

# Synthesis and Properties of Polyesterimides and their Isomers\*

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## Synopsis

A new type of polyesterimide has been synthesized by polycondensation of a dicarboxylic acid containing an internal imide group with ethylene glycol. The dicarboxylic acid was synthesized by reacting aminobenzoic acid with trimellitic acid anhydride in *N,N*-dimethylformamide solution. Three isomeric (ortho, meta, and para) polyesterimides were prepared from the respective isomer of the dicarboxylic acid. The solubility characteristics, solubility parameters, solution viscosity behavior, density, crystallinity, and thermal properties of these three isomeric polyesterimides were discussed. Some generalizations about structure–property relationship in polyesterimides were also made. It was found that while the ortho and meta isomers of the polyesterimide are amorphous, the para isomer tends to be somewhat crystalline and consequently less soluble, even in polar solvents. The thermal behavior of the meta isomer resembles closely that of the para isomer. The thermal stability of these isomers follows the order para  $\geq$  meta  $>$  ortho.

## INTRODUCTION

One of the major limitations of the versatile applications of synthetic polymers is their poor thermal resistance compared with other materials, especially metals and alloys. To overcome the poor heat stability of organic polymers, a new generation of polymers capable of withstanding high temperatures has been prepared during the last decades. In many respects these polymers are significantly different from the conventional addition or condensation polymers.

It has long been recognized that the intrinsic thermal and oxidative stability of aromatic and/or heterocyclic rings may be exploited to develop new thermostable polymers by linking them with stable groups such as amides,<sup>1</sup> esters,<sup>2</sup> imide,<sup>3</sup> and sulfones.<sup>4,5</sup> Alternatively, benzene and other heterocyclic rings may be linked in such a way that ladder, layered, or network structures are obtained. Unfortunately, the linkage or the structure that confers excellent thermal stability to polymers<sup>6</sup> gives rise to insolubility and infusibility leading to great processing difficulty. The processing difficulty again interferes with the applications of polymer materials.

Aromatic polyimides are one such type of highly thermostable polymers for use as films, adhesives, and laminates in applications requiring high-temperature ( $>250^{\circ}\text{C}$ ) resistance, better mechanical strength, and superior electrical/insulating properties.<sup>7–11</sup> However, polyimides have extremely poor processability compared with other traditional engineering plastics. This is due to a number of factors: (a) The high glass transition temperature ( $T_g$ ) of the polyimides makes molding processes difficult. (b) Since polyimides are insoluble in most

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of the commercial solvents, solution processing is also difficult. (c) The pre-polymer of polyimides, i.e., polyamic acid, is very corrosive, and hence its handling/processing is difficult and requires a special type of alloy steel.<sup>12</sup> (d) In the final curing, i.e., conversion of polyamic acid to polyimide, elimination of water results in extensive pores and voids in the final article.

Thus, it becomes apparent that high-temperature stability and ease of processability in polymers do not go together. A compromise is therefore desirable where a certain degree of temperature stability is sacrificed to achieve processability in polymers in general and in polyimides in particular. Following this general principle, copolyimides such as polyesterimides<sup>13-15</sup> and polyamideimides<sup>16,17</sup> have been developed. Although the thermal behavior of an amide linkage in a polymer resembles closely that of an ester group,<sup>11</sup> the solubility characteristics as well as the processability of a polyesterimide appear to be somewhat better than those of a polyamideimide. Relatively lower cost and better outdoor stability of a polyesterimide are additional advantages.

Most of the information about polyesterimides is available only in the patent literature probably because of their commercial importance. Little or no systematic study has been reported so far on the synthesis, properties, and, particularly, the structure-property relationship of polyesterimides and related polymers. This research was carried out as part of the program to develop polyesterimides and related polymers and evaluate their thermal and other useful properties.

There are a few methods of preparation of polyesterimides.<sup>12-15</sup> All of these involve the reaction of dianhydride group of trimellitic acid anhydride with the amino group of a diamine or amino alcohol or amino acid via the formation of the intermediate amic acid. With the progress of polycondensation reaction, the formation of the imide as well as the ester group continues in the polymer chain. The method described in the present article involves the use of a pre-formed imide group, and therefore conversion of polyamic acid to polyimide does not arise. The polycondensation reaction under discussion is therefore a polyesterification process involving a dicarboxylic acid containing a built-in imide ring and a dihydroxy alcohol. The present report also describes the preparation as well as the comparative evaluation of ortho, meta, and para isomers of polyesterimides.

## EXPERIMENTAL

### Reagents

Trimellitic acid anhydride (TMA) was obtained from Amoco Chemical Corporation (U.S.A.) and was used without further purification.

*p*-Aminobenzoic acid (E. Merck, India), *m*-aminobenzoic acid (Schuchardt, München, West Germany), and *o*-aminobenzoic acid (BDH, England) were used without further purification.

Ethylene glycol (BDH, reagent grade) was purified by refluxing over sodium sulfate and subsequent distilling under vacuum.

*N,N*-Dimethylformamide (DMF) (E. Merck, India) was kept over P<sub>2</sub>O<sub>5</sub> for 24 hr and then vacuum distilled at 20 torr. All other solvents used were purified before use.

### Monomers

**Preparation of *N*-(*p*-Carboxyphenyl) Trimellitimide.**<sup>18</sup> To a three-necked flask equipped with a stirrer and a thermometer, 90 ml DMF, 24.66 g (0.18 mole) *p*-aminobenzoic acid, and 34.56 (0.18 mole) TMA were added. A mild exothermic reaction was noted. The reaction mass was heated and stirred, and the temperature was raised to 132°C in 2½ hr. The initial yellow color of the solution was changed to dark brown. The solution was then poured over four volumes (360 ml) of water, when a precipitate was obtained. This was filtered, washed with water, dilute acetic acid, and finally with water and dried at 110°C to give a yellow high-melting (>290°C) solid.

**Preparation of *N*-(*o*-Carboxyphenyl) Trimellitimide.** Following a similar procedure as described above, *N*-(*o*-carboxyphenyl) trimellitimide was prepared using *o*-aminobenzoic acid and TMA. The reaction was carried out at 145°C for 3 hr. A white crystalline solid mp 252°C was obtained.

**Preparation of *N*-(*m*-Carboxyphenyl) Trimellitimide.** Similarly, *N*-(*m*-carboxyphenyl) trimellitimide was prepared by reacting *m*-aminobenzoic acid with TMA at 130°C for 3½ hr. A pale-yellow solid mp >280°C was obtained.

