

# Synthesis, Characterization, and Study of Thermal Properties of Methyl-Substituted Arylene Sulfone Ether Polyimides, Polyamides, and Poly(amide-Imides)\*

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## Synopsis

A number of methyl-substituted bis[(phenyleneoxy) sulfone] dianilines were synthesized and reacted with pyromellitic dianhydride (PMDA), benzophenone tetracarboxylic acid dianhydride (BTDA), terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), and trimellitic anhydride acid chloride (TMAC) to prepare a series of polyimides, polyamides, and poly(amide-imides), respectively. Low temperature solution and interfacial polymerization techniques were utilized to prepare the above polymers. Most of the polymers prepared formed tough, transparent flexible films. The prepared polymers were characterized by solution viscosity, thermal gravimetric analysis (dynamic and isothermal), and differential scanning calorimetry. The effect of the number and the ring substitution of methyl groups on polymer properties is discussed.

## INTRODUCTION

Aromatic polymers containing aryl ether or aryl sulfone linkages generally have greater chain flexibility, lower glass transition temperatures, and greater tractability than the corresponding polymers without these groups in the repeat units. In addition, aromatic polysulfones are known to have high thermooxidative stabilities.<sup>1-4</sup>

A number of polyimides, polyamides, and poly(amide-imides) have been prepared containing both aryl ether and aryl sulfone linkages.<sup>5-7</sup> They are amorphous, have low glass transition temperatures, and show excellent mechanical properties. Polymers of this general type should have high thermal stability with enhanced tractability and solubility characteristics, making them of potential commercial interest. In addition, polyamides incorporating the semistiff structure of aryl ether sulfone linkages have been proposed as new candidates for thermotropic liquid crystalline polymers.<sup>8</sup>

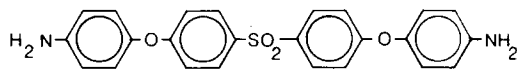
Some of the above polymers have been prepared by reacting a diamine, **1**, with

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the appropriate carboxylic acid derivative using low temperature solution or interfacial polymerization techniques:



These polymers displayed high heat distortion temperatures, good solvent resistance, excellent mechanical properties, high thermal and oxidative stability, and in some cases thermoplastic characteristics.<sup>9</sup>

The purpose of the present study was to modify the basic diamine structure 1 with methyl group substituents and to utilize these novel diamines in the preparation of aromatic polyimides, polyamides, and poly(amide-imides). The effect of the ring substitution on polymer properties have been assessed.

## EXPERIMENTAL

### Procedures

The various starting materials and monomers used in this study were prepared in accordance with literature directions or purchased from supply houses. The carboxylic acid monomers were all recrystallized from the appropriate solvents to constant melting points before use. All solvents used were distilled before use. Pure diamine monomers, anhydrous solvents, and dry apparatus were used. All polymerization reactions, with the exception of the interfacial polymerization reactions, were carried out under a dry nitrogen atmosphere. The polymerization procedures used in this study have been described elsewhere.<sup>5,6,10,11</sup>

Polymer films were prepared by casting polymer solutions in *N,N*-dimethylacetamide onto a glass plate using a doctor blade technique. To ensure complete removal of solvent and imidization, films were heated overnight at 90°C, *in vacuo* for 3 h at 145°C, and then 1 h at 190°C.

### Instrumental Methods

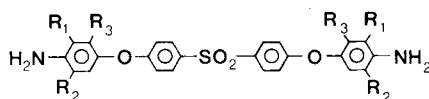
Ubbelohde viscometers were used to determine inherent viscosities of polymer solutions having concentrations of 0.5 g/100 mL in *N,N*-dimethylacetamide. A constant temperature bath was maintained at 25°C.

Thermogravimetric analyses were obtained with a DuPont 950 Thermogravimetric Analyzer in a flowing air environment, unless otherwise indicated. All samples analyzed were films, except for the polyamides which were powders. Sample sizes varied from 1 mg to 2 mg. Heating rate used for the polyamide and poly(amide-imide) determinations was 5°/min. Heating rate used for the polyimide analyses was 10°/min.

The differential scanning calorimetry thermograms were obtained with a DuPont 900 Thermal Analyzer with a DSC cell attachment. All samples analyzed were films, except for the polyamides which were powders. Sample sizes varied from 1.6 mg to 7.0 mg and were analyzed in a flowing nitrogen atmosphere. Rate of heating used was 20°/min.

