alt="bis(3-aminopropyl) sulfide" /></td>
</tr>
<tr>
<td>N-methyl-bis(3-aminopropyl)amine</td>
<td><img src="image" alt="N-methyl-bis(3-aminopropyl)amine" /></td>
</tr>
<tr>
<td>hexamethylenediamine</td>
<td><img src="image" alt="hexamethylenediamine" /></td>
</tr>
<tr>
<td>heptamethylenediamine</td>
<td><img src="image" alt="heptamethylenediamine" /></td>
</tr>
<tr>
<td>nonamethylenediamine</td>
<td><img src="image" alt="nonamethylenediamine" /></td>
</tr>
</tbody>
</table>
Table 2: Assorted dianhydrides used to form polyimides.

![Diagrams of dianhydrides](image)
The intermediate polyamic acids exhibit a variety of properties based upon their structure. Some properties were based on the acid grouping itself, and was lost upon imidization. The polyamic acids were very soluble in a variety of polar solvents, including N,N-dimethyl acetamide. Polyamic acids may be stored for a length of time, under temperature and anhydrous conditions. Polyamic acids were prone to hydrolysis resulting in the degradation of the macromolecule. Since N,N-dimethyl acetamide can release trace quantities of secondary amines into solution, there was the possibility of trans-amidation. Dilute solutions of the dried polyamic acids, c=0.5 g/dL, are used to determine the inherent viscosity. Films of polyimides were formed by first dissolving the polyamic acid (20% solids) in a solvent, usually N,N-dimethyl acetamide followed by heating to induce imidization.

Polyimides, cured from polyamic acids, exhibit a variety of properties and characteristics. These properties arise directly from the polymer structure itself. Polyimides derived from aliphatic diamines show properties generally dependent upon the diamine chain itself. Shorter chain aliphatic diamines, of generally less than seven carbons, yielded polymers with melt viscosities which allowed the preparation of only thick brittle films.8 An exception to this general rule was noted by W. M. Edwards.9 Hexamethylene diamine was reacted with pyromellitic dianhydride followed by dehydration of the polyamic acid, which gave a tough flexible film 7.

\[ \text{H}_2\text{N-}(\text{CH}_2)_6-\text{NH}_2 + \text{n} \begin{array}{c} \text{O} \text{O} \text{O} \text{O} \text{O} \text{O} \\ \text{O} \text{O} \text{O} \text{O} \text{O} \text{O} \end{array} \rightarrow \text{n} \begin{array}{c} \text{O} \text{O} \text{O} \text{O} \text{O} \text{O} \\ \text{O} \text{O} \text{O} \text{O} \text{O} \text{O} \end{array} \]
Polyimides derived from aromatic diamines are the most important commercially, because of their outstanding thermal properties. Aromatic polyimides are resistant to radiation, solvent, bacterial attack, and deformation at elevated temperature. The physical properties of polyimides are retained over prolonged exposure to heat. The following table illustrates this retention of properties by polyimides as a function of both heat and exposure time.

Table 3: Retention of properties for polyimides as a function of time and heat.

<table>
<thead>
<tr>
<th>Temperature [°F(C)]</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>365(185)</td>
<td>20,000</td>
</tr>
<tr>
<td>450(235)</td>
<td>10,000</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis of pyromellitimides showed stability over 500°C in vacuum or inert atmosphere. Isothermal weight loss and film toughness were directly related to polyimide structure. In general, aromatic linkages resulted in stronger, tougher, more stable films, while aliphatic linkages exhibited poorer retention of flexibility and thermal stability. As an example of an aromatic polyimide, the properties of Poly[N,N'-(p,p'-oxydiphenylene) pyromellitimide] are listed in the table on the following page. Aliphatic polyimides using aliphatic linkages showed a lesser stability and lower mechanical values.

Polyimides are characterized by being tough, transparent, thermally stable, and relatively resistant to hydrolysis and degradation.
Table 4. Properties of poly[N,N'-(p,p'-oxydiphenylene pyromellitimide]

<table>
<thead>
<tr>
<th>thermal stability*</th>
<th>Air</th>
<th>Helium</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C</td>
<td>2 hr</td>
<td>22 hr</td>
</tr>
<tr>
<td>400°C</td>
<td>12 hr</td>
<td>2 weeks</td>
</tr>
<tr>
<td>350°C</td>
<td>6 days</td>
<td>1 yr</td>
</tr>
<tr>
<td>300°C</td>
<td>3 mos</td>
<td></td>
</tr>
<tr>
<td>275°C</td>
<td>1 yr</td>
<td></td>
</tr>
<tr>
<td>250°C</td>
<td>8 yr</td>
<td></td>
</tr>
<tr>
<td>melting point</td>
<td>none reported*</td>
<td></td>
</tr>
<tr>
<td>zero strength</td>
<td>815</td>
<td></td>
</tr>
<tr>
<td>temperature, °C</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>specific gravity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>flammability</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>-195°C</td>
</tr>
<tr>
<td>25°C</td>
</tr>
<tr>
<td>200°C</td>
</tr>
<tr>
<td>300°C</td>
</tr>
<tr>
<td>450°C</td>
</tr>
<tr>
<td>tensile strength, psi (\times 10^{-3})</td>
</tr>
<tr>
<td>elongation, %</td>
</tr>
<tr>
<td>tensile modulus, psi (\times 10^{-3})</td>
</tr>
</tbody>
</table>

POLYSULFONAMIDES:

Polysulfonamides were first prepared by G. J. Berchet\(^{13}\) in 1943. A series of aromatic disulfonyl chlorides reacted with aliphatic and aromatic diamines in organic solvents using excess diamine as an acid acceptor. Initial attempts yielded only low molecular weight polysulfonamides, 8, which were not fiber forming.

\[
\begin{align*}
&\text{C}10_2\text{S} - \text{SO}_2\text{Cl} + \text{H}_2\text{N} - \text{O} - \text{O} - \text{NH}_2 \\
&\downarrow \\
&\left[ \text{O}_2\text{S} - \text{SO}_2\text{NH} - \text{O} - \text{O} - \text{NH} \right] \\
&8
\end{align*}
\]

Higher molecular weight polysulfonamides\(^{14, 9}\), were achieved in 1944 by S. Murahashi and T. Takizawa by reacting aliphatic disulfonyl
chlorides with hexamethyline diamine in water or pyridine.

\[
\text{ClO}_2\text{S}-(\text{CH}_2)_6-\text{SO}_2\text{Cl} \quad + \quad \text{H}_2\text{N}-(\text{CH}_2)_6\text{NH}_2
\]

\[
\downarrow
\]

\[
\left[ \text{O}_2\text{S}-(\text{CH}_2)_6-\text{SO}_2\text{NH}-(\text{CH}_2)\text{NH} \right]^{-}
\]

The first high molecular weight polysulfonamides\textsuperscript{15} were prepared by S. A. Sundet, W. S. Murphey, and S. B. Speck in 1959. The diamine, 1,6-hexamethylene diamine, was reacted with 1,3-Benzene disulfonyl chloride, to produce a high molecular weight polymer, 10, in 72% yield.

\[
\text{ClO}_2\text{S} \quad \text{SO}_2\text{Cl} \quad + \quad \text{H}_2\text{N}-(\text{CH}_2)-\text{NH}_2 \quad \rightarrow \quad \left[ \text{O}_2\text{S} \quad \text{O}_2\text{SNH}-(\text{CH}_2)-\text{NH} \right]^{-}
\]

Inherent viscosity of polysulfonamide, 10, was determined to be 1.69 at 30°C in sulfuric acid.

These polymers were synthesized using interfacial polymerization techniques with sodium carbonate as the acid acceptor. Methylene chloride or chloroform were utilized to form the organic phase, while water formed the other immiscible phase.

A novel synthesis of aromatic polysulfonamide was reported by Y. Imai, M. Veda, and T. Iizawa in 1977.\textsuperscript{16} The high molecular weight product, 11, was synthesized from di-1-benzotriazolyl disulfonate
and 4,4'-oxydiphenyl diamine (oxydianiline) in 94% yield.

\[
\begin{align*}
\text{NNN}^-\text{OSO}_2\text{O}-\text{O}-\text{SO}_2\text{O}^-\text{NNN}^- + \text{H}_2\text{NN}^-\text{O}-\text{O}^-\text{NH}_2 \\
\downarrow \\
\text{SO}_2\text{O}-\text{O}-\text{SO}_2\text{NH}-\text{O}-\text{O}^-\text{NH}^- + 2 \text{HO}^-\text{N}^\text{N}
\end{align*}
\]

The reaction was carried out in tetrahydrofuran with triethylamine as the acid acceptor. In 1979 Imai and Veda\textsuperscript{17} prepared various polysulfonamides, 12, by the condensation of aromatic disulfonyl chloride with various diamines.

\[
\text{ClSO}_2^-\text{AR}-\text{SO}_2\text{Cl} + \text{H}_2\text{N}^-\text{AR'}^-\text{NH}_2 \rightarrow \text{HCl} \rightarrow \text{SO}_2^-\text{AR}-\text{SO}_2\text{NH}^-\text{AR'}^-\text{NH}^-
\]

\[\text{AR} = \]