### Polymer Synthesis

Polycondensation reaction was carried out in a cylindrical reaction kettle (1500 ml capacity) fitted with a nitrogen purging tube, a mechanical stirrer, a thermometer, and a vacuum arrangement through the water-cooled condenser. The reaction kettle was heated by means of a vapor bath using different liquids/solids as required. The details of the arrangement are shown in Figure 1. A typical run for polymer synthesis is as follows:<sup>18</sup>

*N*-(*p*-Carboxyphenyl) trimellitimide (para acid), 15.6 g (0.05 mole), was mixed with 10 ml (0.16 mole) ethylene glycol in the reaction kettle, and the mixture was heated under nitrogen atmosphere by an ethylene glycol vapor bath (190°C) for 1 hr. A mixture of antimony trioxide and zinc acetate (0.1 g each) was then added to the reaction mass as the condensation catalyst and the reaction was continued for additional 2 hr. During this period the reaction mass was completely melted and became a homogeneous yellow to brown mass. The ethylene glycol vapor bath was then replaced by a dimethyl phthalate vapor bath (240°C), and the heating was continued for an additional 1 hr. The removal of last traces of volatiles, e.g., excess ethylene glycol and other by-products, was carried out under reduced pressure (~700 torr) during the last 15 min of the reaction. As the polycondensation reaction advanced, the reaction mass became gradually highly viscous and difficult to stir. At the end of the reaction, the molten viscous yellow-brown mass was quickly poured from the kettle under a blanket of nitrogen, which on cooling to room temperature became a solid brittle brown mass.

Following similar procedures, polyesterimides from *N*-(*m*-carboxyphenyl) trimellitimide (meta acid), as well as from *N*-(*o*-carboxyphenyl) trimellitimide (ortho acid) and ethylene glycol, were synthesized.

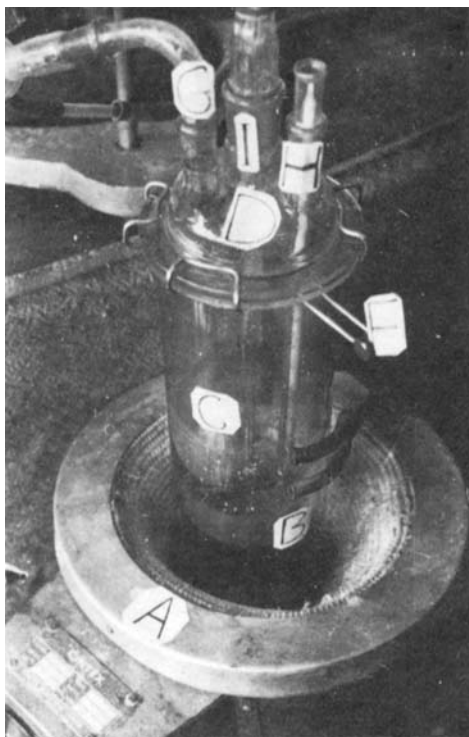


Fig. 1. Experimental setup for polymer synthesis: A, heating arrangement; B, vapor bath; C, reaction kettle; D, lid of reaction kettle; E (not shown), nitrogen inlet; F, screw for closing the lid; G, condenser; H, thermometer; I, stirrer.

### Determination of Equivalent Weight of *N*-(Carboxyphenyl) Trimellitimide

The equivalent weight of these dicarboxylic acids was determined by the method of Fritz.<sup>19</sup> The acid solution in dry DMF was titrated against anhydrous sodium methylate in benzene using cresol red as indicator.

### Characterization of Polyesterimides

**Purification of Polyesterimides.** Polymer samples were purified by repeated precipitations from a solution in DMF using methanol as the nonsolvent. The precipitated polymer was isolated, washed with diethyl ether, and dried in a vacuum oven at 50°C for 24 hr.

**Viscosity Measurements.** These were carried out in 0.5% (g/ml) solutions in DMF at 30°C using a Ubbelohde viscometer. For determining the course of the polycondensation reaction by viscosity measurements, the polymer samples from the reaction kettle were removed at different intervals of time. The polymer samples were immediately precipitated in methanol, isolated, and dried, and then the solution viscosity was measured in DMF.

**Density Measurement.** The density of the polymer samples was determined by means of a small pycnometer in benzene at 30°C.

### Solubility Parameter

Polyesterimide samples (0.02 g) were placed in 2 ml of various solvents and allowed to stand for two weeks.<sup>20</sup> The polymer was then observed in order to judge solvent effects such as swelling and dissolution. A plot of solubility parameters ( $\delta$ ) against hydrogen bonding index ( $\gamma$ ) was prepared. The midpoint of the solubility parameter range was chosen as the solubility parameter of the polymer.

### Thermal Analysis

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were made simultaneously with a Hungarian Mom Derivatograph of Paulik Paulik-Erdey system. The measurements were recorded in air at a heating rate of 5°C/min.

Infrared spectra were recorded on a Perkin-Elmer model 257 spectrometer on a KBr pellet.

X-ray diffraction diagram was recorded with a Dron I (USSR) x-ray diffractometer using Ni-filtered  $\text{CuK}_\alpha$  radiation.

### Hydrolysis of the Para Polymer

The para polymer was refluxed with 10% w/v sodium hydroxide solution for 48 hr. A light-brown solution with some undissolved product was obtained. The solution was filtered and the filtrate acidified with concentrated HCl. Unhydrolyzed polymer and the tricarboxylic acid were obtained as the precipitate. The precipitate was boiled with saturated  $\text{NaHCO}_3$  solution and filtered, and the filtrate was extracted with diethyl ether. The aqueous layer on acidification again with concentrated HCl gave a white precipitate. This was identified as trimellitic acid by melting point determination and IR spectrum.

The original filtrate after first acidification with HCl was made alkaline with NaOH solution. Glacial acetic acid was added dropwise to make the solution slightly acidic (pH 6.5–6.8), and then the solution was extracted with ether. The ether extract was dried over anhydrous sodium sulfate followed by removal of ether to obtain a white product. This was identified as *p*-aminobenzoic acid by melting point determination and IR spectrum. The scheme of hydrolysis and separation of hydrolyzed products is shown in Figure 2.

## RESULTS AND DISCUSSION

### Monomer Synthesis and Characterization

The synthesis of monomers from aminobenzoic acid and TMA may be schematically represented as shown in Figure 3.

Besides DMF, other solvents such as cresol,<sup>12</sup> *N,N*-dimethylacetamide, etc., can also be employed. However, highly polar solvents are necessary to dissolve the dicarboxylic acid monomers (e.g., ortho, meta, and para acids), and these solvents associate strongly with both the monomers and the reactants. This association probably accelerates the reaction.<sup>21</sup>

