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# **Copolyanhydride-Imides**

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### SUMMARY:

Various copolyanhydride-imides have been obtained from diacids containing the preformed imide group by directly reacting of trimellitic anhydride with various aromatic and aliphatic amines. The polymerization process took place in several stages. In the first stage the diacetyl derivatives were obtained from the corresponding diacids by reactions with acetic anhydride. Under special temperature and pressure conditions, polymers were obtained from these derivatives and the chain grew by developing acetic anhydride between contiguous molecules.

The polymers obtained are crystalline, have high thermal stability and good electrical properties. Their structures were determined by IR spectroscopy and elementary analysis and the relationships between their properties and the polymer structures were investigated.

### ZUSAMMENFASSUNG:

Verschiedene copolymere Anhydridimide wurden aus Dicarbonsäuren mit vorgebildeter Imidgruppe erhalten. Dazu wurde zunächst Trimellitsäureanhydrid mit verschiedenen aromatischen und aliphatischen Aminen zu den entsprechenden Dicarbonsäuren mit Imidgruppen umgesetzt. Dann wurden aus diesen Dicarbonsäuren durch Reaktion mit Essigsäureanhydrid die entsprechenden gemischten Anhydride hergestellt. Unter bestimmten Bedingungen wurden daraus dann unter Abspaltung von Essigsäureanhydrid polymere Anhydride gewonnen.

Die Polymeren sind kristallin und zeigen hohe thermische Stabilität und gute elektrische Eigenschaften. Ihre Struktur wurde IR-spektroskopisch und durch Elementaranalyse bestimmt; Beziehungen zwischen Struktur und Eigenschaften wurden untersucht.

# 1. Introduction

Polyanhydrides were described for the first time in 1909 by BUCHER and  $SLADE^1$  as high melting point crystalline polymers. Other researchers have followed in this field and among them HILL and CAROTHERS<sup>2</sup> obtained polyanhydrides from aliphatic diacids resulting in polymers suitable for forming fibres.

In 1957 CONIX published a paper on obtaining polyanhydrides from diacids containing ether linkages and aliphatic and aromatic species<sup>3</sup>. By adding phenylene units the stability or resistance to hydrolysis was significantly increased.

Since then, modifications introduced by other authors<sup>4</sup> have mainly improved thermal properties and the resistance to hydrolysis. This is currently of great interest for obtaining polymers with high thermal stability.

In earlier research we obtained a number of polyester-imides and polyamideimides ranging from perfectly ordered<sup>5</sup> to random<sup>6</sup> structures. High thermal stability polymers have been obtained from monomers with the preformed imide family.

According to WRASIDLO and AUGL<sup>7</sup> obtaining this type of copolymers from monomers with the preformed imide family, has many advantages compared with obtaining them from polyamide acids.

Following this line of thought, and in accordance with our experience, we prepared some anhydride-imide copolymers with which we were able to study the influence of the presence of various groups in the same structure on the final properties of the products.

The first step in synthesis was based on diacids containing the preformed imide ring. These were obtained from the reaction of trimellitic acid anhydride with various aliphatic and aromatic amines in a 2:1 molar ratio. Following the most generally used method for preparing polyanhydrides<sup>8</sup>, the second step was to prepare the diacetyl derivatives of these acids. In the final phase, under special polymerization conditions, the copolymers described in this article were obtained. These polymers were characterized and the relationships between the properties and their molecular structure were investigated.

# 2. Experimental

# 2.1 Materials

Amoco trimellitic anhydride and Panreac acetic anhydride were used without prior purification.

The diamines were conventionally purified. The products used have the following physical constants: Ethylene diamine, bp 115 °C; Hexamethylene diamine, mp 42.5–43 °C; Diaminodiphenylmethane, mp 92 °C; p-Phenylene diamine, mp 142 °C.