- 4,4'-oxydiphenyl disulfonyl chloride (ODSC)
- 4,4'-thiodiphenyl disulfonyl chloride (TDSC)
- 4,4'-disulfonyl diphenyl disulfonyl chloride (SDSC)
- m-benzene disulfonyl chloride (MBSC)
- m-xylene-4,6'-disulfonyl chloride (MXSC)

\[\text{AR} = \]

- bis (4-aminophenyl)ether (ODA)
- bis(4-amino phenyl) methane (MDA)
- m-phenylene diamine (MPDA)

Polymerization was carried out using a variety of conditions, summarized
in the following table.18

Table 5: Polycondensation of Various Aromatic Disulfonyl Chlorides with Aromatic Diamines in Tetra methyl sulfone

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Disulfonyl chloride</th>
<th>Diamine</th>
<th>Acid acceptor</th>
<th>Initial temperatureb (°C)</th>
<th>Polymer Yield (%)</th>
<th>ηinah</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>Pyridine</td>
<td>20</td>
<td>99</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>2-Methylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>2,6-Dimethylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>2,4,6-Trimethylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>Pyridine</td>
<td>10</td>
<td>99</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>2-Methylpyridine</td>
<td>10</td>
<td>99</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>4-Methylpyridine</td>
<td>10</td>
<td>99</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>2-Ethylpyridine</td>
<td>10</td>
<td>99</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>ODA</td>
<td>2-Benzylpyridine</td>
<td>10</td>
<td>99</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>MDA</td>
<td>Pyridine</td>
<td>20</td>
<td>99</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>MDA</td>
<td>2-Methylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>MDA</td>
<td>2,6-Dimethylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>MDA</td>
<td>2,4,6-Trimethylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>MPDA</td>
<td>Pyridine</td>
<td>20</td>
<td>99</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>MPDA</td>
<td>2-Methylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>MPDA</td>
<td>2,6-Dimethylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>TDSC</td>
<td>ODA</td>
<td>Pyridine</td>
<td>20</td>
<td>99</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>SDSC</td>
<td>ODA</td>
<td>2-Methylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>SDSC</td>
<td>MDA</td>
<td>2-Methylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>ODA</td>
<td>2-Methylpyridine</td>
<td>20</td>
<td>99</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>ODA</td>
<td>Pyridine</td>
<td>5</td>
<td>99</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>ODA</td>
<td>2-Methylpyridine</td>
<td>5</td>
<td>99</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>ODA</td>
<td>4-Methylpyridine</td>
<td>5</td>
<td>99</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>ODA</td>
<td>2-Benzylpyridine</td>
<td>5</td>
<td>99</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>ODA</td>
<td>2,6-Dimethylpyridine</td>
<td>5</td>
<td>99</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>ODA</td>
<td>2,4,6-Trimethylpyridine</td>
<td>5</td>
<td>99</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>MBSC</td>
<td>MDA</td>
<td>2-Methylpyridine</td>
<td>5</td>
<td>99</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>MXSC</td>
<td>ODA</td>
<td>2-Methylpyridine</td>
<td>5</td>
<td>99</td>
<td>0.75</td>
<td></td>
</tr>
</tbody>
</table>

*Polymerization was carried out with 2.5 mmole of monomer and 5 mmole of acid acceptor in 5 ml of TMS at 60°C for 24 hr.

bThe temperature at which the polymerization was initiated.

cMeasured at a concentration of 0.5 g/dl in DMAc at 30°C.

The table illustrates the importance of an acid acceptor and initial reaction temperature. Proper selection of these factors was mandatory in ensuring high yield and high molecular weight. If the acid acceptor was not sufficiently reactive, in the medium to pick up all the hydrochloric acid produced, contamination of the system and side reactions occurred, preventing high molecular weight. Starting temperature and reaction temperature were both important. Lower
initial temperatures suppressed side reactions. Solvent selection was very important for formation of high molecular weight polysulfonamides. The reaction of 4,4' oxydiphenyl disulfonyl chloride (ODSC) with 4,4' oxydianiline (ODA) was used to illustrate the effect of solvent/acid acceptor system upon inherent viscosity. The table below illustrates this point. As can be seen, high yield does not necessarily guarantee the formation of a high molecular weight polymer.

Table 6: Polycondensation of ODSC with ODA in Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Acid acceptor</th>
<th>Yield (%)</th>
<th>ηinh a,b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diglyme</td>
<td>2-Methylypyridine</td>
<td>99</td>
<td>0.14</td>
</tr>
<tr>
<td>DMAc</td>
<td>2-Methylypyridine</td>
<td>99</td>
<td>0.16</td>
</tr>
<tr>
<td>TMS</td>
<td>2-Methylypyridine</td>
<td>99</td>
<td>0.37</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Pyridine</td>
<td>99</td>
<td>0.36</td>
</tr>
<tr>
<td>2-Methylypyridine</td>
<td>2-Methylypyridine</td>
<td>99</td>
<td>0.43</td>
</tr>
<tr>
<td>2,6-Dimethylypyridine</td>
<td>2,6-Dimethylypyridine</td>
<td>30</td>
<td>0.07</td>
</tr>
</tbody>
</table>

a Polymerization was carried out with 2.5 mmole of monomer and 5 mmole of acid acceptor in 5 ml of solvent at 60°C for 24 hr.
b Measured at a concentration of 0.5 g/dl in DMAc at 30°C.

To ensure the polymer remains dissolved, the solvent must swell the macromolecule to ensure the reaction is completed. Table 6 indicates this point. The solvents must be anhydrous to prevent the formation of sulfonic acid 13.

\[
\text{ClO}_2\text{S(\text{O})CH}_2\text{(O)-SO}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{ClO}_2\text{S(\text{O})CH}_2\text{(O)-SO}_2\text{H}^{\text{H}}
\]

The formation of sulfonic acid terminated polycondensation and yielded only low molecular weight compounds.

Wholly aromatic polysulfonamides were soluble in strong acids
such as sulfuric, trifluoroacetic, and dichloroacetic acids. These polymers were also soluble in electron donor solvents such as dimethyl formamide, dimethyl sulfonamide, tetramethylene sulfone, and pyridine. They were also soluble in aqueous sodium hydroxide (10%). This was rationalized by the salt formation, 14.

\[
\text{SO}_2\text{NH}^- + \text{NaOH} \rightarrow \text{SO}_2\text{N}_2^- + \text{Na}^+ + \text{H}_2\text{O}
\]

14

Transparent, tough polysulfonamide films were cast from solutions of pyridine (20% solids). Thermal stability was evaluated by thermal gravimetric analysis and differential scanning calorimetry and is summarized in the following table.20

<table>
<thead>
<tr>
<th>Table 7: Thermal Characterization of Aromatic Polysulfonamides</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>I</td>
</tr>
<tr>
<td>II</td>
</tr>
<tr>
<td>IV</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>VII</td>
</tr>
<tr>
<td>VIII</td>
</tr>
<tr>
<td>IX</td>
</tr>
</tbody>
</table>

* A 10% weight loss temperature observed by TGA at a heating rate of 5°C/min.
  
* Determined by thermomechanical analysis of the film sample in helium at a heating rate of 10°C/min.

Regardless of structure, the decomposition of the sulfonamide linkage occurs between 345-395°C in air and 380-400°C in nitrogen. Thermal decomposition is relatively low compared to the polyimides. This was offset by exceptional workability, ease of casting, and film
forming qualities.

Poly(imide-sulfonamide)

Polymer blends of polyimides and polyamides have gained a large portion of the polymer blend market. By copolymerizing two different functionalities into the backbone of the macromolecule an intermediate polymer may be produced. Incorporating a more processable, soluble amide group into a polyimide backbone, it was possible to obtain the best properties of each monomeric unit. The brittle, thermally stable, inert polyimide was converted to a thermally stable, yet workable polymer. The following diagram\textsuperscript{21} (Diagram 1) illustrates the thermal stability of copoly(amide-imides) between that of polyamides and polyimides.

Diagram 1: TGA curves showing the effect of amide and imide backbone composition.