The properties of dicarboxylic acid monomers are presented in Table I. It

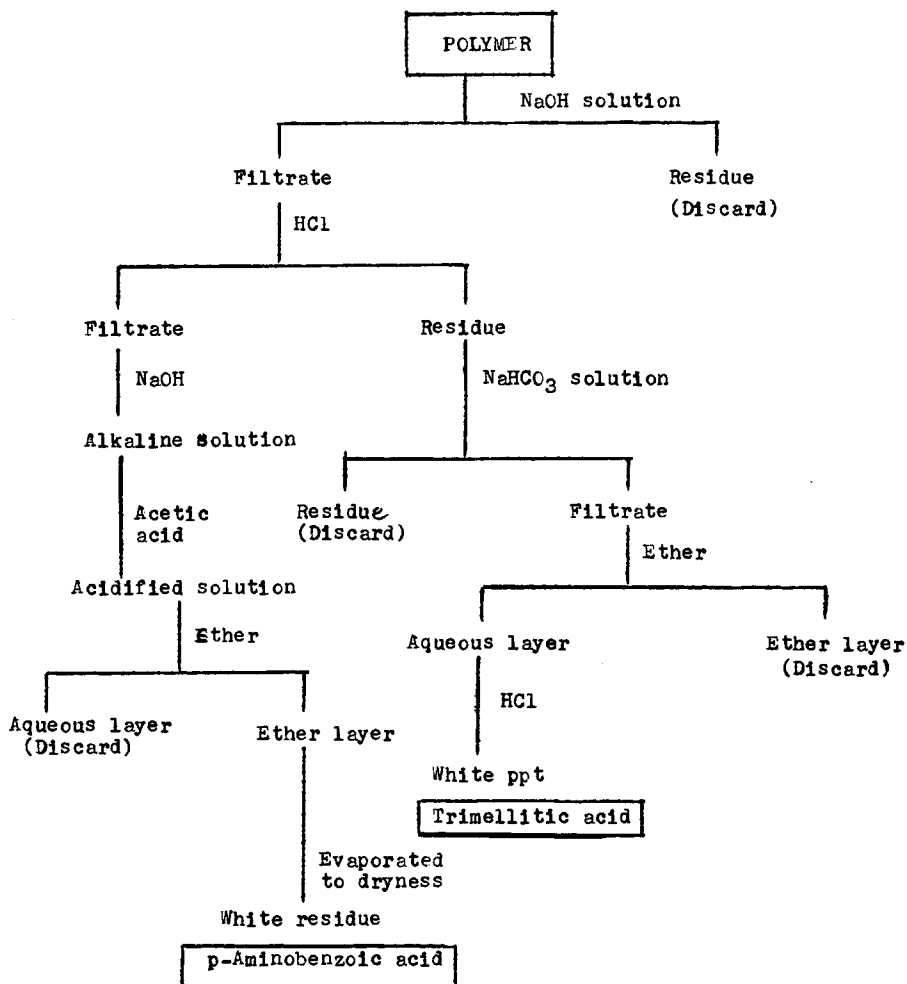
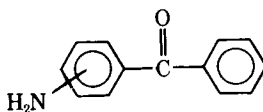


Fig. 2. Scheme of hydrolysis and separation of polyesterimide.

is observed that the yield of monomers is in the order meta acid > para acid > ortho acid. This may be explained by the difference of charge density in these isomeric positions and the steric hindrance. It is expected that the charge density values for the amino group of the aminobenzoic acid follow the order meta position > para position > ortho position. A similar explanation has been advanced by Bell and co-workers.<sup>22</sup> These authors have calculated the charge densities of aminobenzophenones by the Pariser-Parr-Pople self-consistent field method<sup>23</sup> and found the following theoretical charge density values:



*o*-: 1.566

*m*-: 1.682

*p*-: 1.650

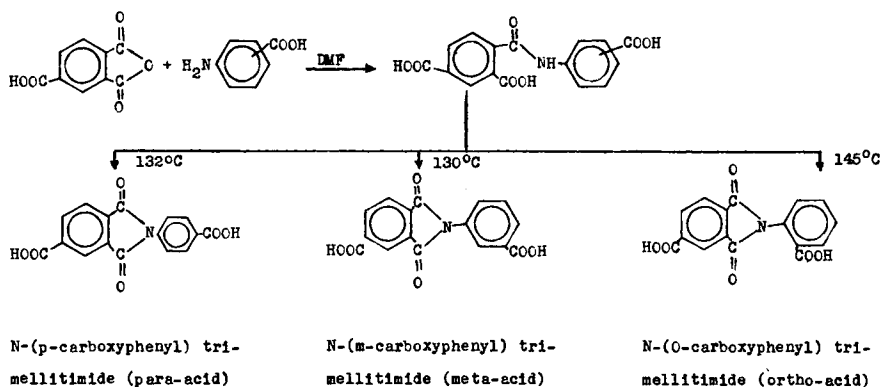
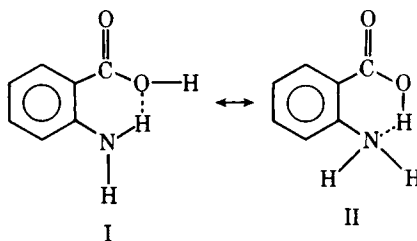


Fig. 3. Schematic of monomer synthesis.

The failure to obtain high yield from *o*-aminobenzoic acid may therefore be due to the inductive deactivation of the amino group. It is likely that the basicity of the *o*-amino group is further decreased by internal hydrogen bonding and the participation of structures I and II to the resonance stabilization of *o*-aminobenzoic acid:



The occurrence of hydrogen bonding in *o*-aminobenzoic acid, but not in the other two isomers, greatly hinders the availability of the amino group for imidization reaction.

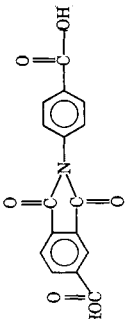
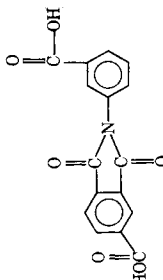
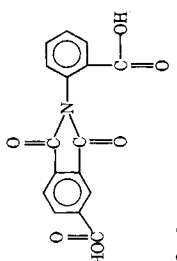
The formation of the internal imide group in the dicarboxylic acid monomers proceeds most likely through the formation of amic acid, as shown in the scheme in Figure 3. The formation of such a type of amic acid was also reported in case of polyimide synthesis from an amine and an anhydride in DMF solution even at room temperature.<sup>24-26</sup>

The IR spectra of these monomer acids are shown in Figure 4. The spectra showed characteristic imide bands at 1725 and 725  $\text{cm}^{-1}$  that are due to carbonyl stretching and ring carbonyl deformation, respectively. The presence of the band at 1680  $\text{cm}^{-1}$  is due to stretching of the carbonyl group. A broad peak appears at 2880  $\text{cm}^{-1}$  owing to the hydroxyl group of the acid moiety.

The results of the elemental analyses are in good agreement with the structural formulas proposed for the monomers (Table I). The structure of the monomers is further confirmed by the nonaqueous titration method of Fritz.<sup>19</sup> The equivalent weight is found to resemble closely the theoretical value (155.5) and is shown in Table I.