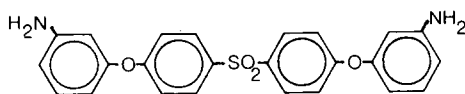
## Diamine Synthesis

A series of methyl-substituted aromatic diamines having the general structure **2** was prepared:



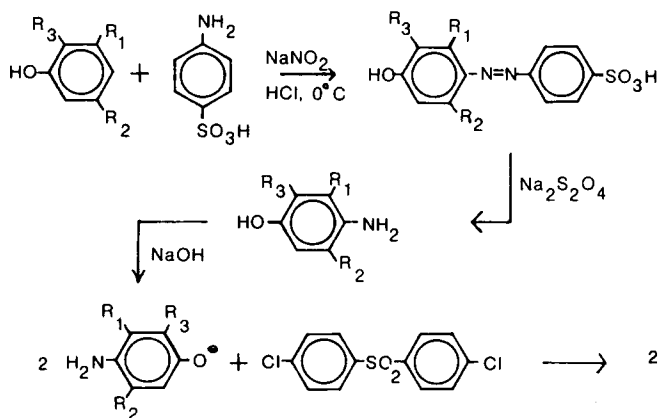
- 2a)  $R_1=R_2=R_3=H-$   
 b)  $R_1=R_2=H, R_3=CH_3-$   
 c)  $R_2=R_3=H, R_1=CH_3-$   
 d)  $R_1=H, R_2=R_3=CH_3-$   
 e)  $R_1=R_2=CH_3, R_3=H-$

In addition, meta-linked diamine **2f** was prepared:



2f

The above diamines were prepared, using a method described by Kawakami and co-workers,<sup>12</sup> by the direct condensation of a sodium salt of the appropriately methyl-substituted aminophenol with 4,4'-dichlorophenyl sulfone. The methyl-substituted aminophenols were obtained by a reduction of the azocompound formed by a diazo coupling reaction of phenol with sulfanilic acid.<sup>13</sup> The general reaction scheme for the preparation of the diamines is shown below:



The meta-linked sulfone ether diamine **2f** is prepared by using *m*-aminophenol in the above sequence.

The diamines were purified by recrystallization or reprecipitation from the appropriate solvents. They were shown to be pure, single compounds on the basis of thin layer chromatography and elemental analyses. The properties of the diamines **2a-f** are summarized in Table I.

TABLE I  
Properties of Diamines

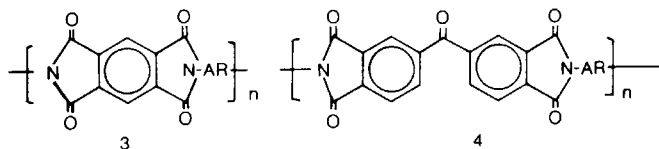
Diamine	mp (°C)	$R_f^a$		Elemental analyses			
				C	H	N	S
2a	189-91	0.48	Calcd	66.66	4.66	6.48	7.40
			Found	66.44	4.69	6.12	7.71
2b	78-80	0.48	Calcd	67.83	5.22	6.09	6.96
			Found	68.52	5.25	5.94	6.85
2c	152-53	0.53	Calcd	67.83	5.22	6.09	6.96
			Found	67.73	5.12	5.98	7.07
2d	91-93	0.54	Calcd	68.85	5.74	5.74	6.56
			Found	68.66	5.88	5.60	6.48
2e	184-86	0.59	Calcd	68.85	5.74	5.74	6.56
			Found	68.64	5.63	5.64	6.53
2f	132-33	0.67	Calcd	66.66	4.66	6.48	7.40
			Found	66.62	4.53	6.30	7.58

<sup>a</sup> Diamines were chromatographed on silica gel using a solvent mixture of benzene:ether:ethanol (5:4:1) by volume.

## RESULTS AND DISCUSSION

### Methyl-Substituted Arylene Sulfone Ether Polyimides

A series of novel polyimides have been prepared from the reaction of pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic acid dianhydride (BTDA) and diamines 2a-f. Low-temperature-solution polymerization techniques were used to first prepare the polyamic acid intermediates which were treated thermally to achieve imidization. The polyimides have general structures 3 and 4 as shown below:



where the AR group represents diamine structures 2a-f.

Polyimides 3a and 4a, i.e., polyimide 3 or 4 prepared from diamine 2a, have been characterized and reported in the literature to have excellent mechanical properties, with good to excellent thermooxidative stability and environmental stress aging characteristics.<sup>5</sup> Most of the modified polyimides prepared in this study were soluble and formed tough, transparent, flexible films. They have been characterized by solution viscosity, thermal gravimetric analysis, and differential scanning calorimetry. The properties of polyimide series 3a-f and 4a-f are summarized in Table II.