![TGA curves](image)

Thermal breakdown occurred at approximately 550°C for the polyimide. Although the polyimide showed good thermal stability, it was not easily fabricated. The polyamide curve showed thermal weight loss at 390°C, a low value relative to the polyimide. The copoly(amide-imide) showed good thermal stability with decomposition occurring at 485°C.
This same idea was the basis in combining the polyimide and the polysulfonamide. By incorporating the sulfonamide group into a polyimide backbone, an intermediate macromolecule was the logical result. The most dramatic work was performed by Y. Imai and H. Orunoyama in 1973.\(^2\) A two step cyclopolycondensation was utilized by reacting various diamines with 4-chlorosulfonyl phthalic anhydride to yield a new class of poly(imide-sulfonamides). The general reaction scheme was as follows:

\[
\begin{align*}
H_2N-R-NH_2 + & \xrightarrow{\text{HCOOH}} \quad \n_{\text{ClO}_2S} \\
\xrightarrow{\text{CONH-R-SO}_2NH} & \quad \n \quad 15 (a-d) \\
\xrightarrow{-H_2O} & \quad \n \quad 16 (a-d)
\end{align*}
\]

\[R = a -\underset{\text{o}}{\text{O}}-\underset{\text{o}}{\text{O}} ; b -\underset{\text{o}}{\text{O}}-\text{CH}_2-\underset{\text{o}}{\text{O}} ; c -\underset{\text{o}}{\text{O}}-\text{SO}_2-\underset{\text{o}}{\text{O}} ; d -\text{(CH}_2\text{)}_{12}\]

The results of these polymerizations are summarized in the following table.\(^2\)
Table 8: Preparation of Poly(amic sulfonamide) from 4-chlorosulfonyl phthalic anhydride and Various Diamines

<table>
<thead>
<tr>
<th>Diamine</th>
<th>Solvent*</th>
<th>Acid acceptor*</th>
<th>Polymerization conditions</th>
<th>Polymer yield, %</th>
<th>η abolished*</th>
</tr>
</thead>
<tbody>
<tr>
<td>-′(CH₂)₄−</td>
<td>MEK-water</td>
<td>Na₂CO₃</td>
<td>25, 0.5</td>
<td>66, 0.14</td>
<td></td>
</tr>
<tr>
<td>-O−</td>
<td>THF-water</td>
<td>Na₂CO₃</td>
<td>25, 0.5</td>
<td>89, 0.21</td>
<td></td>
</tr>
<tr>
<td>-CH₃−</td>
<td>DCM</td>
<td>NMM</td>
<td>25, 3</td>
<td>98, 0.17</td>
<td></td>
</tr>
<tr>
<td>-O−</td>
<td>TMS</td>
<td>NMM</td>
<td>50, 3</td>
<td>99, 0.17</td>
<td></td>
</tr>
<tr>
<td>-O−</td>
<td>TMS</td>
<td>NMM</td>
<td>25, 3</td>
<td>98, 0.21</td>
<td></td>
</tr>
<tr>
<td>-O−</td>
<td>DMAc</td>
<td>NMM</td>
<td>25, 3</td>
<td>98, 0.19</td>
<td></td>
</tr>
<tr>
<td>-O−</td>
<td>DMAc</td>
<td>NMM</td>
<td>-15 to +25, 3</td>
<td>99, 0.67</td>
<td></td>
</tr>
<tr>
<td>-O−</td>
<td>DMAc</td>
<td>NMM</td>
<td>-15 to +25, 3</td>
<td>98, 0.44</td>
<td></td>
</tr>
<tr>
<td>-O−</td>
<td>DMAc</td>
<td>NMM</td>
<td>-15 to +25, 3</td>
<td>96, 0.14</td>
<td></td>
</tr>
</tbody>
</table>


These reactions were carried out using solution and interfacial polymerization techniques. The interfacial polymerization technique failed to give high molecular weight polyamic acid. This was attributed to the low reactivity of the sulfonyl chloride. Solution polymerization in dichloromethane also yielded low molecular weight polyamic acid, due to its insolubility in the solvent. High molecular weight polymer was achieved using low temperature solution polymerizations with N,N-dimethyl acetamide as a solvent, and an organic acid acceptor.

The polymers were soluble in aprotic solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide, and N,N-dimethyl acetamide. Solubility was observed in organic bases, such as pyridine, and...
inorganic bases, such as sodium hydroxide. These results are summarized in the following table.25

Table 9: Solubility of Polymers

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PSAA from ODA</th>
<th>PSI from ODA</th>
<th>PSI from HMDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>95% Sulfuric acid</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Dimethylacetamide</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Pyridine</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>10% Aqueous sodium hydroxide</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>86% Formic acid</td>
<td>-</td>
<td>-</td>
<td>±</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>±</td>
<td>±</td>
<td>±</td>
</tr>
<tr>
<td>Acetone</td>
<td>±</td>
<td>-</td>
<td>±</td>
</tr>
<tr>
<td>Ethanol</td>
<td>±</td>
<td>-</td>
<td>±</td>
</tr>
</tbody>
</table>

* (+ +) soluble at room temperature; (+) soluble by heating; (±) partially soluble or swelling; (−) insoluble.

Poly(sulfonamide-imide) films were formed by casting solutions of polyamic acids in N,N'-dimethyl acetamide, followed by heating at 280°C for three hours. The films were generally transparent, yellow, and brittle. Differential scanning calorimetry showed an exothermic shift around 350°C. Glass transition temperature of 295°C were observed. Thermal gravimetric analysis showed decomposition beginning at 350°C with a 10% weight loss at 430°C.

Aromatic poly(sulfonamides imides) showed greater thermal stability than poly-sulfonamides yet lesser stability than structurally related polyimides. These poly(sulfonamide-imides) showed better film forming qualities and workability than polyimides, yet less than poly(sulfonamides).

The poly(imide-sulfonamides) showed properties intermediate of those of polyimide and polysulfonamides as predicted.
DISCUSSION OF RESULTS

The strategy for the synthesis of the title polymers involved a four step process; (1) synthesis of a diacetanilide containing two sulfonamide linkages, (2) deblocking of the diacetanilides to form dianiline monomers, (3) solution polymerization of the dianiline monomers with the appropriate dianhydride to form the poly(amic acid-sulfonamide), (4) thermal curing of the poly(amic acid-sulfonamide) to produce the poly(imide-sulfonamide).

Synthesis of the novel diacetonilides was accomplished by reacting various commercially available diamines with N-acetyl sulfanilyl chloride in glacial acetic acid with anhydrous sodium carbonate as the acid acceptor (see general reaction procedure A, Experimental Section, pg. 41). The diamines used were 4,4'-oxydianiline, 4,4'-methylenedianiline, 4,4'-diamino diphenyl sulfone, and 1,12-diaminododecane to yield the following diacetonilides:

- 4,4'-[oxy bis(p-phenylene sulfonamido)] diacetonilide, 17a,
- 4,4'-[methylene bis(p-phenylene sulfonamido)] diacetonilide, 17b,
- 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] diacetonilide, 17c,
- and 4,4'-[1,12-dodecamethylene bis(p-phenylene sulfonamido)] diacetonilide, 17d, respectively.

The following equation illustrates this general reaction.

\[
\text{H}_2\text{N-R-NH}_2 + 2 \text{CH}_3\text{CNH(O)SO}_2\text{Cl} \rightarrow \text{H}_2\text{N-R-NH}_2 + 2 \text{CH}_3\text{CNH(O)SO}_2\text{Cl}
\]
The crude diacetanilides were obtained in 80% yield when a 2.2:1 molar ratio of N-acetyl sulfanilyl chloride to diamine was used. A slight excess of N-acetyl sulfanilyl chloride was used to ensure a complete reaction. Thin layer chromatography (ethylacetate-hexane, 3:1 v/v) showed a mixture containing the sulfonic acid of N-acetyl sulfanilyl chloride, the desired diacetanilide, and the monoacetanilide. The monoacetanilide, 18, was a contaminant and resulted from the diamine reacting with only one mole of N-acetyl sulfanilyl chloride.

Attempts to purify the crude mixture by recrystallization were unsuccessful. The formation of the monoacetaniline was attributed to poor mixing and high reactant concentration. Water in the reaction vessel and solvents were responsible for the formation of the sulfonic acid. This problem was solved by changing the reaction conditions.
to ensure good-mixing, lower reactant concentration, and the exclusion of water.

General reaction procedure B used tetrahydrofuran in which both reactants were soluble. Pyridine was used as the acid acceptor (see general reaction procedure B, Experimental Section, pg. 41). N-acetyl sulfanilyl chloride was only moderately soluble in tetrahydrofuran, but with the addition of pyridine, the remainder of the sulfonyl chloride dissolved. Large volumes of tetrahydrofuran were used to dissolve the diamines. The diamine solution was added dropwise to the N-acetyl sulfanilyl chloride with mechanical stirring. Tetrahydrofuran and pyridine were dried over molecular sieves. Diacetanilides were obtained in yields of 75 to 90%.

Thin layer chromatography showed a slight trace of the monoacetanilide, a large concentrated spot which corresponded to the diacetanilide, and a spot at the origin corresponding to the sulfonic acid. The diacetanilide was purified by recrystallization. The results are summarized in Table 10.

Table 10: Summary of the reaction of N-Acetyl Sulfanilyl Chloride with Diamines to Produce Diacetanilides.