The yellow color of the para monomer may be due to the possibility of for-

TABLE I  
Properties of Dicarboxylic Acid Monomers

Structure/name	Equivalent weight <sup>a</sup>	Yield, %	Physical state	Melting point, °C	Analysis, %		
					C	H	N
 N-( <i>p</i> -Carboxyphenyl)trimellitamide Para monomer	155	67.8	yellow crystalline	290	calcd 61.73 found 60.20	2.89 2.96	4.50 5.01
 N-( <i>m</i> -Carboxyphenyl)trimellitamide Meta monomer	154	71.5	very pale yellow crystalline solid	280	calcd 61.73 found 61.95	2.89 2.57	4.50 3.87
 N-( <i>o</i> -Carboxyphenyl)trimellitamide Ortho monomer	153	65.5	white crystalline solid	256	calcd 61.73 found 61.50	2.89 2.25	4.50 4.45

<sup>a</sup> Experimentally determined by the method of Fritz.<sup>19</sup>



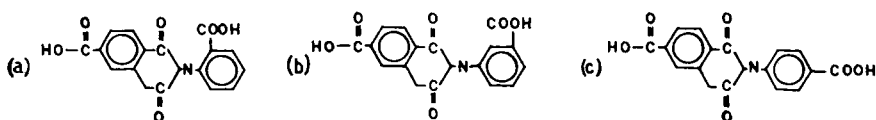
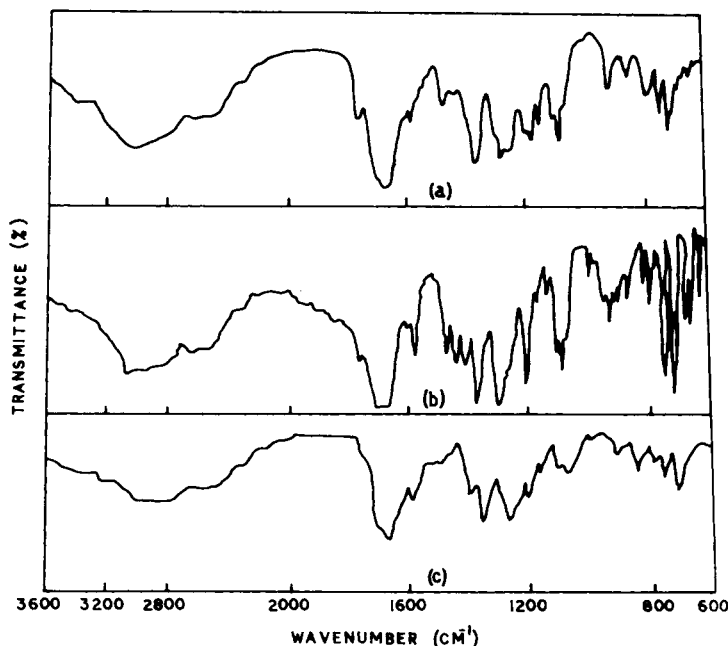
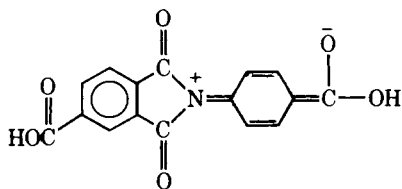


Fig. 4. Infrared spectra of imidodicarboxylic acid monomers: (a) ortho acid; (b) meta acid; (c) para acid.

mation of the quinonoid structure:



### Polymer Synthesis and Characterization

The polycondensation reaction between *N*-(carboxyphenyl)trimellitimide and ethylene glycol is in effect a polyesterification process involving dicarboxylic acid and a dihydroxy alcohol. The reaction scheme is shown in Figure 5. The polymerization proceeds via melt polycondensation technique using a  $\text{Sb}_2\text{O}_3/\text{Zn}$  acetate combination as the esterification catalyst. Ethylene glycol is used in excess to act as the solvent for ease of dissolution of the components in the melt. Depending on the end use of the polyesterimides, the polycondensation reaction may be controlled by temperature, time, and the catalyst concentration used. The preformed imide ring in the monomer acids, i.e., *N*-(carboxyphenyl)trimellitimides, makes the polycondensation process a simple polyesterification

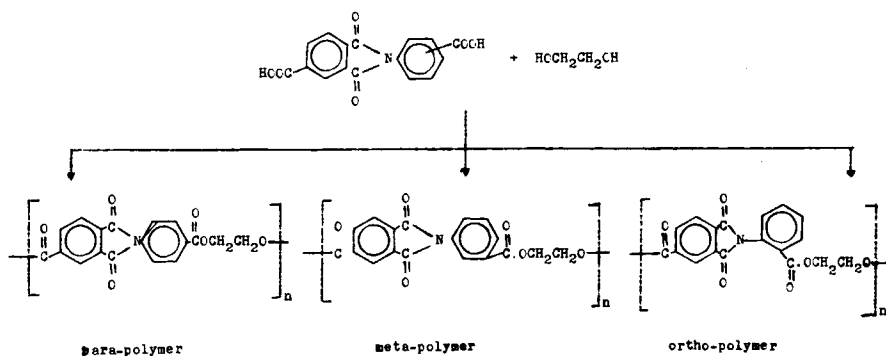


Fig. 5. Schematic of polymer synthesis.

reaction and not the polyamic acid formation, and subsequently its cyclization and simultaneous polyesterification as in other routes to polyesterimides.<sup>12-14</sup>

The general characteristics of the polymers are shown in Table II. It appears that the yield (based on purified polymer in each case) of the ortho polymer is maximum. This seems to be unlikely because of the steric effect. However, the ortho acid has the lowest melting point of all the isomers. Since one of the necessary conditions for melt polymerization is that the reactants should preferably be in the form of melt, the ortho acid, under identical melt polycondensation, starts melting earlier and therefore polymerizing earlier than the other isomers. It was also experimentally observed that the orthoisomer undergoes

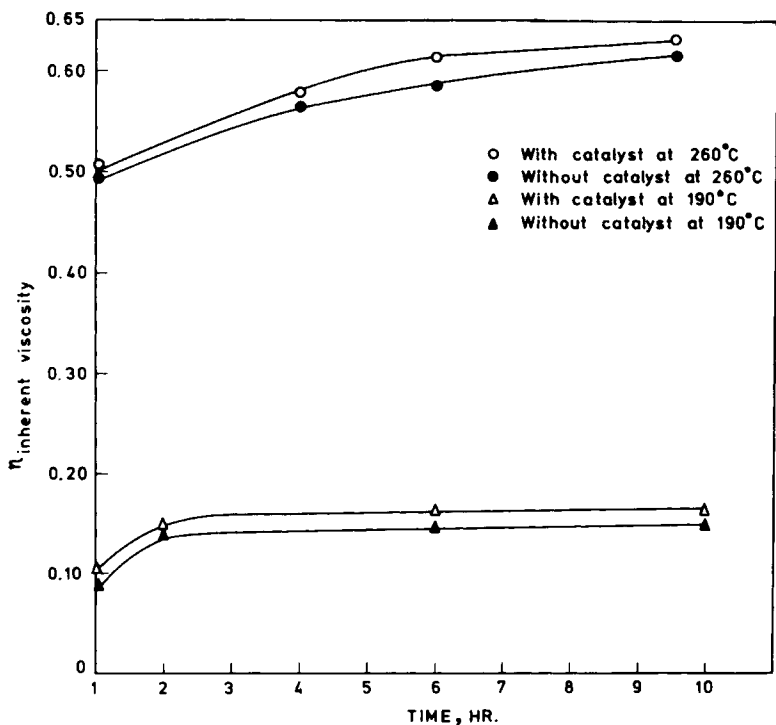
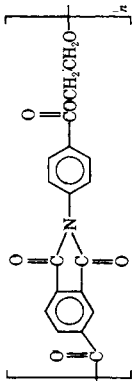
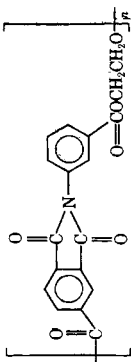
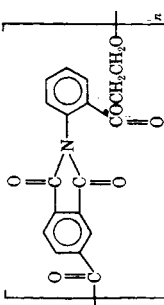


Fig. 6. Effect of time, temperature, and catalyst concentration on the polycondensation of ortho acid.