The inherent viscosities of the 3a-f PMDA series vary from 0.29 to 0.51 dL/g and the 4a-f BTDA series vary from 0.31 to 0.45 dL/g. In spite of the low apparent viscosities, all these polyimides had film-forming properties. The methyl groups ortho to the amine group, particularly in diamine 2e may lower the molecular weight by sterically reducing the reactivity of the amine group and/or prevent the final imidization ring closure from occurring and instead allow in-

TABLE II  
Properties of Polyimides from PMDA, BTDA, and Aromatic Sulfone Ether Diamines

Polyimide	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)	TGA <sup>c</sup>			
			Air <sup>d</sup>	N <sub>2</sub>	% wt loss at 500°C	
					AIR	N <sub>2</sub>
<b>3</b>						
a	0.51	335 <sup>e</sup>	400	420	12	14
b	0.45	300	400	420	10	14
c	0.49	310	415	450	15	6
d	0.41	310	395	415	20	18
e	0.29	340	405	420	18	8
f	0.45	265	430	440	8	12
<b>4</b>						
a	0.38	280 <sup>f</sup>	400		12	
b	0.31	240	390		12	
c	0.45	265	400		14	
d	0.37	280	400		13	
e	0.32	280	400		12	
f	0.35	225	410		5	

<sup>a</sup> Dimethyl acetamide at 25°C, concn = 0.5 g/100 mL.

<sup>b</sup> Obtained on a DuPont 900 Thermal Analyzer with a differential scanning calorimeter.

<sup>c</sup> Obtained on a DuPont 950 Thermogravimetric Analyzer.

<sup>d</sup> The polymer decomposition temperature (PDT) taken as the onset of rapid decomposition.

<sup>e</sup> A  $T_m$  of 435°C was observed.

<sup>f</sup> A  $T_m$  of 400°C was observed—all other samples did not show a  $T_m$ .

termolecular crosslinking side reactions to occur during the thermal cyclization. This generally results in insoluble polymers with unusually high glass transition temperatures. We observe brittle films for polyimides **3e** and **4e**, and also for the polyimides prepared with diamine **2d**.

The glass transition temperatures  $T_g$  for the **3a–f** PMDA series and BTDA series are given in Table II. As expected, both PMDA and BTDA polyimides prepared from the nonlinear meta-linked diamine **2f** have the lowest  $T_g$  values in their respective series. As the number of the methyl groups increases in the diamine segment, the  $T_g$  decreases except in polyimides **3e** and **4e**. In these polyimides the  $T_g$  values are almost identical to the  $T_g$  values of polyimides **3a** and **4a**, which were prepared from the unsubstituted para-linked diamine. This may be due to either the symmetrical arrangement of the methyl groups in the diamine segment or to the formation of a polyimide with some crosslinks.

Polyimides **3a** and **4a** show crystalline melting points of 435°C and 400°C, respectively. Crystalline melting points were not observed for the other polyimides. These polyimides, **3b–f** and **4b–f**, have a variety of methyl substituents and meta-linkage present in their structures, which will affect packing efficiency and hence their ability to crystallize.

Fairly good thermal stability was shown by both polyimide series with the PMDA series showing slightly higher polymer decomposition temperatures than the BTDA series. The temperature for the onset of rapid weight loss or decomposition was taken as the polymer decomposition temperature. The polymer decomposition temperature for most of the polyimides prepared was about 400°C. Thermal gravimetric data is summarized in Table II. The thermograms for polyimide series **3a–f** and **4a–f** are illustrated in Figures 1 and 2, respectively.

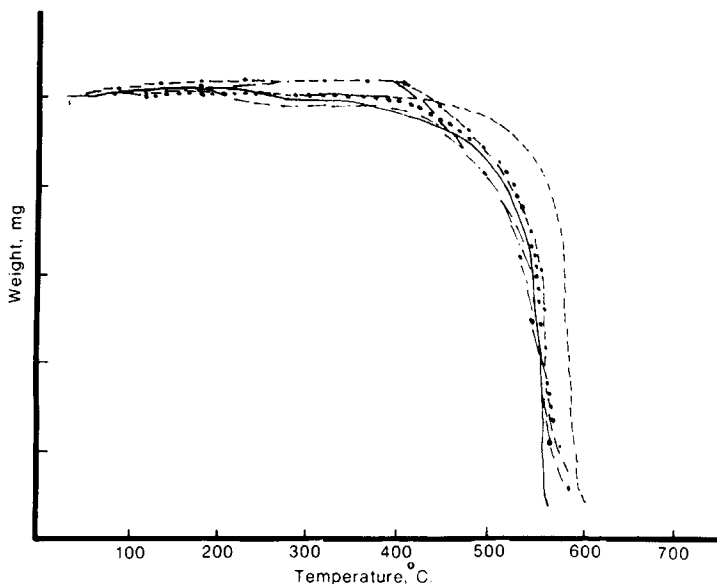


Fig. 1. Thermogravimetric analyses of polyimides from PMDA and aromatic sulfone ether diamines in air: (—) 3a; (.....) 3b; (---) 3c; (- - - -) 3d; (---) 3e; (---) 3f.

