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Synthesis of p,p′-Phenolphthalein-bis(trimellitic) Dianhydride

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ABSTRACT

p,p′-Phenolphthalein-bis(trimellitic) dianhydride was obtained by the reaction of diacetyloxyphenolphthalein with trimellitic anhydride. The structure of the new compound was proved by elementary analysis, infrared spectroscopy, and acid value determination. The course of acidolysis reaction was examined in the temperature range of 240-280°C. The compound obtained is a powder having a melting point of 135-138°C, has high thermal stability, and is easily soluble in many organic solvents and low-molecular epoxy resins. Application of p,p′-phenolphthalein-bis(trimellitic) dianhydride in synthesis of soluble polyesterimides and as a hardening agent for low molecular weight epoxy resins is proposed.

This paper deals with the synthesis of p,p′-phenolphthalein-bis(trimellitic) dianhydride, which contains in the molecule both ester groups and a large polar group, i. e., the lactone ring. Research to find a new dianhydride was undertaken with the goal of its further use in the

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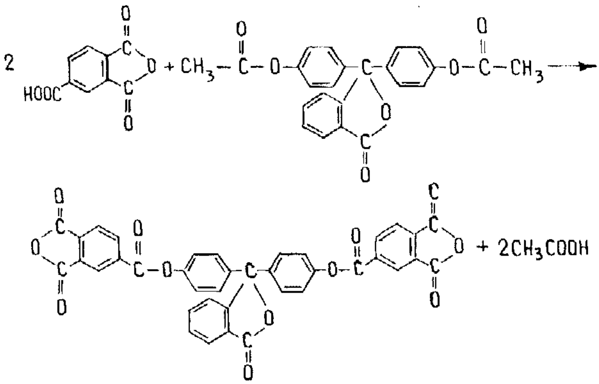
synthesis of thermally resistant, regularly alternating polyesterimides which are soluble in typical organic solvents. According to the concept set forth by Korshak and his associates [1-3] the presence of large polar groups in macromolecules increases polymer solubility due to the decrease of the polymer chain density and better polymer solvation with polar solvents.

p,p'-Phenolphthalein-bis(trimellitic) dianhydride was obtained from 2 moles of trimellitic anhydride reacted with 1 mole of diacetyloxyphenolphthalein in accordance with the acidolysis reaction given by Loncrini [4].



The acidolysis reaction was conducted in a high boiling solvent, and, in order to increase the reaction yield, the resulting acetic acid was continuously removed by distillation.

EXPERIMENTAL

Apparatus and Methods of Characterization

Infrared spectral analysis was carried out by using a Zeiss UR-10 spectrophotometer (Jena, GDR).

Thermal analysis was conducted in air by means of the OD-102 derivatograph (MOM, Budapest, Hungarian DR), which is based on the Paulik, Paulik, and Erdey system.

Differential scanning calorimetry (DSC) was carried out under nitrogen by using a Perkin-Elmer DSC-1B differential microcalorimeter.

Melting points were determined in a capillary in a Tottoli apparatus (W. Büchi, Switzerland).

Elementary analysis was carred out by employing a Perkin-Elmer apparatus in ultrapure oxygen at a combustion temperature of 950-1000°C.

The content of carboxyl groups in hydrolyzed compound was determined by potentiometric titration with 0.1 N KOH solution following the method described in the literature [5].

The content of free carboxyl groups was determined by potentiometric titration with a tertiary amine in anhydrous medium [6].

Materials

Trimellitic anhydride (benzene 1,2,4-tricarboxylic acid) had anhydride content, 97%; trimellitic acid content, 2%; acid value about 870; melting point, 166°C and was obtained from Schuchardt, Germany.

Phenolphthalein, analytically pure, melting point 261°C was from POCH, Poland.

Chlorinated triphenyl (as Aroclor 5432, pure) was obtained from Monsanto Chemical Co., U. S. A. It had viscosity (ASTM D-88) 50-60 (98.9°C), specific gravity 1.290 (15.5°C), and acid value 0.014.

n-Heptane, pure, boiling point 98.4°C and n-hexane, pure, boiling point 69°C were from VEB, Jenapharm, Laborchemie, Apolda, GDR. Both n-heptane and n-hexane were dried with anhydrous calcium sulfate preparatory to the experiments.

Acetic anhydride, analytically pure, boiling point 139.6°C was from Oswiecim Chemical Works, Poland.