TABLE II  
Properties and Elemental Analyses of the Polyesterimides

Repeat unit	Yield, %	Inherent viscosity, <sup>a</sup> dl/g	Density, g/cm <sup>3</sup>	<i>T<sub>g</sub></i> , °C	Analysis, %		
					C	H	N
 Para polymer	91.7	0.25	1.380	280	calcd 64.09 found 63.50	3.26 4.03	4.15 4.29
 Meta polymer	79.4	0.37 <sup>b</sup>	1.259	220	calcd 64.09 found 63.45	3.26 4.19	4.15 4.86
 Ortho polymer	95.0	0.20	1.140	180	calcd 64.09 found 64.02	3.26 4.15	4.15 3.95

<sup>a</sup> 0.5% solution in DMF at 30°C.

<sup>b</sup> The solution on standing for more than 72 hr develops haziness and a precipitate.

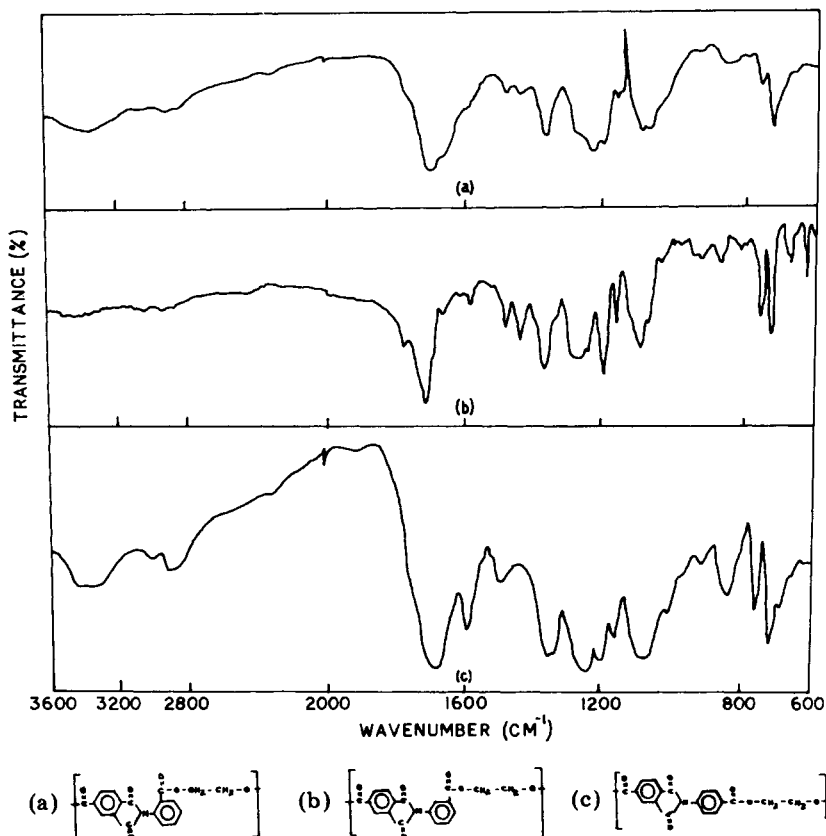


Fig. 7. Infrared spectra of polyesterimides: (a) ortho polymer; (b) meta polymer; (c) para polymer.

polycondensation, as is evident from the increase in viscosity of the reaction mass, during the first hour of the reaction, while the other isomers remain practically unaffected. This probably points to the fact that the threshold or floor polymerization temperature (i.e., the temperature below which polymerization does not take place) is the lowest for the ortho acid. Further work is necessary to understand the process before any definite conclusion can be made.

Table II shows that the inherent viscosity for the para polymer is greater than that of the meta polymer and the latter is again greater than that of the ortho polymer.

#### Effect of Catalyst

The combination of antimony trioxide and zinc acetate was found to be an effective system for polyesterification reaction. Increasing the catalyst concentration results in the decrease of reaction time. However, the molecular weight of the polyesterimide depends very little on the catalyst concentration (Fig. 6).

### Effect of Time and Temperature

Figure 6 shows that the molecular weight of the polymer increases with reaction time, as is usual in polycondensation processes. However, when the reaction was carried out at a lower temperature ( $\sim 190^\circ\text{C}$ ), the increase in molecular weight with time is not appreciable, indicating that the rate of polycondensation below or near  $190^\circ\text{C}$  is probably not significant. It was found that the polymer formed at or near  $190^\circ\text{C}$  is of gum type having a lower molecular weight. When the reaction was carried out at or above  $240^\circ\text{C}$ , the increase in molecular weight with time is significant (Fig. 6).

### Polymer Characterization

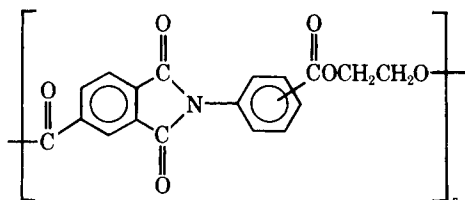
The polyesterimides prepared were characterized by elemental analyses, IR spectra, ultrasonic studies, and hydrolysis method.

The IR spectra for the polymers are shown in Figure 7. The IR spectra show characteristic imide bands at  $1785\text{ cm}^{-1}$  due to symmetrical carbonyl stretching vibration, at  $1730\text{ cm}^{-1}$  due to asymmetric carbonyl stretching, and at  $725\text{ cm}^{-1}$  due possibly to ring carbonyl deformation. The presence of aryl ester groups is indicated by the bands at  $1710\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  stretching and at  $1250$  and  $1180\text{ cm}^{-1}$  due to  $\text{C}-\text{O}$  stretching. The small band at  $2950\text{ cm}^{-1}$  appears to be due to  $\text{CH}_2$  groups.

The identification of the polyesterimide structure from IR spectra is not very easy because of the fact that the strongest band of the ester group is that of the carbonyl group, which unfortunately coincides with the strong imide absorption at  $1730\text{ cm}^{-1}$ . Owing to this difficulty of complete identification of polyesterimide from its IR spectrum, we would like to stress the importance, whenever any detailed information is required, of proper examination of the resin by hydrolysis followed by separation and identification of the hydrolyzed products.<sup>27</sup> The results of our hydrolysis experiment also confirmed the structure of polyesterimide (Fig. 2).