Some of the polyimide samples analyzed showed a slight 1–4% weight increase at temperatures from 150°C to 300°C. Since the determinations were carried out in a flowing air atmosphere, air oxidation reactions with methyl substituents are possible.<sup>14</sup> With the exception of polyimides 3f and 4f prepared from the meta-linked diamine 2f, all the polyimides showed almost identical thermal behavior.

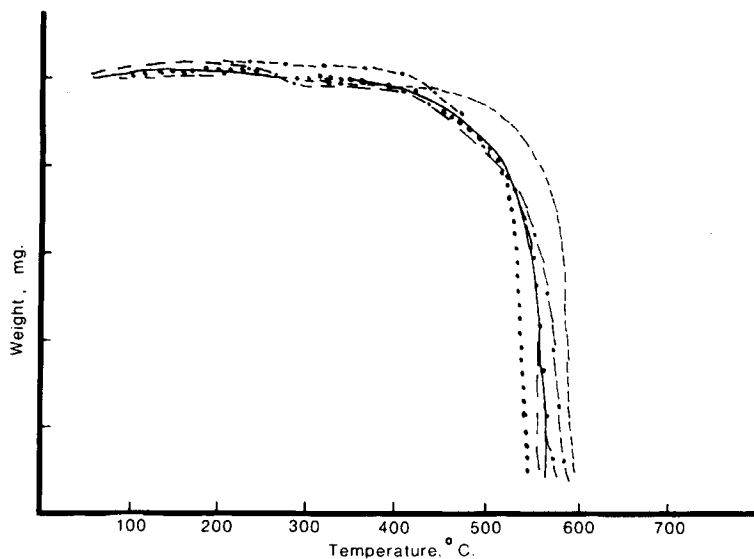


Fig. 2. Thermogravimetric analyses of polyimides from BTDA and aromatic sulfone ether diamines in air: (—) 4a; (.....) 4b; (---) 4c; (- - - -) 4d; (---) 4e; (---) 4f.

TABLE III  
Isothermal Gravimetric Analyses of Polyimides from PMDA, BTDA, and Sulfone Ether Diamines at 325°C in Air

Polyimide	% Weight loss <sup>a</sup>					
	4 h	1 day	2 days	3 days	6 days	8 days
<b>3</b>						
a	8.5	4.4	8.2	11.4	11.4	11.4 <sup>b</sup>
b	2.9	0.2	3.3	8.4	20.5	23.8
c	9.2	7.2	7.9	13.9	25.2	34.5
d	2.4	+0.3	10.3	18.1	26.0	28.4
e	2.4	+2.9	28.4	39.7	43.4	50.5
f	3.9	2.1	8.1	10.4	10.4	11.7 <sup>b</sup>
<b>4</b>						
a	12.4	11.9	11.9	17.1	17.1	17.1 <sup>b</sup>
b	5.2	7.7	11.6	16.1	19.5	20.9
c	6.8	6.8	6.8	8.1	8.8	8.7 <sup>b</sup>
d	4.0	9.6	19.7	25.5	32.5	37.4
e	6.7	5.2	10.4	16.9	25.6	27.3
f	7.2	5.2	5.2	7.2	7.3	7.2 <sup>b</sup>

<sup>a</sup> All samples were films, except 3d and 4d, which were powders.

<sup>b</sup> These film samples retained their mechanical strength; they were flexible and could be folded many times without breaking.

Polyimides 3f and 4f showed considerably greater thermal stability than all of the other polyimides in their respective series. These polyimides also showed the lowest percent weight loss at 500°C. As can be seen in Figures 1 and 2, the methyl substituents in the diamine structural unit appear to have little influence on thermal stability since the polymer decomposition temperature and the