Phenolphthalein Acetylation

The acetylation of phenolphthalein was carried out by following the procedure described by Morgan [7]. A 30 g portion of phenolphthalein, 300 ml of acetic anhydride, and 1.2 g of potassium acetate were heated at the anhydride boiling point under reflux for 3 hr. The resulting product was precipitated with a 70/30 mixture (w/w) of water and methanol. The precipitate was filtered off, thoroughly washed with the water/methanol mixture, and then dried under reduced pressure (about 10 Torr) at a temperature of 80°C. The melting point of diacetyloxyphenolphthalein prepared was 145°C (lit. mp. 146°C according to the Morgan [7]).

Synthesis of p,p'-Phenolphthalein-bis(trimellitic) Dianhydride

Trimellitic anhydride (38.4 g, 0.2 mole), 40.2 g (0.1 mole) of diacetyloxyphenolphthalein, and 200 g of chlorinated triphenyl (Aroclor

5432) were placed in a reactor equipped with a stirrer, thermometer, and Dean-Stark receiver. First the stirrer was switched on, then the reaction mixture was heated to 200-205°C until a clear mass was formed.

With further heating, the acetic acid slowly distilled off at a temperature of 235-240°C. The reaction was continued with gradually increased temperature up to 275-280°C. At this temperature, the reaction was allowed to proceed until the evolution of acetic acid was completed. Then, the temperature was increased to 300°C followed by blowing nitrogen through the reaction mass to remove completely all remaining acetic acid. A total of 11.6 g of acetic acid, i. e., 96.7% of theoretical yield, was received within about 3 hr.

The course of acidolysis was studied at 240 ± 1°C, 260 ± 1°C, and 280 ± 1°C by determining the quantity of acetic acid evolved during the reaction being run at a continuous nitrogen flow. The content of acetic acid in the distillate was determined by titration with 0.5 N NaOH solution. The course of the reaction at the temperatures studied is shown in Fig. 1.

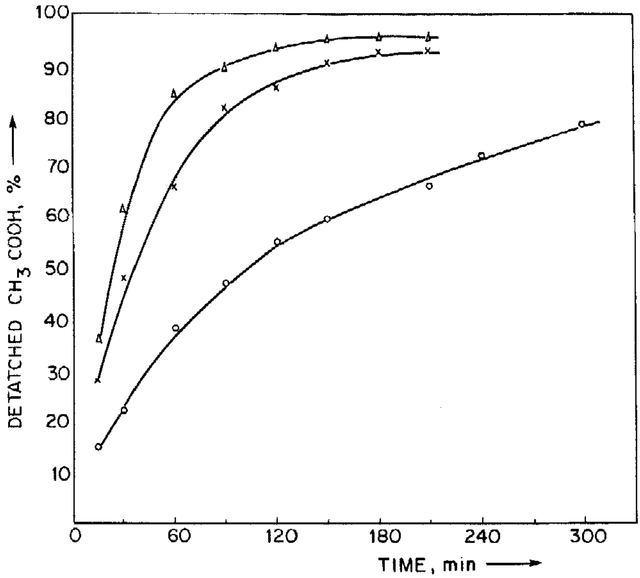


FIG. 1. Effect of temperature on the course of reaction of diacetyloxyphenolphthalein with trimellitic anhydride: (○) 240°C; (×) 260°C; (△) 280°C.

When the acidolysis was completed, the reaction mixture was cooled to about 80°C and then poured slowly into 3 to 4-fold excess of n-heptane. The suspension formed was agitated with a high-speed stirrer to precipitate the dianhydride that was filtered off and washed several times with n-heptane and then dried under reduced pressure (about 10 Torr), first at room temperature, then at 70-80°C. The yield of beige powder was 62.8 g (94% of theoretical yield).

Preparation of Pure Product

The 62.8 g of crude reaction product was mixed with 250 ml of benzene, resulting in a suspension to which acetic anhydride was gradually added in a minimum quantity to dissolve the precipitate while keeping it continuously stirred.

The solution was heated with active carbon for 30 min under reflux, then filtered off, and cooled. This solution was poured slowly into a 5 to 6-fold excess volume of dry n-hexane or n-heptane and continuously agitated. The precipitate formed was filtered off and washed with n-hexane or n-heptane and then dried under reduced pressure (about 10 Torr) in the presence of phosphorus pentoxide at 30-40°C followed by drying at 70-80°C. A white powder 42.9 g, (approximately 68% of theoretical yield) was obtained.