<table>
<thead>
<tr>
<th>Number</th>
<th>Diamine-R-group</th>
<th>% yield</th>
<th>M.P. °C</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>17a</td>
<td>-O-</td>
<td>80</td>
<td>238-240</td>
<td>0.28</td>
</tr>
<tr>
<td>17b</td>
<td>-O-CN₂-O'</td>
<td>90</td>
<td>148-152</td>
<td>0.28</td>
</tr>
<tr>
<td>17c</td>
<td>-SO₂-</td>
<td>75</td>
<td>161-162</td>
<td>0.20</td>
</tr>
<tr>
<td>17d</td>
<td>-(CH₂)₆</td>
<td>88</td>
<td>152-154</td>
<td>0.31</td>
</tr>
</tbody>
</table>

TLC conditions were ethyl acetate:hexane (3:1). A slight trace of monoacetanilide was observed in each case at an Rf 0.08 higher than the diacetanilide.
The diacetanilides were deblocked (see general reaction procedure C. Experimental Section, pg. 42), without any difficulties. The diacetanilides were heated at reflux temperatures with 6N hydrochloric acid from one to four hours to yield dianiline monomer 19a-d. Hydrolysis of 17a, 17b, 17c and 17d yielded 4,4'-(oxy bis(p-phenylene sulfonamido)) dianiline, 19a, 4,4-[methylene bis(p-phenylene sulfonamido)] dianiline, 19b, 4,4-[sulfonyl bis(p-phenylene sulfonamido)] dianiline, 19c, and 4,4'-(dodecamethylene bis(p-phenylene sulfonamido)) dianiline, 19d, respectively. The equation illustrating this reaction is shown below.

\[
\begin{align*}
\text{CH}_3\text{CNH-} & \quad \text{SO}_2\text{NH-R-NHO} \\
\text{O} & \quad \text{S} \quad \text{O} \quad \text{NHCCH}_3
\end{align*}
\]

17

\[1.6N \text{ HC1}\]

\[2.\text{Na}_2\text{CO}_3\]

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

19

Where R= \[\text{O} \quad \text{O}\] 19a

Where R= \[\text{O} \quad \text{CH}_2 \quad \text{O}\] 19b

Where R= \[\text{O} \quad \text{SO}_2 \quad \text{O}\] 19c

Where R= \[-(\text{CH}_2)_2\] 19d

Thin layer chromatography was used to monitor the progress of the deblocking procedure. Diacetanilides 17a and 17b required only one hour of reflux to fully deblock the monomer. These were the only two compounds to completely dissolve in the refluxing 6N hydrochloric acid. Diacetanilides 17c and 17d did not completely dissolve and required four hours to fully deblock. Yields for the deblocking
procedure ranged from 80 to 95%. Thin layer chromatography showed the sulfonic acid, the deblocked monoacetanilide and the deblocked diacetanilide. The dianiline monomers 19a, 19b, 19c, and 19d were purified by column elution chromatography (3:1 ethyl acetate:hexane on silica gel). These results are summarized in Table 11.
<table>
<thead>
<tr>
<th>Number</th>
<th>Diamine-R-Group</th>
<th>% Yield</th>
<th>Mp°C</th>
<th>Rf&lt;sup&gt;b&lt;/sup&gt;</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>19a</td>
<td></td>
<td>80</td>
<td>179-180</td>
<td>0.57 Calculated</td>
<td>56.46</td>
<td>4.34</td>
<td>10.97</td>
<td>12.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td>56.43</td>
<td>4.45</td>
<td>10.75</td>
<td>12.05</td>
</tr>
<tr>
<td>19b</td>
<td></td>
<td>87</td>
<td>222.3-223.5</td>
<td>0.41 Calculated</td>
<td>59.04</td>
<td>4.77</td>
<td>11.01</td>
<td>12.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td>59.37</td>
<td>4.68</td>
<td>11.03</td>
<td>12.84</td>
</tr>
<tr>
<td>19c</td>
<td></td>
<td>93</td>
<td>171-173</td>
<td>0.39 Calculated</td>
<td>51.60</td>
<td>3.97</td>
<td>10.03</td>
<td>17.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td>52.03</td>
<td>3.89</td>
<td>9.74</td>
<td>17.50</td>
</tr>
<tr>
<td>19d</td>
<td>-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;12&lt;/sub&gt;</td>
<td>95</td>
<td>175.5-176.3</td>
<td>0.69 Calculated</td>
<td>56.44</td>
<td>7.52</td>
<td>10.97</td>
<td>12.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td>56.67</td>
<td>7.23</td>
<td>10.62</td>
<td>12.38</td>
</tr>
</tbody>
</table>

<sup>a</sup> Melting points were determined on the dianilines after column chromatography

<sup>b</sup> T.L.C. conditions were ethyl acetate-hexane 3:1
All dianiline monomers were dried over phosphorus pentoxide and refluxing toluene in a drying pistol before they were used for polymerization and elemental analysis. All observed elemental analysis were within experimental error and compared favorably to the calculated values as seen in Table 11.

The infrared spectra of the dianiline monomers were taken utilizing potassium bromide pellets (40:60, sample to KBr). Absorbtions at 3480 cm\(^{-1}\) and 3380 cm\(^{-1}\) confirmed the presence of the primary amino group. The loss of the absorbtion at 1680 cm\(^{-1}\), which corresponded to the carbonyl of the blocking acetyl group, indicated complete hydrolysis had occurred.

Eight novel poly(imide sulfonamides) having the structures 1a-1d and 2a-2d shown below, have been synthesized utilizing low temperature solution pooymerization techniques. The dianiline monomers 19a, 19b, 19c, and 19d were reacted with pyromellitic dianhydride and 4,4'-benzophenone tetracarboxylic dianhydride to produce poly(amic acid sulfonamides) 20 (a-d) and 21 (a-d) respectively. Poly(amic acid sulfonamides) 20 (a-d) and 21 (a-d) were cured for three hours at 280°C to produce poly(imide sulfonamides) with the structures 1 (a-d) and 2 (a-d).
Where $R = \text{ } -\text{O-O-} \quad 1a, 2a, 19a, 20a, 21a$

Where $R = \text{ } -\text{O-CH}_2\text{O-} \quad 1b, 2b, 19b, 20b, 21b$

Where $R = \text{ } -\text{O-SO}_2\text{O-} \quad 1c, 2c, 19c, 20c, 21c$

Where $R = \text{ } -(\text{CH}_2)_3 \quad 1d, 2d, 19d, 20d, 21d$
These reactions were characterized as step-growth polymerization.\textsuperscript{26} Characteristics of step-growth polymers are: (a) condensation of two functional groups, (b) elimination of a small molecule, (c) monomers disappear early, (d) molecular weight rises steadily, (e) all molecular species are present at any time.

Polymerizations were carried out using dry apparatus, assembled hot after baking in an oven at 120° C for six hour. The dianiline monomers were purified by recrystallization and showed only one spot on a T.L.C. plate. The reaction solvent, N,N-dimethyl acetamide was distilled from calcium hydride to ensure the exclusion of water. The reaction temperature was started at 0° C, but allowed to warm to 25° C.

Initial polymerization attempts yielded brittle polymeric materials having dilute solution viscosity of 0.09. Due to the low inherent viscosities, one of the requirements for polymerization must have been violated. Monomer purity was suspect. Instead of using just recrystallized dianiline monomers, column chromatography was performed on these compounds. Using rigorously dried dianiline monomers that were purified by column techniques (ethyl acetate-hexane 3:1 and the maintainance of 0° C), a second series of polymerizations were carried out. These prepared polymers were characterized by infrared spectroscopy, thermal gravimetric analysis, differential scanning calorimetry and dilute solution viscosity. These properties were summarized on Table 12.
Table 12: Inherent Viscosities, Thermal Gravimetric Analysis, and Differential Scanning Calorimetry of the Prepared Poly(imide-sulfonamides).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Inherent Viscosities</th>
<th>TGA</th>
<th>Differential Scanning Calorimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.53</td>
<td>8.9</td>
<td>182</td>
</tr>
<tr>
<td>2a</td>
<td>0.49</td>
<td>12.7</td>
<td>249</td>
</tr>
<tr>
<td>1b</td>
<td>0.32</td>
<td>19.0</td>
<td>194</td>
</tr>
<tr>
<td>2b</td>
<td>0.36</td>
<td>6.8</td>
<td>248</td>
</tr>
<tr>
<td>1c</td>
<td>0.21</td>
<td>24.0</td>
<td>132</td>
</tr>
<tr>
<td>2c</td>
<td>0.23</td>
<td>34.0</td>
<td>214</td>
</tr>
<tr>
<td>1d</td>
<td>0.13</td>
<td>42.0</td>
<td>105</td>
</tr>
<tr>
<td>2d</td>
<td>0.19</td>
<td>42.0</td>
<td>103</td>
</tr>
</tbody>
</table>

a Determined in N,N'-dimethyl acetamide at 25°C and a concentration of 0.5g/100ml on the poly(amic acid sulfonamides).

b Percent weight loss at 400°C in nitrogen at a heating rate of 20°C/min.

c Observed by differential scanning calorimetry at a heating rate of 20°C/min. in nitrogen.
Inherent viscosities of the prepared polymers ranged from 0.13 to 0.53 in N,N-dimethyl acetamide at 25°C and a concentration of 0.5 grams per 100 ml. Despite these relatively low inherent viscosities polymers containing ether and methylene units, polymers 1a, 2a, 1b and 2b, formed tough, transparent yellow, flexible films. Inherent viscosities of these films were 0.53, 0.49, 0.32, and 0.36 respectively. Polymers 1c and 2c, containing the sulfonyl group, having inherent viscosities of 0.21 and 0.23 did not form films. This was attributed to both the rigid bulky sulfonyl groups, which would prevent packing into a well ordered structure needed to form films, and the low inherent viscosity. Polymers 1d and 2d, containing the dodecamethylene group, having inherent viscosities of 0.13 and 0.19, did not form films. This was attributed to low molecular weight.

Differential scanning calorimetry was utilized to determine the glass transition temperatures (Tg°C) of the polymer. The glass transition temperature was the temperature at which a macromolecule changes from a hard, brittle material to a rubbery amorphous compound, which was a measure of the torsion of the polymer backbone.

The glass transition temperature was dependent upon the structure of the polymer. The greater the ordering the higher the glass transition temperature. Factors such as hydrogen bonding and symmetry allow the polymer chains to order themselves resulting in an increased glass transition temperature. Large bulky groups and highly rigid backbones prevent close packing therefore decreasing the glass transition temperature.