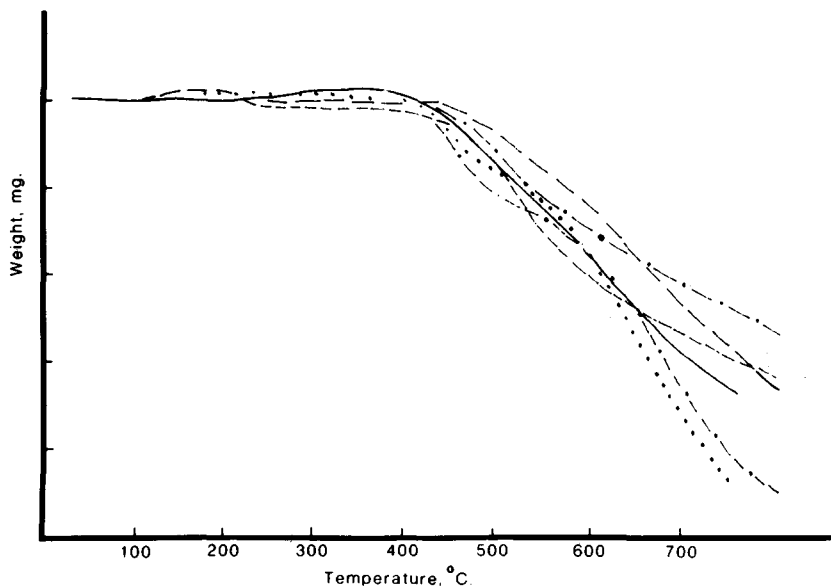


Fig. 3. Thermogravimetric analyses of polyimides from PMDA and aromatic sulfone ether diamines in nitrogen: (—) 3a; (·····) 3b; (---) 3c; (- - - -) 3d; (- · - ·) 3e; (---) 3f.

thermograms of the prepared polyimides are similar in these dynamic studies.

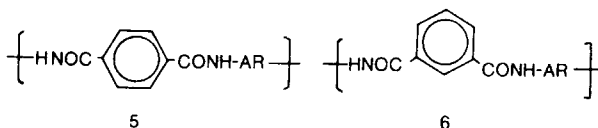
The polymer decomposition temperatures for the PMDA polyimides 3a-f increased 10–20°C when the TGA determinations were carried out in a flowing nitrogen atmosphere. These data are summarized in Table II. The thermograms for these polyimides are illustrated in Figure 3.

Isothermal gravimetric analyses of polyimides 3a-f and 4-f are summarized in Table III. These studies were carried out at 325°C and illustrate the effect of methyl substituents on the thermal stability. After an initial weight loss (2.4–12.4%) most polyimide film samples showed a small weight increase (0.5–5.3%). The weight loss is believed to be due to entrapped solvent, incomplete imidization reaction, and/or crosslinking reactions while the following weight gain is attributed to thermooxidative reactions.

After 24 h all samples steadily lost weight. With the exception of polyimide 4c, polyimides modified with methyl substituents all showed a considerably greater weight loss than those polyimides prepared from unsubstituted para- and meta-linked diamines. Polyimide films 3a, 3f, 4a, 4c, and 4f retained their mechanical strength after eight days of heating. They were flexible and could be folded many times without breaking.

### Methyl-Substituted Arylene Sulfone Ether Polyamides

A series of novel polyterephthalamides and polyisophthalamides have been prepared from the reaction of terephthaloyl chloride and isophthaloyl chloride with diamines 2a-f, respectively. The polyamides were prepared using an interfacial polymerization technique with water and cyclohexanone as the immiscible solvents. The polyamides have the general structures 5 and 6 as shown below:



where the AR group indicates the structures of diamine 2a-f. Most of the modified polyamides prepared formed though transparent flexible films. They have been characterized by solution viscosity, thermal gravimetric (dynamic and isothermal) analysis, and differential scanning calorimetry. In addition, several of the prepared polyamides, considered to be novel candidates for thermotropic liquid crystalline polymers, were characterized by X-ray diffraction analysis and optical birefringence. The results of this study have been described elsewhere.<sup>8</sup> The properties of the polyterephthalamides, series 5a-f, and the poly(isophthalamides) series 6a-f are summarized in Table IV.

The inherent viscosities of the para-linked series 5a-f are greater than those for the meta-linked series 6a-f, as might be expected from considerations of the structure. Both polyterephthalamide and polyisophthalamide prepared from diamine 2e have the lowest inherent viscosities. Diamine 2e has methyl substituents at all ortho positions to the amino groups, a structure which can sterically reduce the reactivity of the amine groups and thus prevent the formation of a high molecular weight polyamide.



TABLE IV  
Properties of Polyamides from Terephthaloyl Chloride, Isophthaloyl Chloride, and Aromatic Sulfone Ether Diamines

Polyamide	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)	$T_m$ (°C)	TGA <sup>c</sup>	
				Air <sup>d</sup> (°C)	% wt loss at 500°C
<b>5</b>					
a	Insoluble	260 (215) <sup>e</sup>	425	405	17
b	0.63	210		360	26
c	1.06	220	287	370	24
d	0.54	230	330	350	39
e	0.29	265		360	35
f	0.50	195		410	12
<b>6</b>					
a	0.98	255	325	400	19
b	0.52	240	325	360	28
c	0.46	215	295	360	24
d	0.51	225	335	360	30
e	0.23	250		360	29
f	0.34	195	255	405	16

<sup>a</sup> Dimethyl acetamide at 25°C, concentration = 0.5 g/100 mL.