The ultrasonic interferometer technique, developed in our laboratory, was also used to establish the polymer repeat unit.<sup>28</sup>

From the elemental analyses, IR spectra, hydrolysis experiment, and ultrasonic study, the structure of the polyesterimide has been shown to be



Thus, the polyesterimide discussed in this article has the following sequence of groups: imide-ester-ester-imide in the macromolecular chain.

## Polymer Properties

### *Solubility Characteristics*

Solubility of the polyesterimides is summarized in Table III. Polyesterimides are found to be soluble only in highly polar solvents. The solubility characteristic of the polymer is in the order: ortho polymer > meta polymer  $\geq$  para polymer. The para polymer is insoluble in most of the solvents except DMF, *m*-cresol, *N*-methyl pyrrolidone and dimethyl sulfoxide. The poor solubility of the para polymer may be due to its higher chain symmetry and higher molecular weight compared with the other two isomers.

### *Solubility Parameter*

A plot of solubility parameter ( $\delta$ ) versus hydrogen bonding ( $\gamma$ ) for solvents shown in Table III is illustrated in Figure 8. The solubility parameter may be calculated from Small's group contributions.<sup>28,29</sup> The molar attraction constant

TABLE III  
Solubility of Polyesterimides

Solvent	Solubility parameter $\delta$	Hydrogen bonding index $\gamma$	Solubility <sup>a</sup>		
			Ortho polymer	Meta polymer	Para polymer
Diacetone alcohol	9.77	6.9	—	—	—
Cyclohexanone	10.42	6.4	++	+	—
<i>N,N</i> -Dimethylformamide	11.79	6.4	++	+	+
1,4-Dioxane	10.13	5.7	++	+	—
Acetone	9.62	5.7	—	—	—
<i>N</i> -Methylpyrrolidone	11.00	5.6	++	++	+
Tetrahydrofuran	9.10	5.3	++	+	—
Methyl acetate	9.46	5.2	±	—	—
Cyclopentanone	10.53	5.2	++	+	—
Ethyl acetate	8.91	5.2	—	—	—
Dimethyl sulfoxide	13.00	5.0	++	++	+
Ethyl methyl ketone	9.45	5.0	±	±	—
Methyl benzoate	10.19	4.5	++	—	—
Toluene	8.93	3.8	—	—	—
Nitrobenzene	10.00	3.2	±	±	—
Methylene chloride	9.88	2.7	±	—	—
Ethylene dichloride	9.86	2.7	++	—	—
Chlorobenzene	9.67	2.7	±	±	—
Benzene	9.67	2.7	—	—	—
Chloroform	9.16	2.2	++	—	—
Hexane	7.27	2.2	—	—	—
Formic acid			++	++	—
<i>m</i> -Cresol			++	++	+
Conc. H <sub>2</sub> SO <sub>4</sub>			++	++	+
Cyclohexane	8.19	2.2	—	—	—
Carbon tetrachloride	8.55	2.2	—	—	—
Pentane	7.02	2.2	—	—	—
Decane	7.74	2.2	—	—	—

<sup>a</sup> Solubility keys: (++) soluble; (+) soluble on heating; (±) partly soluble or swelling; (—) insoluble.

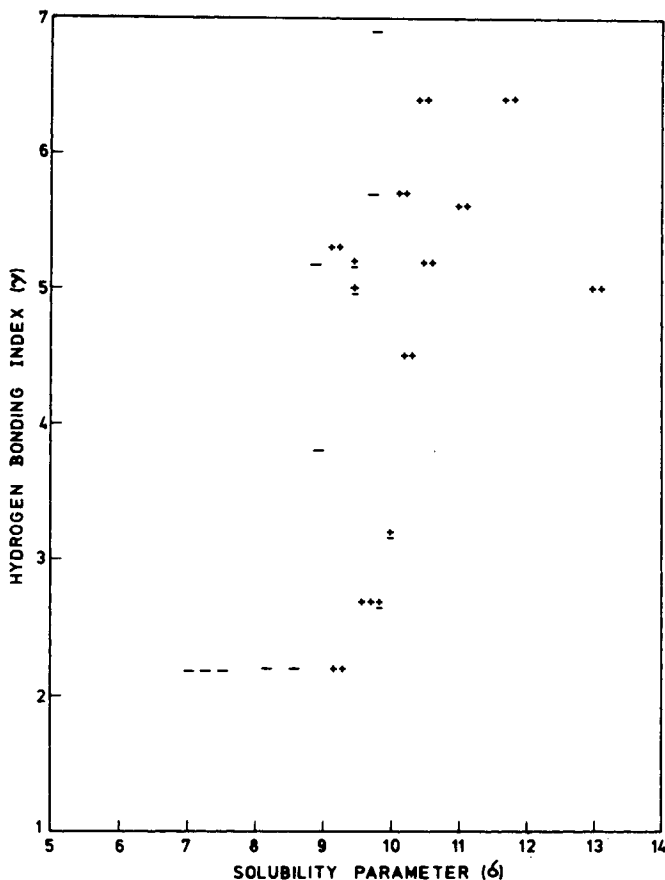


Fig. 8. Solubility map of the ortho polymer: (++) soluble, (+) soluble on heating, (±) partly soluble or swelling, and (-) insoluble.

$G$  values used here have been reported by Hoy.<sup>29-31</sup> The  $G$  values for various groups are shown in Table IV. These are used to calculate the solubility parameter  $\delta$  of the ortho polymer using the relationship

$$\delta = \rho \left( \frac{\sum G}{M} \right)$$

where  $\sum G$  is the sum of Small's group contribution (i.e., molar attraction values),  $M$  is the formula weight of the polymer repeat unit, and  $\rho$  is the density of the polymer. The  $\delta$  value at the midpoint of the solubility map (Fig. 8), which is found to be 9.8, agrees well with the calculated value of  $\delta$ , i.e., 9.66 (Table IV).

#### *Solution Viscosity Behavior*

The inherent viscosity of the polyesterimides solution (0.5% w/v) in DMF at 30°C follows the order para polymer > meta polymer > ortho polymer. This indicates perhaps that the molecular weight of the para polymer thus prepared is the highest of all the three polymers. Highest inherent viscosities have also been found in solutions of para-substituted aromatic polyimides by Bower and

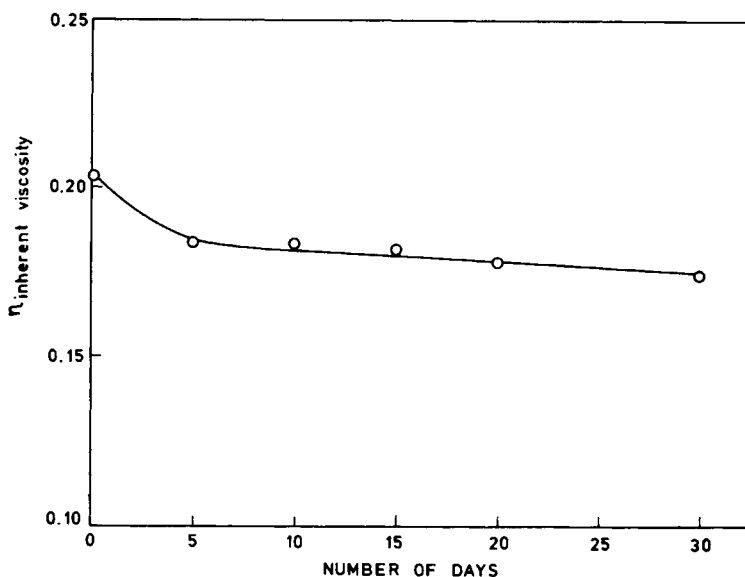


Fig. 9. Effect of aging of ortho polymer solution (0.5%) in DMF at 30°C on the inherent viscosity.