The glass transition temperatures for the 4,4'-benzophenone
tetracarboxylic dianhydride series were 249°C for R=diphenyl ether 2a, 248°C for R=diphenyl methylene 2b, 214°C for R=diphenyl sulfone 2c, and 105°C for R=1,12 dodecamethylene 2d. The glass transition temperatures for the series of polymers derived from pyromellitic dianhydride were 182°C for R=diphenyl either 19, 194°C for R=diphenyl methylene 1b, 132°C for R=diphenyl sulfone 1c, and 103°C for R=1,12 dodecamethylene 1d.

The series of polymers derived from 4,4'-benzophenone tetracarboxylic dianhydride showed a significantly higher glass transition temperature than the polymers derived from pyromellitic dianhydride. This is not ordinarily the case. Usually polymers derived from pyromellitic dianhydride show a greater glass transition temperature. Polymers of 1,12 dodecamethylene, 1d and 2d, were not affected by the change in dianhydride.

Polymers 2a, 2b, and 2c showed glass transition temperature of 249°C, 248°C, and 214°C, respectively, which were quite high. These high temperatures indicate a high degree of order in the polymer backbone. Hydrogen bonding may be one factor involved in such ordering as illustrated below.
The 4,4'-benzophenone tetracarboxylic dianhydride has an extra carbonyl in the backbone of its structure that is not present in pyromellitic dianhydride. This carbonyl can serve as a site for hydrogen bonding. Moreover, when hydrogen bonding occurs, the benzene rings adjacent to the sulfonamide and the benzene ring of the benzophenone linkage may align resulting in TT-cloud overlap. These interactions would result in greater ordering and a higher glass transition temperature. Other factors include degradative crosslinking and flex. The carbonyl of the benzophenone may act as a site for a crosslink to occur. In this situation an elevated glass transition temperature would be observed. The carbonyl may also be responsible for a deceptive inherent viscosity. The flexibility of the carbonyl would allow the polymer chain to fold over itself and pack more polymer into a given area resulting in a deceptively low molecular weight. If the polymer was a higher molecular weight species than indicated, there would be an elevated glass transition temperature.

Polymers 1a, 1b, and 1c with glass transition temperatures of 182°C, 194°C, and 132°C respectively, did not have this extra carbonyl to enhance order which resulted in net lower glass transition temperatures.

Polymers utilizing R equal to diphenyl ether and diphenyl methylene show similar values, changing only with the dianhydride used. This was attributed to the similar flex and bulk characteristics of these linkages. The R equal to diphenyl sulfone group resulted in a net lower glass transition temperature than the above two species. This was attributed to greater bulk and decreased flex of the sulfone group which impeded close packing.
The polymers of pyromellitic dianhydride and 4,4'-benzophenone tetracarboxylic dianhydride derived from R=1,12 diaminododecane were the only exceptions to the previously mentioned macromolecules. This was attributed to the decrease in torsion of the polymeric back bone inherent in most polymers containing large aliphatic linkages.

The thermal stability of the poly(imide-sulfonamides) were determined by thermal gravimetric analysis (TGA) at a heating rate of 20°C/minute in a nitrogen atmosphere. All polymers showed a 0.5% to 1.5% weight loss at 150°C which was attributed to the loss of entrapped solvent. The individual TGA curves for the poly(imide-sulfonamide) la (Figure 19), 2a (Figure 20), 1b (Figure 21), 2b (Figure 22), 1c (Figure 23), 2c (Figure 24), 1d (Figure 25), 2d (Figure 26). Percent weight loss at 400°C for the polymers is summarized in Table 12.

Polymers 1a (R=4,4'-oxydianiline and pyromellitic dianhydride) and 2b (R=4,4'-methylene dianiline and 4,4'-benzophenone tetracarboxylic dianhydride) showed no depressions on major weight until thermal breakdown occurred at 400°C. This indicates a high degree of thermal stability. Polymers 1b (R=4,4'-oxydianiline and 4,4'-benzophenone tetracarboxylic dianhydride) and 2a (R=4,4'-methylene dianiline and pyromellitic dianhydride) showed a depression at 200°C followed by major thermal degradation at 400°C. The depression at 200°C was attributed to incomplete imidization where the weight loss corresponded to the elimination of water.

Polymers 1c, 2c, 1d, and 2d did not show any depression at 200°C. Polymer degradation began at 350°C followed by a sharp weight loss. This was attributed to low molecular weight.
In every case the higher the inherent viscosity resulted in greater thermal stability was observed. This higher inherent viscosity implies higher molecular weight. Combining thermograms of each R group used 1a, 2a (Figure 27), 1b, 2b (Figure 28), 1c, 2c (Figure 29), 1d, 2d (Figure 30) there is not correlation observed based on R linkage or dianhydride.

Thermal stability does appear intermediate between the poly sulfonamide and the polyimide as predicted.
CONCLUSION

Eight novel poly(amide-sulfonamides) were synthesized and characterized. Poly(amide-sulfonamides 1a, 1b, 2a, and 2b containing the 4,4'-oxydianiline and 4,4' methylene dianiline groupings showed the best physical and chemical properties. They all formed tough flexible films. These malina show promise as potential candidates for ultrafiltration and reverse osmosis membranes and should be investigated further.
EXPERIMENTAL

General Information

Melting Point: Melting points were carried out on a Mettler FP-5 with a polarizing microscope attachment.

Infrared spectroscopy: All infrared spectra were obtained using potassium bromide pellets, 10%, on a Perkin-Elmer 681 spectrophotometer using the following parameters—scan mode at % T, slit at 5, and Time constant at 1. All peaks were reported in reciprocal centimeters (cm⁻¹) where S, M, and W stand for strong, medium, and weak absorptions respectively.

Inherent Viscosity: Viscosities of poly(amic acid sulfonamide) solutions, concentration 0.5g/100 ml in N,N-dimethyl acetamide, were determined in a Ubelode viscometer at a constant temperature of 25°C.

Elemental Analysis: Analysis were performed by the Baron Consulting Co. Inc. of Orange, Connecticut. The diamine monomers were dried in vacuo over phosphorus pentoxide and boiling toluene in a drying pistol to ensure the removal of water and solvent.

Reagents and Solvents: All reagents and solvents were purchased from the Aldrich Chemical Company or the Eastman Kodak Company. Acetamide benzene sulfonyl chloride was recrystallized from chloroform and petroleum ether (4:1 by volume). All diamines were recrystallized from pure methanol before use. N,N-dimethyl acetamide
was distilled from calcium hydride under reduced pressure and stored over molecular sieves. Pyromellitic dianhydride was purified by sublimation. Benzophenone tetracarboxylic dianhydride was recrystallized from acetic anhydride, washed with cold anhydrous ether, and stored in an evacuated desiccator.

**Thermal Gravimetric Analysis (TGA):** Thermal gravimetric analysis were performed on the cured polymer films utilizing a Perkin-Elmer TGS-2 Thermogravimetric Analyzer. Polymers were heated at a rate of 20°C per minute in a nitrogen atmosphere.

**Differential Scanning Calorimetry (DSC):** Glass transition temperatures of the cured polymer films were determined on a Perkin-Elmer DSC-4 Differential Scanning Calorimeter with a Nitrogen purge, heating rate of 10°C/min., and a range of 10 mcal/sec.

**Thin Layer Chromatography (TLC):** Thin layer chromatography was performed on blocked and deblocked diamines utilizing Eastman Kodak Chromatograms with fluorescent indicator (no. 13181). The solvent used was ethyl acetate:hexane (3:1 v/v).

**Column Elution Chromatography:** Column chromatography was utilized for the purification of the diamino monomers. Woelm Silica Gel (EM. 60F254) was the stationary phase while ethyl acetate:hexane (3:1 v/v) was used as the mobile phase.
General Procedure A for the Preparation of Blocked Diamine Monomers

Diamine (0.05 moles) and 100 ml glacial acetic acid were placed in a 500 ml round bottom flask equipped with a magnetic stirrer, thermometer, and condenser. The mixture was heated to reflux temperature (110°C). To this heated mixture was added N-acetyl sulfanilyl chloride (0.1125 moles, 25% excess), in one portion. Immediately, 0.5 mole anhydrous sodium acetate was added to the stirring mixture. Anhydrous sodium acetate was added in 0.25, 0.125, 0.125, and 0.25 molar portions every fifteen minutes. After the final addition, the mixture was refluxed and stirred for two hours. The mixture was cooled to room temperature, transferred to a Waring blender with 500 ml water. The precipitate was filtered and washed as follows: 2 X 100 ml cold 10% acetic acid, 2 X 100 ml cold 5N hydrochloric acid.

The crude product was dried in a vacuum oven at 30°C for six hours.

General Procedure B for the Preparation of Blocked Diamine Monomers.

N-Acetyl sulfanilyl chloride (0.11 moles, 10% excess), 250 ml tetrahydrofuran, and 9.70 ml pyridine (0.11 moles) were placed in a 2.0 liter round bottom flask equipped with a mechanical stirrer and a condenser. The mixture was heated to reflux. To this heated mixture was added dropwise, diamine (0.05 moles) in 250 ml tetrahydrofuran. The mixture was stirred for two hours, cooled, and the tetrahydrofuran was decanted from a dark viscous oil. The oil was poured into a beaker of ice water to give a precipitate. The
precipitate was collected and dried in vacuo at 110°C for six hours.