## 2.2 Synthesis of Diacids

# 2.2.1 Synthesis of Ethylene-bis- (N-trimellitimide)

50 g (0,25 moles) of trimellitic anhydride and 500 ml of dry methanol were mixed together in a three-necked flask. When the mixture was completely dissolved, a

#### Copolyanhydride Imides

7,2 g (0,125 moles) solution of ethylene diamine in 25 ml of methanol was allowed to mix with the first solution drop by drop at room temperature. As the second solution was added, a white precipitate began forming until all of this solution had been added to the first. When this reaction was complete, the precipitate was filtered out, washed repeatedly with methanol, and finally dried at 25 °C in a vacuum drying oven. The resulting product was a mixture of diacid with open and closed rings as checked by IR spectroscopy.

In order to close all of the rings the intermediate product was suspended in diphenyl oxide at 248 °C for one hour. The product was filtered, successively washed with benzene and sulphuric acid, and finally dried. A white powder, mp 362 °C, was obtained (yield 80 %). Absorption bands: --OH carboxylic at 2 500-3 050 cm<sup>-1</sup>, C=O carboxylic at 1 700 cm<sup>-1</sup>, C=O imide at 1 780 and 1 720 cm<sup>-1</sup> and imide ring at 730 cm<sup>-1</sup>.



Analysis: (C<sub>20</sub> H<sub>12</sub> N<sub>2</sub>) calcd. C 58.82 H 2.94 N 6.86 found C 58.78 H 2.96 N 7.02

# 2.2.2 Synthesis of Hexamethylene-bis- (N-trimellitimide)

Similar to the above procedure, when 2:1 methanol hexamethylene diamine and trimellitic anhydride react in solution, an intermediate compound which gives the corresponding acid-imide after heat treatment in diphenyl oxide. A white powder with mp 321 °C was obtained (yield 82 %). Absorption bands: —OH carboxylic at 2 500–3 000 cm<sup>-1</sup>, C=O carboxylic at 1 700 cm<sup>-1</sup>, C=O imide at 1 780 cm<sup>-1</sup> and 1 720 cm<sup>-1</sup>, and imide ring at 735 cm<sup>-1</sup>.



Analysis: (C<sub>24</sub> H<sub>20</sub> N<sub>2</sub>) calcd. C 62.06 H 4.31 N 6.03 found C 62.21 H 4.23 N 6.15

# 2.2.3 Synthesis of p-Phenylene-bis- (N-trimellitimide)

At room temperature 20 g (0.1 mol) of trimellitic anhydride were dissolved in 200 ml of dry methanol in a three necked 500 ml flask. 5 g (0.05 moles) of p-phenylene diamine, dissolved in 25 ml of methanol, were allowed to drip into this solution. When it was all added, a large amount of yellow precipitate was obtained. This precipitate was filtered, repeatedly washed with methanol and dried in a vacuum at room temperature (yield 94 %). The resulting product was a tetra-acid with the following structure:



which has no established melting point. Analysis:  $(C_{24} H_{16} O_{10} N_2)$  calcd. C 58.53 H 3.25 N 5.69 found C 58.28 H 3.27 N 5.89

This compound was suspended in diphenyl oxide and heated to boiling point for two hours, and resulted in a yellow product with mp 370 °C. Absorption bands: —OH carboxylic at 2 500 to 3 100 cm<sup>-1</sup>, C=O carboxylic at 1 700 cm<sup>-1</sup>, C=O imide at 1 785 and 1 725 cm<sup>-1</sup> and imide ring at 725 cm<sup>-1</sup>.



Analysis: (C<sub>24</sub> H<sub>12</sub> O<sub>8</sub> N<sub>2</sub>) calcd. C 63.15 H 2.63 N 6.14 found C 63.35 H 2.72 N 6.00

# 2.2.4 Synthesis of 4.4'-bis- (N-trimellitimide)-diphenylmethane

10 g (0.05 moles) of diamine-diphenylmethane were dissolved in 100 ml of mcresol in a four-necked flask with a central stirrer, gas inlet and outlet and thermometer, and heated to 80–90 °C. At this temperature, 20 g (0.1 moles) of trimellitic anhydride are gradually added and the solution was heated to 160-170 °C for three hours, at the end of that time a large amount of precipitate was obtained. This was filtered, washed several times with methanol and benzene, and finally dried at 25 °C, in a vacuum drying oven. The yellowish product has a mp of 362 °C (yield 81 %). Its IR spectrum shows absorption bands of —OH carboxylic at 2500-3050 cm<sup>-1</sup>, C=O carboxylic at 1700 cm<sup>-1</sup>, C=O imide at 1785 and 1720 cm<sup>-2</sup>, and imide ring at 725 cm<sup>-1</sup>.