Frost.<sup>21</sup> It was reported earlier<sup>15</sup> that the inherent viscosity of polyesterimides in DMF remains practically unaffected even after 30 days at room temperature. In the present case, the inherent viscosity decreases to some extent during the initial period of five days and thereafter remains practically the same (Fig. 9).

TABLE IV  
Calculated Solubility Parameters for the Polyesterimides

Functional group	G value, (cal-cm <sup>3</sup> ) <sup>1/2</sup>	No. of functional groups/substitutions in the polymer repeat unit	Total G value for polymers, (Cal-cm <sup>3</sup> ) <sup>1/2</sup>		
			Ortho	Meta	Para
—CH <sub>2</sub> —	131.5	2	263.00	263.00	263.00
—CH=, (Aromatic)	117.12	7	819.84	819.84	819.84
=C=, (Aromatic)	98.12	5	490.60	490.60	490.60
>C=O	262.96	2	525.92	525.92	525.92
—N— 	61.08	1	61.08	61.08	61.08
—COO—	326.58	2	653.16	653.16	653.16
Five-membered ring	20.99	1	20.99	20.99	20.99
Six-membered ring	-23.44	2	-46.88	-46.88	-46.88
Para substitution	40.33	1	40.33	40.33	
		2			80.66
Ortho substitution	9.69	1		9.69	9.69
		2	19.38		
Meta substitution	6.60	1	6.60		6.60
		2		13.20	
		ΣG	2854.02	2850.93	2884.66
Solubility parameter δ			9.66	10.65	11.82



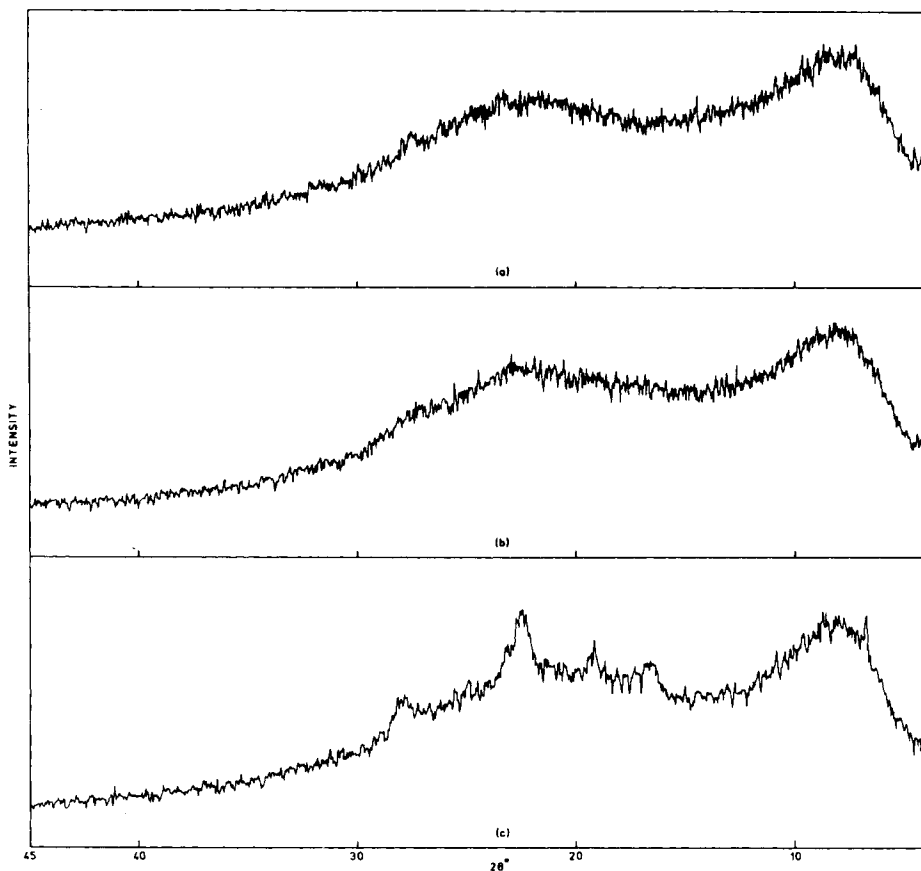


Fig. 10. X-ray diffraction diagram showing intensity vs. scattering angle ( $2\theta$ ) for (a) ortho polymer, (b) meta polymer, and (c) para polymer.

The decrease of inherent viscosity during this period of 25 days is about 5% of the initial value. This is in contrast to the behavior of soluble polyamic acids, which do not generally form stable solution. The viscosity of such solution on standing decreases.<sup>17,24,32</sup>

#### *Density and Crystallinity*

The density of the polyesterimides indicates the following order: para polymer > meta polymer > ortho polymer (Table II). This is consistent with the concept of close packing of the crystal lattice due to the chain symmetry in polymers. The x-ray diffraction diagrams of the polymers are shown in Figure 10. The diagrams indicate that the para polymer has some degree of crystallinity, while the other two polymers—meta and ortho—are amorphous in nature. The x-ray study, therefore, corroborates the highest density and poor solubility of the para polymer. The greater chain symmetry leads to closer chain packing, which in turn results in a higher degree of crystallinity. This is reflected in the solubility, density, and thermal and possibly mechanical behavior of the polymers.