Characterization and Identification of p,p'-Phenolphthaleinbis(trimellitic) Dianhydride (PPTD)

The resulting product was purified twice as described above before determining its molecular formula and physicochemical properties. After the second purification, the tested compound melted in a more narrow range of temperatures. The melting point of the compound purified three times did not differ from that of the compound purified twice. Table 1 presents the physicochemical properties of the compound obtained and the elementary analysis results.

The infrared spectrum of p,p'-phenolphthalein-bis(trimellitic) anhydride is shown in Fig. 2. The sample for IR analysis was prepared by means of the pressed KBr disk technique. The compound content in a disk was 2 mg/1200 mg of KBr. The IR analysis conditions were as follows: rate of scanning, 50 cm^{-1}/min; pen deflection time, 32 sec; slit width, 8; the time constant, 2.

The purified dianhydride was also analyzed by means of the differential scanning calorimetry. The DSC curve was recorded at a constant rate of temperature increase of 16°C/min and a sensitivity of 4 mcal/sec, on a weighed portion of 3.5 mg of compound. The curve obtained is shown in Fig. 3.

TABLE 1. Physical and Chemical Properties of p,p'-Phenolphthalein-bis(trimellitic) Dianhydride

Characteristics	
Appearance	White powder
Melting point, °C	135-138
Elementary analysis	
Calculated for $C_{38}O_{12}H_{18}$, %	C, 68.46; H, 2.70
Found, %	C, 67.87; H, 2.88
Acid value, mg KOH/g	
Calculated	336
Found	335
Content of free carboxy groups, %	0.73
Solubility in solvents	Acetone methyl ethyl ketone Glacial acetic acid Acetic anhydride Dimethylformamide Dimethyl sulfoxide Cresol, Dioxane Low-molecular epoxy resins Methanol (hot) Ethanol (hot)
Insolubility in solvents	Ethyl ether Petroleum ether Extraction naphtha n-Hexane n-Heptane

In order to determine the thermal resistance of p,p'-phenolphthalein-bis(trimellitic) dianhydride, the usual derivatographic method was employed. The thermal curves shown in Fig. 4 were recorded at a rate of temperature increase of about 8°C/min.

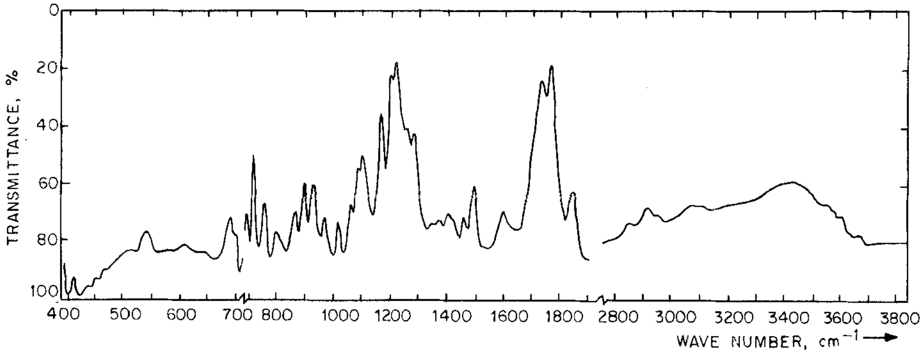


FIG. 2. Infrared spectrum of p,p'-phenolphthalein-bis(trimellitic) dianhydride.