Analysis: (C<sub>31</sub> H<sub>17</sub> O<sub>8</sub> N<sub>2</sub>) caled. C 68.13 H 3.29 N 5.12 found C 68.29 H 3.45 N 5.24

#### 2.3 Diacetylate Derivatives

The diacetylate derivatives were obtained from the above acids by reaction with acetic anhydride at boiling point and with reaction times ranging between 16 and 24 hours. Due to the low solubility of the diacids in acetic anhydride, a low diacid

concentration was used. The dianhydrides were precipitated in the final solution by evaporation of the solvent.

The precipitated dianhydrides obtained were purified by recrystallization in acetic anhydride.

In the spectroscopic analyses, all showed the characteristic bands of anhydride grouping at 1810 to  $1825 \text{ cm}^{-1}$ , and  $1720 \text{ to } 1740 \text{ cm}^{-1}$ , and the imide grouping at 1780, 1720 and 725 cm<sup>-1</sup>, while the bands corresponding to the carboxyl group disappeared.

The following elementary analyses were obtained for the compounds:

Diacetylate derivative of ethylene-bis- (N-trimellitimide)

 $\begin{array}{c} ({\rm C}_{24} \ {\rm H}_{16} \ {\rm O}_{10} \ {\rm N}_2) & {\rm caled.} \ {\rm C} \ 58.53 & {\rm H} \ 3.25 & {\rm N} \ 5.69 \\ {\rm found} \ {\rm C} \ 58.67 & {\rm H} \ 3.25 & {\rm N} \ 5.99 \end{array}$ 

Diacetylate derivative of hexamethylene-bis- (N-trimellitimide)

 $\begin{array}{c} ({\rm C}_{28} \ {\rm H}_{24} \ {\rm O}_{10} \ {\rm N}_2) & {\rm calcd.} \ {\rm C} \ 61.31 & {\rm H} \ 4.18 & {\rm N} \ 5.10 \\ & {\rm found} \ {\rm C} \ 61.34 & {\rm H} \ 4.37 & {\rm N} \ 5.23 \end{array}$ 

Diacetylate derivative of p-phenyl-bis- (N-trimellitimide)

 $\begin{array}{c} ({\rm C}_{28} \; {\rm H}_{16} \; {\rm O}_{10} \; {\rm N}_2) & {\rm caled.} \; {\rm C} \; 62.22 & {\rm H} \; 2.96 & {\rm N} \; 5.18 \\ {\rm found} \; {\rm C} \; 62.13 & {\rm H} \; 2.79 & {\rm N} \; 5.23 \end{array}$ 

Diacetylate derivative of 4.4'-bis- (N-trimellitimide)- diphenylmethane

 $\begin{array}{c} ({\rm C}_{35} \, {\rm H}_{22} \, {\rm O}_{10} \, {\rm N}_2) & {\rm calcd.} \, {\rm C} \, 66.66 & {\rm H} \, 3.49 & {\rm N} \, 4.44 \\ & {\rm found} \, {\rm C} \, 66.49 & {\rm H} \, 3.65 & {\rm N} \, 4.35 \end{array}$ 

### 2.4 Polymerization

The intermediate anhydrides were polymerized in reaction tubes equipped with gas inlet and outlet valves. A weighed amount of intermediate compound was heated in these tubes in an oil bath at 220–260 °C for about three hrs. at 16–18 mm Hg pressure. Acetic anhydride was eliminated during the reaction. The entire polymerization process was carried out in N<sub>2</sub> atmosphere. The products extracted from the reaction tube were analyzed to determine their most important properties and structure.