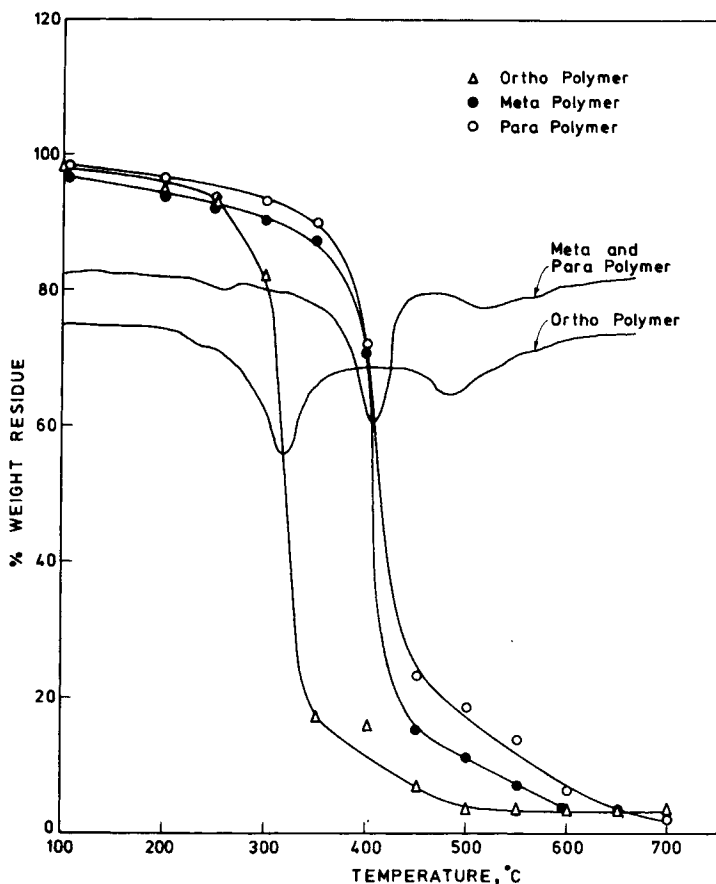


Fig. 11. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) of (a) ortho polymer, (b) meta polymer, and (c) para polymer in air at heating rate of 5°C/min.

### Thermal Behavior

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) data of the three polymers in air are presented in Figure 11. The TGA data indicated that the order of thermal stability is para polymer  $\geq$  meta polymer  $>$  ortho polymer. The para and meta polymers undergo less than 10% weight loss at 300°C in air. The slightly better thermal stability of the para polymer than the meta polymer may be ascribed to its higher crystallinity. It was pointed out by Bower and Frost<sup>21</sup> that orientation of groups on the benzene ring did not generally have a great effect on the thermal stability but was a factor in flexibility and viscosity. Our observation in the present study indicates that although the thermal stability of meta and para polyesterimides is comparable, the ortho polymer has relatively inferior thermal stability. In our opinion, the question of flexibility and thermal and/or oxidative stability as well as strength properties in polymers is very complex. It should be considered as owing largely to two general factors: (1) intrachain and (2) interchain factors interrelated with each other. The chain symmetry is responsible for flexibility or the free movement of the chain around its own axis. This also contributes to the close packing and crystallinity of the material. In ortho substitution the benzene ring is highly

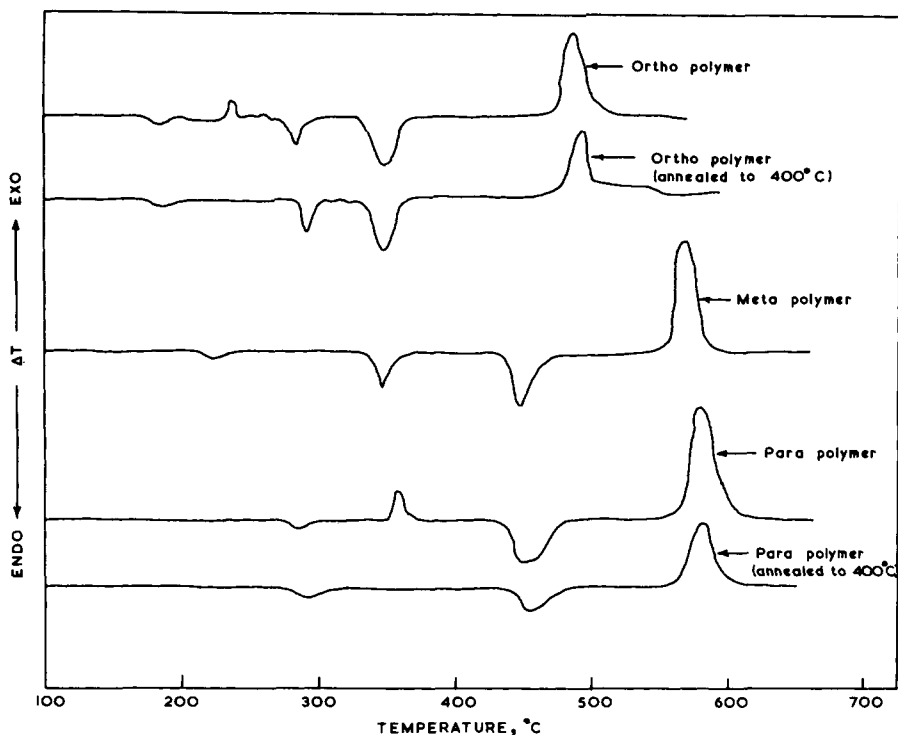


Fig. 12. Differential thermal analysis (DTA) of (a) ortho polymer, (b) meta polymer, and (c) para polymer in air at heating rate of 5°C/min.

unsymmetrical about the macromolecular chain axis, while in the para substitution the benzene ring is perfectly symmetrical. In the meta substitution a compromise is attained between these two. The slight unsymmetrical nature of the meta substitution prevents the close packing of molecules, as does the para substitution, and thus strikes a balance between the highly ordered structure of para substitution and the complete amorphous structure of the ortho substitution. This may probably be the reason for the greater success of meta-substituted polymers in applications requiring thermal stability and chain flexibility, e.g., in high-temperature cable insulation. The temperature for maximum rate of weight loss,  $T_{\max}$ , is 440°C for both meta and para polymers, while that for the ortho polymer is only 340°C (Table V). The maximum weight loss region was also confirmed by DTG curves.

#### *Isomer Effects on Glass Transition Temperature*

The DTA curves shown in Figure 12 exhibit a discontinuous shift of the baseline toward the endothermic side in the temperature range at 180, 220, and 280°C for the ortho, meta, and para polymers, respectively. These endothermic peaks represent the glass transition temperature  $T_g$  of the respective polyesterimides. These results are consistent with the fact that meta and ortho substitution in polymer chains are more effective than para substitution in decreasing the glass transition temperature.<sup>21,33</sup> The sharp endothermic peaks at 260 and 340°C for ortho and meta polymers are due to the melting/softening

TABLE V  
Thermal Properties of Polyesterimides in Air

Polymer	$T_g$ , °C	$T_m$ , °C	Decomposition temperature at various percent weight loss, °C				$T_{max}$ , °C
			10%	20%	30%	40%	
Ortho polymer	180	260	280	310	325	340	340
Meta polymer	220	340	312	385	420	425	440
Para polymer	280	360	360	400	420	430	442

point ( $T_m$ ) of polymers. For the more symmetrical para polymer, this endothermic transition was not observed. This may be due to the overlap of endothermic transition with some exothermic decomposition or stress relief. This exothermic transition was not observed in the DTA thermogram of the para polymer when the sample was annealed to 400°C under nitrogen atmosphere, cooling it to room temperature, and running the same sample again for DTA (see Fig. 12). The stress relief effect is also observed as an exothermic peak at 230°C for the ortho polymer, but the peak was absent in the DTA curve of the annealed sample (Fig. 12). The broad endothermic peaks at 340, 440, and 442°C are due to maximum weight loss for the ortho, meta, and para polymers, respectively. The sudden rise of the exothermic peak at 480, 560, and 580°C for the ortho, meta, and para polymers, respectively, is due to the onset of oxidative degradation of the polymer in air.

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