**General Procedure C for the Preparation of Diamine Monomers.**

Into a one neck round bottom flask equipped with a condenser and magnetic stirrer was placed (0.05 moles) blocked diamino compound 120 ml 6N hydrochloric acid (8 times by weight). The mixture was refluxed for one hour, cooled, poured into 1000 ml ice water, and neutralized with anhydrous sodium carbonate. The product, formed upon neutralization, was washed with cold water and dried at 30°C in vacuo for six hours.

**General Procedure D for the Polymerization of Diamino Monomer and Dianhydride**

To a 50 ml round bottom flask, equipped with a drying lobe and magnetic stirrer, was placed 3.0 ml freshly distilled N,N-dimethyl acetamide. The solvent was cooled to 0°C in an ice bath and dianhydride (0.005 moles) was added in one portion. Once the dianhydride dissolved, diamino monomer (0.005 moles) was added in a single addition. The mixture was stirred for six hours, poured into 250 ml distilled water, collected, and dried in vacuo for six hours at 100°C.

**Reaction of 4,4'-oxydianiline with N-Acetylsulfanilyl Chloride to Prepare 4,4'-[oxy bis (p-phenylene sulfonamido)] diacetanilide, 17a.**

Using general procedure A, 10.00 grams (0.0499 moles) of 4,4'-o
oxydianiline was reacted with 26.0 grams (0.1125 moles) N-acetyl sulfanilyl chloride to produce 15.01 grams, 84% yield, of 17a, (m.p. 152-178°C). Thin layer chromatography showed three spots. Purification by recrystallization was unsuccessful.

Reaction of 4,4'-Methylene Dianiline with N-Acetyl Sulfanilyl Chloride to Prepare 4,4'-[methylene bis (p-phenylene sulfonamido)] diacetanilide, 17b.

Using general procedure A, 1.98 grams (0.010 moles) of 4,4'-methylene dianiline was reacted with 5.85 grams (0.0225 moles) N-acetyl sulfanilyl chloride to produce 5.334 grams, 90% yield, of 17b, (m.p. 120-140°C). Thin layer chromatography showed three spots. Purification by recrystallization was unsuccessful.

Reaction of 4,4'-Diaminodiphenyl Sulfone with N-Acetyl Sulfanilyl Chloride to Prepare 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] diacetanilide, 17c.

Using general procedure A, 7.45 grams (0.03 moles) of 4,4' diamino diphenyl sulfone was reacted with 17.40 grams (0.075 moles) N-acetyl sulfanilyl chloride to produce 16.07 grams, 83% yield, of 17c (m.p. 175-180°C). Thin layer chromatography showed three spots. Purification by recrystallization was unsuccessful.
Reaction of 1,12 Diaminododecane with N-Acetyl sulfanilyl Chloride to Prepare 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)] diacetanilide, 17d.

Using general procedure A, 6.06 grams (0.0271 moles) 1,12-diamino dodecane was reacted with 17.55 grams (0.075 moles) N-acetyl sulfanilyl chloride to produce 6.42 grams, 40% yield, of 17d (m.p. 140°-142°C). Thin layer chromatography showed three spots. Purification by recrystallization was unsuccessful.

Reaction of 4,4'-Oxydianiline with N-Acetyl Sulfanilyl Chloride to Prepare 4,4'-[oxy bis (p-phenylene sulfonamido)] diacetanilide, 17a.

Using general procedure B, 11.68 grams (0.05 moles) of 4,4'-oxydianiline was reacted with 25.00 grams (0.11 moles) N-Acetyl sulfanilyl chloride to produce 23.76 grams, 80% yield of 17a (m.p. 192-198°C). Thin layer chromatography showed two major spots and a trace spot at $R_f$=0.0, 0.28, and 0.31 respectively. The spot at $R_f$=0.28 corresponded to the desired product. The crude material was recrystallized from methanol:chloroform (30:70 v/v) to give a white powder (m.p. 238-240°C).

See Figure 3 for infrared spectra.

Reaction of 4,4'-Methylene Dianiline with N-Acetyl Sulfanilyl Chloride to Prepare 4,4'-[methyl bis (p-phenylene sulfonamido)] diacetanilide, 17b.

Using general procedure B, 9.95 grams (0.05 moles) of 4,4'-
methylene dianiline was reacted with 25.70 grams (0.11 moles) N-acetyl sulfanilyl chloride to produce 26.67 grams, 90% yield, of 17b (m.p. 142-146°C). Thin layer chromatography showed two major spots and a trace spot at R_f=0.0, 0.28, and 0.31 respectively. The spot at R_f=0.21 corresponded to the desired product. The crude material was recrystallized from methanol:chloroform (30:70 v/v) to give a white powder (m.p. 148-152°C).

See Figure 4 for infrared spectra.

Reaction of 4,4'-Diamino diphenyl Sulfone with N-Acetyl Sulfanilyl Chloride to Prepare 4,4'-[sulfonyl bis (p-phenylene sulfonamido)] diacatanilide, 17c.

Using general procedure B, 12.40 grams (0.05 moles) of 4,4'-diaminodiphenyl sulfone was reacted with 25.79 grams (0.11 moles) N-acetyl sulfanilyl chloride to produce 24.23 grams, 75% yield of 17c (m.p. 156-158°C). Thin layer chromatography showed two major spots and a trace spot at R_f=0.0, 0.20, and 0.22 respectively. The spot at R_f=0.20 corresponded to the desired product. The crude material was recrystallized from methanol:chloroform (30:70 v/v) to give a tan powder (m.p. 161-162°C).

See Figure 5 for infrared spectra.
Reaction of 1,12-Diaminododecane with N-Acetyl sulfanilyl Chloride to Prepare 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)] diacetanilide, 17d.

Using procedure B, 10.0 grams (0.05 moles) of 1,12-diaminododecane was reacted with 25.00 grams (0.11 moles) N-acetyl sulfanilyl chloride to produce 26.17 grams, 88% yield of 17d (m.p. 140-142°C). Thin layer chromatography showed two major spots and a trace spot at Rf=0.0, 0.31 and 0.39 respectively. The spot at Rf=0.31 corresponded to the desired product. The crude material was recrystallized from methanol-chloroform (20:80 v/v) to give a white powder (m.p.=152-154°C).

See Figure 6 for infrared spectra.

Deblocking of 4,4'-[oxy bis(p-phenylene sulfonamido)] diacetanilide 17a, to Prepare 4,4'-[oxy bis(p-phenylene sulfonamido)] dianiline, 19a.

Using general procedure C, 10.00 grams (0.017 moles) of 4,4'-[oxy bis(p-phenylene sulfonamido)] diacetanilide, 17a, was deblocked with 80 ml, 6N hydrochloric acid to produce 7.60 grams, 80% yield of 4,4'-[oxy bis(p-phenylene sulfonamido)] dianiline, 19a, (m.p.=175-176°C). Thin layer chromatography showed two major spots and a trace spot at Rf=0.0, 0.57, and 0.63 which corresponded to the sulfonic acid of N-acetyl sulfanilyl chloride, monomer 19a, and the 1:1 substituted product, respectively. The dianiline monomer was purified by column elution chromatography utilizing ethyl acetate-
hexane (3:1 v/v) as the mobile phase on a stationary phase of silica gel. The monomer, 19a (m.p. 179-180°C), was collected and dried in vacuo at 110°C for twelve hours.

Infrared Spectrum: Infrared spectrum of 19a showed major absorptions at 3480 cm⁻¹ and 3380-3250 cm⁻¹ which corresponded to the sulfonamide and primary amine respectively. (See Figure 7). Other absorptions were observed at 1660(m), 1595(m), 1500(s), 1330(s), 1240(s), 1220(s), 1150(s), 1090(s), 1010(w), 910(w), 870(m), 830(s), 680(m) cm⁻¹.

Deblocking of 4,4'-[methyl bis(p-phenylene sulfonamide diacetanilide, 17b, to Prepare 4,4'-[methyl bis p-phenylene sulfonamido)] dianiline, 19b.

Using general procedure G, 10.00 grams (0.0169 moles) of 4,4'-[methyl bis(p-phenylene sulfonamido)] diacetanilide, 19b, was de-blocked with 80 ml, 6N hydrochloric acid to produce 7.54 grams, 87% yield of 4,4'-[methyl bis(p-phenylene sulfonamido)] dianiline 17b. Thin layer chromatography showed two major spots and a trace spot at R=0.0, 0.41, and 0.48 which corresponded to the sulfonic acid of N-acetyl sulfanilyl chloride, monomer 19b, and the 1:1 substituted product, respectively. The dianiline monomer was purified by column elution chromatography utilizing ethyl acetate-hexane (3:1 v/v) as the mobile phase on a stationary phase of silica gel. The monomer, 19b (m.p. 222.3-223.5°C), was collected and dried in vacuo at 110°C for twelve hours.

Elementary Analysis:

Calculated: C, 59.01; H, 4.77; N, 11.01; S, 12.60.