### 2.5 Characterization of the Polymers

### 2.5.1 Thermal Properties

The polymer melting points were measured with a TOTTOLI type BÜCHI melting and boiling points device.

n conditions Elementary analysis	ure Time C H N	Hg) (h) $(\%)$ $(\%)$ $(\%)$	4 caled. 61.53 2.56 7.17 found 61.13 2.77 6.97	6 calcd. 64.57 4.03 6.27 found 64.27 4.10 6.33	6 4 caled. 65.75 2.28 6.39 found 64.67 2.51 6.25	t 4 caled. 70.45 3.03 5.30 found 70.22 3.15 5.27
Polymerizatio	Temp. Press	(mm) (C)	220 10	220 11	240 10	- 260
Structure			-000 CO N-(CH <sub>2</sub> ) <sub>2</sub> -N OC OC CO	-000 <sup>CO</sup> N <sup>-(CH<sub>2</sub>)<sub>6</sub>-N<sup>OC</sup> OC CO<sup>-</sup> CO<sup>-</sup></sup>		
 Polymon	NO		I	п	III	IV

Table 1. Synthesis of polyanhydrides.

126

## Copolyanhydride-Imides

The thermogravimetric analyses were carried out with a DU PONT model 950 thermobalance. Measurements were taken in  $N_2$  atmosphere at a heating rate of 10 and 15 °C/min.

The differential thermal analyses of the copolymers were made in a DU PONT 900 differential calorimeter. Table 2 shows the obtained results calculated by graphic integration of the curves obtained, using the melting point of indium as a basis.

Polymer No.	$(\mathbf{T}_{\mathbf{m}})_{\mathbf{ap}}.$ (°C)	(H <sub>m</sub> ) <sub>ap</sub> . (cal/g)	10 % weight lost (°C)
I	440	36.4	450
II	240	11.0	425
	415	16.6	
III	460	38,4	450
IV			475

Table 2. Thermal properties of the polymers.

# 2.5.2 Electrical Properties

The electrical properties were measured by a system consisting of a General Radio type 716 C capacitance bridge, a General Radio type 1311 oscillator, and a General Radio type 1232 A zero detector and a syntonized amplifier. The samples were heated in a 1050 °C ADAMEL oven. Current of  $10^4$  c/s was used (Table 3).

Table 3.	Electrical	properties*
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Polymer	Sample	Dielectric constant	Power factor	Volume Resistivity (Ω cm)
I	t = 1.003  mm $a = 19.6 \text{ mm}^2$	5.87	0.0041	$1.05 \cdot 10^{15}$
II	t = 1.202  mm $a = 19.6 \text{ mm}^2$	5.51	0.0040	$2.47 \cdot 10^{15}$
III	t = 1.004  mm $a = 13.0 \text{ mm}^2$	3.29	0.0045	4.60 · 10 <sup>11</sup>
IV	t = 1.25  mm $a = 19.6 \text{ mm}^2$	7.35	0.0040	$1.28 \cdot 10^{15}$

\* Discs of the materials were prepared in an evacuable die by compression at  $4.10^3$  Kp/cm<sup>2</sup>. a = area, t = thickness.

### 2.5.3 Crystallinity

A "Norelco" X-Ray defractometer was used. Working conditions: Goniometer and Chart speed  $2^{\circ}/\text{min}$  and 1 inch/min respectively. Divergence receiving and scattering slits:  $1^{\circ}$ ,  $0,1^{\circ}$ ,  $1^{\circ}$ .

# 3. Results and Discussion

Two steps were taken to obtain these polyanhydrides: first diacids containing imide groups were obtained, and second these were polymerized with acetic anhydride by a method discusses here below.

As explained in the experimental section, diacids containing preformed imide groups were obtained by direct reaction of trimellitic anhydride with aliphatic and aromatic diamines in a 2:1 molar ratio. The method generally used was a reaction in solution, first obtaining open amide tetra-acid; then the chains were closed by heat treatment under special conditions.



R depends on the type of diamine used. In this experiment ethylene diamine, hexamethylene diamine, diaminodiphenylmethane, and p-phenylene diamine were used.

The yields of diacid imides were high, and their elementary analyses and characteristic bands on the IR spectra agree with the proposed structures.

The following equations show the steps taken to polymerize these diacids with acetic anhydride:





In the first step the diacetylate derivative is obtained by the direct reaction of the diacids with acetic anhydride. This reaction which is carried out in the backflow of acetic anhydride is described in the experimental section. These dianhydrides have also been isolated and characterized. IR spectroscopy and elementary analysis show that the experimental results agree with those calculated according to theory.