<sup>b</sup> Obtained on a DuPont 900 Thermal Analyzer with a differential scanning calorimeter.

<sup>c</sup> Obtained on a DuPont 950 Thermogravimetric Analyzer.

<sup>d</sup> The polymer decomposition temperature, PDT, taken as the onset of rapid decomposition.

<sup>e</sup> Glass transition temperature observed after quenching with liquid nitrogen.

The  $T_g$ 's for the 5a-f polyterephthalamide series are slightly greater (5–20°) than for the polyisophthalamide series 6a-f, as shown in Table IV. Both polyamides 5f and 6f prepared from the meta-linked diamine 2f have the lowest  $T_g$  value in their respective series, 195°C. The methyl substituents appear to lower the glass transition temperatures except in polyamides 5e and 6e. In these cases the  $T_g$  values are almost identical to  $T_g$  values of polyamides 5a and 6a prepared from the unsubstituted para-linked diamine. These higher values may be due to a symmetry factor—the order arrangement of the methyl substituents in the diamine segment. The same increase in  $T_g$  was observed in polyimides 3e and 4e.

With the exception of polyamides 5b, 5e, 5f, and 6e, all the prepared polyamides showed an endotherm varying from 255°C to 425°C. Examination of cast unstretched polyamide films under a low power microscope with crosspolarizing filters did not show crystallites. The X-ray diffraction patterns also have indicated low degree of crystallinity.<sup>8</sup>

Good thermal stability with similar polymer decomposition temperatures was shown by both polyamide series, as shown in Table IV. The thermograms for polyamide series 5a-f and 6a-f are illustrated in Figures 4 and 5, respectively. Some of the polyamide samples showed a small 1–4% weight gain at temperatures from 150°C to 300°C, attributable to air oxidation reactions. Polyamides 5f and 6, prepared from the meta-linked diamine 2f, showed greater thermal stability than all the other polyamides in their respective series similarly to the observations for the polyimides. They also showed the lowest percent weight loss at 500°C. The polyamide structures modified with methyl substituents in the diamine segment appear to be more susceptible to decomposition reactions and lose weight rapidly at temperatures between 350°C and 370°C. This can be seen

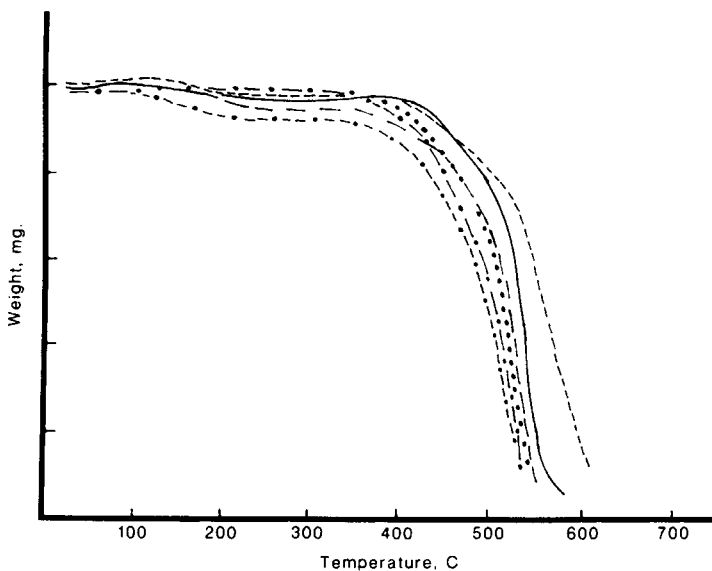


Fig. 4. Thermogravimetric analyses of polyamides from terephthaloyl chloride and aromatic sulfone ether diamines: (—) 5a; (.....) 5b; (--) 5c; (- · - · -) 5d; (---) 5e; (---) 5f.

in Figures 4 and 5. Isothermal gravimetric analyses of polyterephthalamides 5a, 5c, 5e, and 5f and polyisophthalamides 6a–f carried out in a flowing air atmosphere at 500°C also showed that methyl substitution generally increased weight loss.