Found: C, 59.32; H, 4.68; N, 11.03; S, 12.84.
Infrared Spectrum:

Infrared spectrum of 19b, showed major absorptions at 3485 cm\(^{-1}\) and 3380-3250 cm\(^{-1}\) which corresponded to the sulfonamide and corresponded to the sulfonamide and primary amino respectively. (See Figure 8). Other absorptions were observed at: 2930(w), 1640(s), 1600(s), 1505(s), 1450(m), 1390(m), 1310(s), 1190(m), 1150(s), 1090(s), 910(m), 860(m), 700 cm\(^{-1}\)(m).

Deblocking of 4,4'-[sulfonyl bis(p-phenylene sulfonamido) diacetanilide, 17c, to Prepare 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] dianiline, 19c.

Using general procedure C, 10.00 grams (0.015 moles) of 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] diacetanilide, 17c, was deblocked with 80 ml, 6N hydrochloric acid to produce 7.81 grams, 93% yield of 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] dianiline, 19c, m.p. (162-168°C). Thin layer chromatography showed two major spots and a trace spot at R\(_f\)=0.0, 0.39, and 0.42 which corresponded to the sulfonic acid of N-acetyl sulfanilyl chloride, monomer 19c, and the 1:1 substituted product, respectively. The dianiline monomer was purified by column elution chromatography utilizing ethyl acetate-hexane (3:1 v/v) as the mobile phase on a stationary phase of silical gel. The monomer, 19c (m.p. 171-173°C), was collected and dried in vacuo at 110°C for twelve hours.

Elementary Analysis:

Calculate: C, 51.60; H, 397; N, 10.03; S, 17.22

Found: C, 52.03; H, 3.89; N, 9.74; S, 17.50

Infrared spectrum of 19c, showed major absorptions at 3450 cm\(^{-1}\)
and 3360-3220 cm\(^{-1}\) which corresponded to the sulfonamide and primary amine respectively. (See Figure 9). Other absorptions were observed at: 1625(m), 1590(s), 1500(m), 1275(m), 1140(s), 1100(s), 1070(w), 825(m), 715(w), 690(w) cm\(^{-1}\).

Deblocking of 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)] diacetanilide, 17d, to Prepare 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)] dianiline, 19d.

Using general procedure C, 10.0 grams (0.017 moles) of 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)] diacetanilide, 17d, was deblocked with 80 ml, 6N hydrochloric acid to produce 8.160 grams, 95% yield of 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)] dianiline, 19d (m.p.=172-175\(^\circ\)C). Thin layer chromatography showed two major spots and a trace spot at R\(_f\)=0.0, 0.69, 0.79, which corresponded to the sulfonic acid of N-acetyl sulfanilyl chloride, monomer 19d. and the 1:1 substituted product, respectively. The dianiline monomer was purified by column elution chromatography utilizing ethyl acetate-hexane (3:1 v/v) as the mobile phase on a stationary phase of silica gel. The monomer, 19d (m.p 175.5-176.3\(^\circ\)C), was collected and dried in vacuo at 110\(^\circ\)C for twelve hours.

Elementary Analysis: (C\(_{24}\)H\(_{28}\)O\(_4\)N\(_4\)S\(_2\))

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Infrared Spectrum:

Infrared spectrum of 19d, showed major absorptions at 3410 cm\(^{-1}\), 3280 cm\(^{-1}\) and 3110 cm\(^{-1}\) which corresponded to the primary amine
and the sulfonamide respectively (see Figure 10).

Other absorptions were observed at: 2920(s), 2850(s), 1660(s), 1590(s), 1540(s), 1400(s), 1320(s), 1300(s), 1260(m), 1150(s), 1085(s), 1010(w), 830(m), 815(m), 725(m), 700(m), 635(s), 620(s) cm⁻¹.

Polymerization of 4,4'-[oxy bis(p-phenylene sulfonamido)]
dianiline, 19a, with Pyromellitic Dianhydride to
Prepare Poly 4,4'-[oxy bis(p-phenylene sulfonamido)]
pyromellitimide 1a.

Using general procedure D, 1.8796 grams (0.003 moles) dianiline monomer, 19a, was reacted with 0.7313 grams (0.003 moles) pyromellitic dianhydride in N,N-dimethyl acetamide to produce 2.48 grams, 95% yield, poly(amic acid sulfonamide), 20a, having an inherent viscosity of 0.53. A solution of poly(amic acid sulfonamide), 20% solid in N,N-dimethyl acetamide, was cast on a tempered glass plate and cured for three hours at 280°C to produce a film, poly 4,4'-[oxy bis (p-phenylene sulfonamido)] pyromellitimide 1a. Thermal gravimetric analysis showed 8.96% weight loss at 400°C (see Figure 19). Analysis by differential scanning calorimetry gave a glass transition temperature (Tg°C) of 182°C. Polymer 1a produced a tough flexible yellow film.

Infrared spectrum:

Infrared spectrum of 1a showed major absorptions at 3280 cm⁻¹ and 1780-1710 cm⁻¹ which corresponded to the sulfonamide and the imide linkages respectively. (See Figure 11.)
Polymerization of 4,4'-[oxy bis(p-phenylene sulfonamido)] dianiline, 19a, with 4,4'-Benzophenone Tetracarboxylic Dianhydride to prepare Poly 4,4'-[oxy bis(p-phenylene sulfonamido)]-2,5-bis(1,3-Dioisoindolinediyl)carbonyl 2a.

Using general procedure D, 0.8339 grams (0.0015 moles) dianiline monomer, 19a, was reacted with 0.47932 grams (0.0015 moles) 4,4'-benzophenone tetracarboxylic dianhydride in N,N-dimethylacetamide to produce 1.2511 grams, 95% yield, poly(amic acid sulfonamide), 21a, having an inherent viscosity of 0.49. A solution of poly(amic acid sulfonamide), (20% solids in dimethyl acetamide) was cast on a tempered glass plate and cured for three hours at 280°C producing a film poly 4,4'-[oxy bis(p-phenylene sulfonamido)]-2,5-bis(1,3-dioisoindolinediyl) carbonyl, 2a. Thermal gravimetric analysis showed a 12.71% weight loss at 400°C. (see Figure 20). Analysis by differential scanning calorimetry gave a glass transition temperature (Tg°) of 249°C. Polymer 2a produced a tough, flexible yellow film.

Infrared Spectrum:

Infrared spectrum of 2a showed major absorptions at 3280 cm⁻¹ and 1780-1710 cm⁻¹ which corresponded to the sulfonamide and imide linkages respectively. (See Figure 12.)

Polymerization of 4,4-[methyl bis(p-phenylene sulfonamido)] dianiline, 19b, with Pyromellitic Dianhydride to Prepare poly 4,4'-[methyl bis(p-phenylene sulfonamido)] pyromellitimide, 1b.

Using general procedure D, 0.67079 grams (0.001 moles) dianiline monomer, 19b, was reacted with 0.26192 grams (0.001 moles) pyromel-
litic dianhydride in N,N'-dimethyl acetamide to produce 0.9047 grams, 97% yield of poly(amic acid sulfonamide) 20b, having an inherent viscosity of 0.32. A solution of the poly(amic acid sulfonamide), 20% solids in dimethylacetamide, was cast on a tempered glass plate and cured for three hours at 280°C to produce poly 4,4'-[oxy bis(p-phenylene sulfonamido)] pyromellitimide, 1b. Thermal gravimetric analysis showed a 19% weight loss at 400°C (see Figure 21). Differential scanning calorimetry gave a glass transition temperature (Tg°) of 194°C. Polymer 1b produced a tough, flexible, yellow film.

Infrared Spectrum:

Infrared spectrum of 1b showed major absorptions at 3275 cm⁻¹ and 1780-1720 cm⁻¹ which corresponded to the sulfonamide and imide linkages respectively (see Figure 13).

Polymerization of 4,4'-[methyl bis(p-phenyl sulfonamido)] dianiline, 19b, with 4,4'-Benzophenone Tetracarboxylic Dianhydride to prepare Poly 4,4'[methyl bis(p-phenyl sulfonamido)]-2,5-bis (1,3-dioxoisoiindolinediyI) carbonyl 2b.

Using general procedure D, 0.4012 grams (0.0007 moles) dianiline monomer, 19b, was reacted with 0.2311 grams (0.0007 moles) 4,4'-benzophenone tetracarboxylic dianhydride in N,N-dimethylacetamide to produce 0.6133 grams, 97% yield, of poly(amic acid sulfonamide), 21b, having an inherent viscosity of 0.36. A solution of poly(amic acid sulfonamide), 20% solids in dimethyl acetamide, was cast on a tempered glass plate and cured for three hours at 280°C to produce poly 4,4'-[oxy bis(p-phenylene sulfonamido)]-2,5-bis(1,3-dioxoisoiindolinediyI)carbonyl 2b. Thermal gravimetric analysis showed a
6.83% weight loss at 400°C (see Figure 22). Differential scanning calorimetry gave a glass transition temperature (Tg°) of 248°C. Polymer 2b produced a tough, flexible, yellow film.

**Infrared spectrum:**

Infrared spectrum of 2b showed major absorptions at 3290 and 1780-1690 cm\(^{-1}\) which corresponded to the sulfonamide and imide linkages, respectively. (See Figure 14.)