When these intermediate compounds are heated to high temperatures at a low pressure, as is described in Table 1, the separation of the final acetyl groups takes place. This is done by means of a process of interchange of anhydride between adjacent molecules. The growth of the chains and the formation of polyanhydrides of high molecular weight is achieved.

The stages of this process may be followed by IR spectroscopy. Fig. 1 shows the IR spectrum of one of the diacids. The presence of the following bands may be noted: carboxylic acid at 2500 to  $3000 \text{ cm}^{-1}$  and at  $1700 \text{ cm}^{-1}$ , and the imide grouping at 1780, 1720 and 725 cm<sup>-1</sup>. From Fig. 2, which corresponds to the diacetylate derivative from the same diacid, it is noted that the typical acid absorption bands have disappeared, and at 1820 and 1720 cm<sup>-1</sup> bands corresponding to the anhydride function appear; the imide function bands remain unaltered. From Fig. 3, which corresponds to the polymer derived from the earlier dianhydride, it is noted that the C=O anhydride bands move to lower frequencies (about 20 cm<sup>-1</sup>). This is due to the increasing conjugation resulting from the lengthening of the chains. Also noted is a clear decrease in the intensity of these bands, due, no doubt, to the smaller percentage that the anhydride function has in the structural unit of the polymer in comparison to the dianhydride monomer molecule. However, the bands corresponding to the imide grouping remain unaltered.

This spectrographic study and the exceptionally good results of the elementary analyses of the polymer structural units confirm the validity of our structure proposals.

The linear character was shown by a study of solubility. It was observed that they are soluble in very polar solvents such as DMF, DMAc, mcresol and DMSO. The polymers I and II are the most soluble due to





Fig. 1. IR-Spectrum of the diacid obtained from trimellitic anhydride and diamino diphenylmethane.



Fig. 2. IR-Spectrum of the diacetylate derivative of the diacid from Fig. 1.



Fig. 3. IR-Spectrum of polymer IV.

the introduction of methylene units in the dorsal column of these two polymers.

130

## Copolyanhydride-Imides

The influence of the various groups introduced was also made clear in the study of the thermal behavior of these materials. From the thermogravimetric analyses (refer to Fig. 4 graphs) it is deduced that these polymers are highly resistant to heat, since in no case they begin to break down before 400 °C. As expected, the higher the concentration of aromatic nuclei, the more heat resistant is the polymer, as can be seen by comparing the thermograms in the graphs mentioned before. These show, for example, that the polymer containing diaminodiphenylmethane does not lose 10 % of its weight until it reaches 475 °C.



Fig. 4. Thermogravimetric analyses of the polymers.

To confirm further the crystalline characteristics of these polymers they have been subjected to differential calorimetry. By this method, the temperatures and apparent melting enthalpies were calculated. These values, deduced from the calorimetric diagrams, are summarized in Table 2. As expected, the transition temperature significantly increases with the aromatic character of the macromolecules. Since the estimate of the crystalline natur of the polymer is not quantitative, it is not possible to establish a correlation between the crystalline nature and the melting enthalpy. Nevertheless, it is evident that the polymers derived from p-phenylene diamine, since they are most rigid, show the highest apparent enthalpy despite being less crystalline.

One of the main fields of use of this type of polymer is for electrical insulation. Therefore, with an eye to possible later use, the electrical properties of these materials have been studied. Table 3 shows the values obtained for the dielectric constant, the factor of strength and resistivity in volume at room



Fig. 5. X-Ray spectra of the polymers.



Fig. 6. Dielectric constants of the polymers in dependence upon temperature.

132



Fig. 7. Power factor of the polymers in dependence upon temperature.

temperature. These values are in line with those corresponding to other polymers and resins commonly used in this way. Given the polar nature of the compounds obtained, the temperature influences the values of the electrical properties. Nevertheless, given the thermal stability and high transition temperatures, this influence is not significant until 200 °C is reached, as shown by Fig. 6 and 7.

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