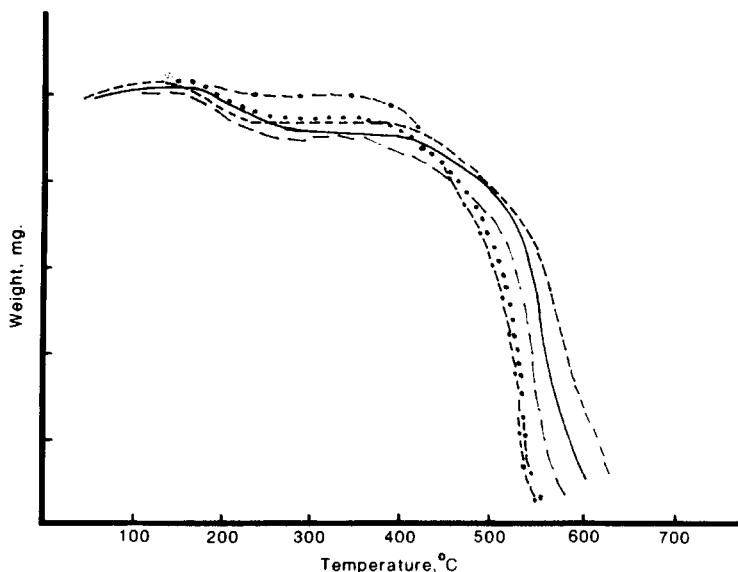


Fig. 5. Thermogravimetric analyses of polyamides from isophthaloyl chloride and aromatic sulfone ether diamines: (—) 6a; (.....) 6b; (--) 6c; (- · - · -) 6d; 6e; (---) 6f.

TABLE V  
Properties of Poly(amide-Imides) from Trimellitoyl Chloride and Aromatic Sulfone Ether Diamines

Poly(amide-imide)	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)	$T_m$ (°C)	TGA <sup>c</sup>	
				Air <sup>d</sup> (°C)	% wt loss at 500°C
7					
a	0.49	218	315	405	22
b	0.32	203	275	309	23
c	0.36	183	262 <sup>e</sup>	360	23
d	0.37	208	305 <sup>e</sup>	350	28
e	0.30	238	282 (486) <sup>e</sup>	360	28
f	0.44	192	351	405	18

<sup>a</sup> Dimethyl acetamide at 25°C, concn = 0.5 g/100 mL.

<sup>b</sup> Obtained on a DuPont 900 Thermal Analyzer with a differential scanning calorimeter.

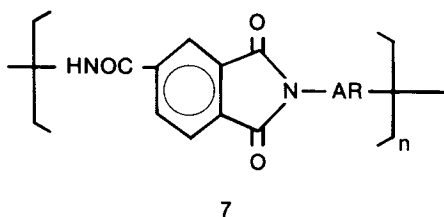
<sup>c</sup> Obtained on a DuPont 950 Thermogravimetric Analyzer.

<sup>d</sup> The polymer decomposition temperature (PDT) taken as the onset of rapid decomposition.

<sup>e</sup> Sharply defined endotherms; all others were broad.

### Methyl-Substituted Arylene Sulfone Ether Poly(amide-Imides)

A series of novel poly(amide-imides) have been prepared from the reaction of trimellitoyl chloride and diamines 2a-f. Low temperature solution polymerization techniques were used first to prepare the soluble poly(amic acid) intermediates which were treated thermally to achieve imidization. The general structure 7 of the poly(amide-imide) is shown below:



where the AR group indicates the diamine structures 2a-f.

Poly(amide-imide) 7a has been prepared, characterized, and reported in the literature to exhibit an excellent combination of moldability, thermal stability, mechanical properties, and solvent resistance.<sup>6</sup> All of the modified poly(amide-imides) prepared here formed tough, transparent films. They have been characterized by solution viscosity, thermal gravimetric analysis, and differential scanning calorimetry. The properties of poly(amide-imide) series 7a-f are summarized in Table V.

All the poly(amide-imide)s prepared formed tough, transparent films in spite of their low inherent viscosities. Films of poly(amide-imide)s 7a, 7d, and 7f were strong and flexible while the others in this series were brittle. As in the case of the polyimide series, methyl groups ortho to the amine functionality in diamines 2d and 2e may lower the molecular weight by sterically reducing the reactivity of the amine group. Crosslinking reactions in this poly(amide-imide) series, however, may also occur to some extent as in the polyimide series 3 or 4. Since