**Polymerization of 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] dianiline 19c with Pyromellitic Dianhydride to Prepare Poly 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] pyromellitimide, 1c.**

Using general procedure D, 2.3357 grams (0.0045 moles) dianiline monomer, 19c, was reacted with 0.9120 grams (0.0045 moles) pyromellitic dianhydride in N,N-dimethylacetamide to produce 3,1181 grams, 96% yield, poly(amic acid sulfonamide), 20c, having an inherent viscosity of 0.21. A solution of dry poly(amic acid sulfonamide), 20% solids in dimethyl acetamide, was cast on a tempered glass plate and cured for three hours at 280°C to produce poly 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] pyromellitimide), 1c. Thermal gravimetric analysis showed a 24% weight loss at 400°C (see Figure 23). Analysis by differential scanning calorimetry gave a glass transition temperature (Tg°) of 132°C. Polymer 1c was not film forming.

**Infrared Spectrum:**

Infrared spectrum of 1c showed major absorptions at 3230 cm\(^{-1}\) and 1780-1720 cm\(^{-1}\) which corresponded to the sulfonamide and imide linkages, respectively. (See Figure 15.)
Polymerization of 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] dianiline 19c with 4,4'-Benzophenone Tetracarboxylic Dianhydride to Prepare Poly 4,4'-[sulfonyl bis(p-phenylene sulfonamido)]-2,5-bis(1,3-dioxoisoindolinediyl)carbonyl 2c.

Using general procedure D, 2.8470 grams (0.0051 moles) dianiline monomer, 19c, was reacted with 1.6423 grams (0.0051 moles) 4,4'-benzophenone tetracarboxylic dianhydride in N,N-dimethyl acetamide to produce 4.4011 grams 98% yield, of poly(amic acid sulfonamide), 21c, having an inherent viscosity of 0.23. A solution of poly(amic acid sulfonamide), 10% solids in dimethyl acetamide, was cast on a tempered glass plate and cured for three hours at 280°C to produce poly 4,4'-[sulfonyl bis(p-phenylene sulfonamido)]-2,5-bis(1,3-dioxoisoindolinediycarbonyl], 2c. Thermal gravimetric analysis showed a 34% weight loss at 400°C (see Figure 24). Differential scanning calorimetry gave a glass transition temperature (Tg°) of 214°C.

Infrared Spectrum:

Infrared spectrum of 2c showed major absorptions at 3290 cm⁻¹ and 1800-1660 cm⁻¹ which corresponded to the sulfonamide and imide linkages, respectively. (See Figure 16.)

Polymerization of 4,4'-[dodecamethylene bis(p-phenylene sulfonamido) dianiline, 19d, with Pyromellitic Dianhydride to Prepare Poly 4,4'-[dodecamethylene bis (p-phenylene sulfonamido)] pyromellitimide 1d.

Using general procedure D, 0.8790 grams (0.0017 moles) dianiline monomer, 19d, was reacted with 0.3754 grams (0.0017 moles) pyromellitic dianhydride in N,N-dimethyl acetamide to produce 1.2295 grams,
98% yield, poly(amic acid sulfonamide), 20d, having an inherent viscosity of 0.13. A solution of poly(amic acid sulfonamide), 20% solids in dimethyl acetamide, was cast on a tempered glass plate for three hours at 280°C to produce poly 4,4'-[sulfonyl bis(p-phenylene sulfonamido)] pyromellitimide, 1d. Thermal gravimetric analysis showed 42% weight loss at 400°C (see Figure 25). Analysis by differential scanning calorimetry gave a glass transition temperature (Tg°) of 105°C. Polymer 1d was not film forming.

**Infrared Spectrum:**

Infrared spectrum of 1d showed major absorptions at 3310-3280 and 1760-1710 cm⁻¹ which corresponded to the sulfonamide and imide linkages, respectively. (See Figure 17.)

**Polymerization of 4,4'-[dodecamethylene bis(p-phenylene sulfonamido) dianiline, 19d, with 4,4'-Benzophenone Tetracarboxylic Dianhydride to Prepare Poly 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)]-2,5-bis (1,3-dioxoisindolinediyi) carbonyl, 2d.**

Using general procedure D, 0.6515 grams (0.0013 moles) dianiline monomer, 19d, was reacted with 0.4111 grams (0.0013 moles) 4,4 benzophenonetetracarboxylic dianhydride in N,N-dimethyl acetamide to produce 1.009 grams, 95% yield, of poly(amic acid sulfonamide), 21d, having an inherent viscosity of 0.19. A solution of poly(amic acid sulfonamide), 20% solids in dimethyl acetamide, was cast on a tempered glass plate for three hours at 280°C to produce poly 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)]-2,5-bis(1,3-dioxoisindolinediyi)carbonyl, 2d. Thermal gravimetric analysis showed
a 42% weight loss at 400°C (see Figure 26). Differential scanning calorimetry gave a glass transition temperature (Tg°) 103°C. Polymer 2d was not film forming.

**Infrared Spectrum:**

Infrared spectrum of 2d showed major absorptions at 3305-3260 cm\(^{-1}\) and 1780-1700 cm\(^{-1}\) which corresponded to the sulfonamide and imide linkages, respectively. (See Figure 18.)
(figure 3): Infrared Spectrum of 4,4'-[oxy bis(p-phenylene sulfonamido)] diacetanilide 17a.
(figure 4): Infrared Spectrum of 4,4'-[methyl bis(p-phenylene sulfonamido)]diacetanilide 17b.
(figure 5): Infrared Spectrum of $4,4''\text{-}[\text{sulfonyl bis( p-phenylene sulfonamido)}]\text{diacetanilide}$ 17c.
(figure 6): Infrared Spectrum of 4,4′-[dodecamethylene bis(p-phenylene sulfonamido)]diacetonilide 17d.
(figure 7): Infrared Spectrum of 4,4'-[oxy bis(p-phenylene sulfonamido)]dianiline 19a.
(figure 10): Infrared Spectrum of 4,4'-[dodecamethylene bis(p-phenylene sulfonamido)]dianiline 19d.
(figure 14): Infrared Spectrum of Polymer 2b.
(figure 15): Infrared Spectrum of Polymer 1c.
(figure 20): TGA curve of Polymer 2a.

EJK 2-11

WT: 5.9980 mg RATE: 20.00 deg/min

FROM: 150
TO: 400
WT % CHANGE: 12.71

PERKIN-ELMER Thermal Analysis

FILE: QSAVE.TG
DATE: 84/09/28 TIME: 12:08
(figure 21): TGA curve of Polymer 1b.

EJK2-1

WT: 15.8670 mg RATE: 20.00 deg/min

% WEIGHT

FROM: 150.38
TO: 330.02
WT % CHANGE: 9.54

TEMPERATURE (C)

EJK FILE: QSAVE.TG
DATE: 04/09/28 TIME: 11:23

PERKIN-ELMER Thermal Analysis
(figure 22): TGA curve of Polymer 2b.

EJK2-3

WT: 6.2780 mg  RATE: 20.00 deg/min

100.00

98.58%

91.63%

FROM: 150
TO: 400
WT % CHANGE: 6.94

EJK FILE: RITO2.TG
DATE: 04/09/28  TIME: 10:42

PERKIN-ELMER Thermal Analysis
(figure 23): TGA curve of Polymer 1c.

EJK 2-18

WT: 23.7706 mg  RATE: 20.00 deg/min

FROM: 150
TO: 400
WT % CHANGE: 24.53

99.57%

75.03%
(figure 24): TGA curve of Polymer 2c.

EJK2-20

WT: 15.4705 mg  RATE: 20.00 deg/min

FROM: 150  TO: 400  WT % CHANGE: 34.96

99.43%

64.47%

% WEIGHT

TEMPERATURE (C)

EJK  FILE: QSAVE.TG

DATE: 84/09/28  TIME: 14:06

PERKIN-ELMER Thermal Analysis
(figure 27): TGA curves of 1a and 2a.

EJK2-5 1a

--- = EJK 2-11 2a

% WEIGHT

60.00

20.00

60.00 120.00 180.00 240.00 300.00 360.00 420.00 480.00 540.00 600.00 660.00

TEMPERATURE (C)

TG

DATE: 84/09/28  TIME: 09:29

PERKIN-ELMER Thermal Analysis
(figure 28): TGA curves of 1b and 2b.

EJK2-3 : 2b

--- = EJK2-1 : 1b

WT: 6.2780 mg  RATE: 20.00 deg/min

EJK  FILE: RIT02. TG
DATE: 84/09/28  TIME: 10:42

PERKIN-ELMER Thermal Analysis
(figure 29): TGA curves of 1c and 2c.

EJK2-20: 2c
--- = EJK 2-18: 1c

EJK FILE: R108.TG
DATE: 84/09/28 TIME: 14.06

PERKIN-ELMER Thermal Analysis
(Figure 30): TGA curves of 1d and 2d.

EJK2-16: 2d

WT: 11.6165 mg  RATE: 20.00 deg/min

EJK2-14: 1d

% WEIGHT

TEMPERATURE (C)

DATE: 84/09/28  TIME: 12:55
REFERENCES


Ibid. p122.
Ibid. p124.


Ibid.


Ibid. p1490.
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Ibid. p1489.
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References (con't.)

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<td>23.</td>
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<td>24.</td>
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