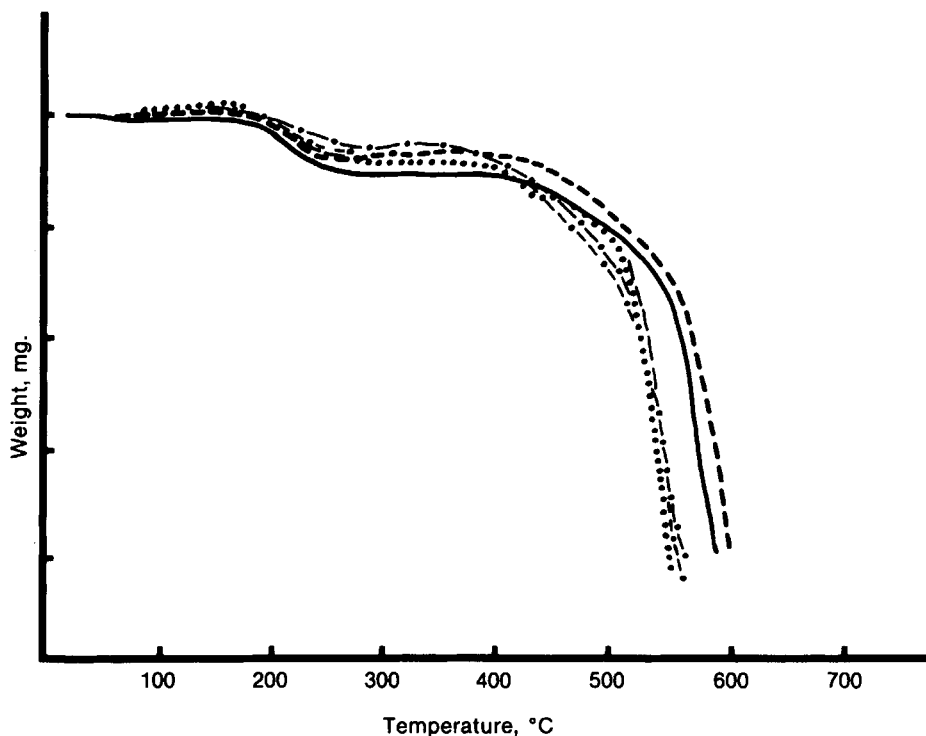


Fig. 6. Thermogravimetric analyses of poly(amide-imides) from trimellitoyl chloride and aromatic sulfone ether diamines: (—) 7a; (····) 7b; (--) 7c; (- - - -) 7d; (- - -) 7e; (---) 7f.

some brittle films were observed, especially in 7e, crosslinking reactions may have taken place.

The  $T_g$ 's for the poly(amide-imide) series are shown in Table V. The poly(amide-imide) 7f prepared from the meta-linked diamine exhibited a lower  $T_g$  than poly(amide-imide) 7a, as expected. As the number of methyl group substituents increase in the diamine segment, the observed  $T_g$  decreases except in poly(amide-imide) 7e. This polymer shows the highest  $T_g$ , 238°C, of all the poly(amide-imide)s prepared in the series. Similar glass transition behavior was observed in the polyimide and the polyamide series. All of the prepared poly(amide-imide)s showed endotherms, while those for poly(amide-imide)s 7c, 7d, and 7e were particularly sharp.

Thermal gravimetric analyses of the prepared poly(amide-imide)s as shown in Table V indicated thermal stabilities intermediate between the polyimide and the polyamide series prepared from the same diamine. Poly(amide-imide)s 7a and 7f prepared from the unsubstituted para- and meta-linked diamine showed the highest decomposition temperature, 405°C. Poly(amide-imide)s prepared with methyl-substituted diamines decomposed from 15°C to 55°C lower. The thermograms for the poly(amide-imide) series 7a-f are illustrated in Figure 6. The methyl-substituted poly(amide-imide)s 7b-e all showed a small weight gain at temperatures from 150°C to 200°C, attributable to air oxidation reactions.

Poly(amide-imide) 7f, prepared from the meta-linked diamine 2f, showed greater stability than all the others in this series. Polymer 7f also showed the lowest percent weight loss, 18%, at 500°C. Similar thermal stabilities were also

observed in polyimides 3f and 4f and polyamides 5f and 6f, all prepared from the same meta-linked diamine. The methyl-substituted poly(amide-imide)s, as in the case of methyl-modified polyimides and polyamides, appear to be more susceptible to thermal decomposition and rapidly lose weight at temperatures between 350°C and 390°C.

### CONCLUSION

We have prepared a series of polyimides, polyamides, and poly(amide-imide)s all containing the aryl sulfone ether structural unit in the polymer repeat unit. The aryl sulfone ether unit, containing both a flexible ether and a highly polar sulfone linkage, has been modified by substituting methyl groups at various positions on the aryl ether ring. In general, methyl groups present in these polymers tend to lower the glass transition temperatures, lower the thermal stability, and allow for air oxidations to occur. Methyl groups ortho to the amino functionality appear to sterically reduce the reactivity of the diamine and in the case of the polyimides and poly(amide-imide)s allow for the possibility of crosslinking reactions to occur.

Surprisingly, all the polymers prepared from the meta-linked unsubstituted diamine showed either identical or superior thermal properties to the corresponding polymer prepared from the para-linked unsubstituted diamine. The meta linkage, in addition to imparting thermal stability to these structures, also lowered glass transition temperatures.

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