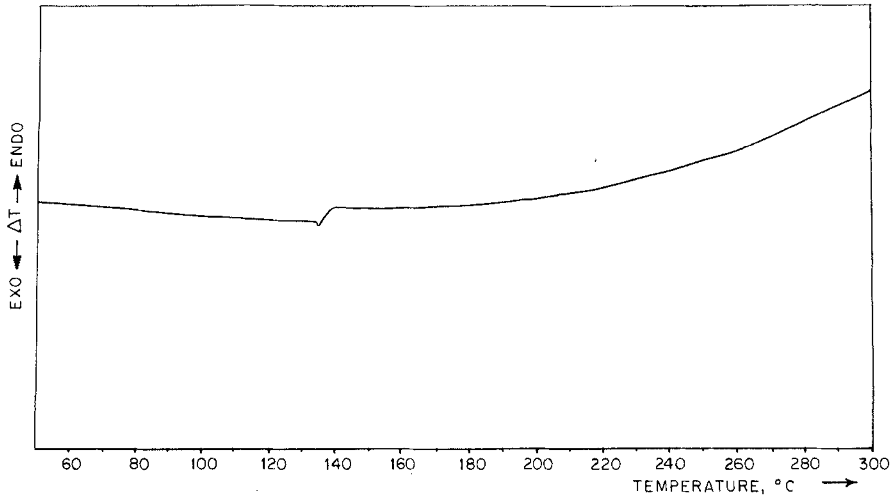


FIG. 3. DSC curve of p,p'-phenolphthalein-bis(trimellitic) dianhydride. Heating rate, 16°C/sec; sample, 3.5 mg; sensitivity, 4 mcal/sec.

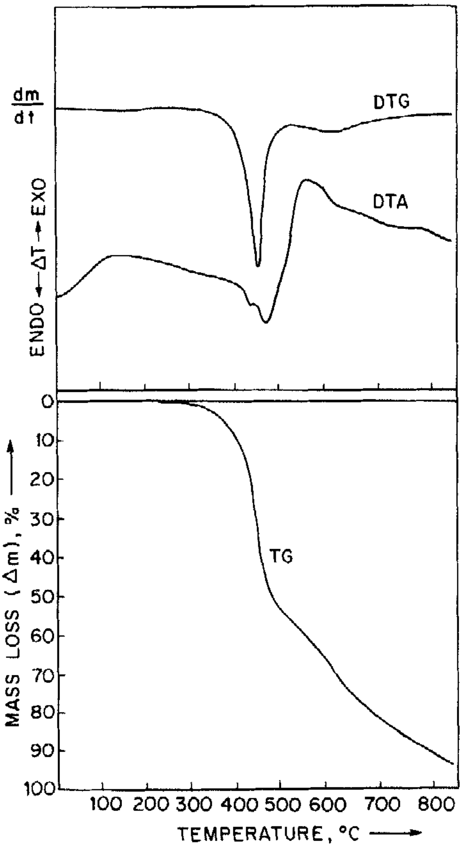


FIG. 4. TGA, DTA, DTG of p,p'-phenolphthalein-bis(trimellitic) dianhydride.

DISCUSSION RESULTS AND CONCLUSIONS

Examinations of the course of reaction between trimellitic anhydride and diacetyloxyphenolphthalein in a high-boiling solvent at 240, 260, and 280° C proved that the higher temperature, the higher reaction rate in the given temperature range. It may be concluded from the curves shown in Fig. 1 that the reaction yield, as determined from acetic acid evolved, was only 59% at 240° C after 2.5 hr while the yields were 90 and 95% at 260° C and 280° C, respectively, for the same time of processing.

The purified reaction product is a solid powder which melts at 135-138° C. The DSC analysis proved that the compound had an amorphous structure, i. e., it passed from the solid to the liquid state without any latent heat effect, increasing only its specific heat. This is illustrated in Fig. 3, where the DSC curve shows an inflection in the temperature range of 135-138° C corresponding to the melting point range mentioned above.

The assumed molecular formula of the compound was proved by elementary analysis and acid value determinations. It was also proved that one molecule of diacetyloxyphenolphthalein attached to two molecules of trimellitic anhydride in the reaction.

The acidolysis mechanism, according to which only the carboxy groups of trimellitic anhydride take part in this reaction, and the molecule structure were established from the IR spectrum presented in Fig. 2. That spectrum has an absorption doublet at 1773 and 1850 cm^{-1}, which is characteristice of cyclic acid anhydrides [8], no specific band for carboxyl C=O stretching vibrations which is present in the spectrum of trimellitic anhydride at 1711.9 cm^{-1}. Furthermore, the IR spectrum contains absorption bands characteristic of the ester group, i. e., the band at 1736 cm^{-1} related to the absorption of carbonyl group stretching [8a], the bands at 1000-1300 cm^{-1} caused by stretching vibrations of both –C–O– and –C–C– groups [8b], as well as the –C–O–C– group characteristic for acid anhydrides [9]. The absorption band specific for C=O of the lactone group and present in the spectrum of phenolphthalein at 1730 cm^{1}, is not visible in the spectrum of the prepared compound because it is overlapped by the absorption band of the ester carbonyl group.

The p,p'-phenolphthalein-bis(trimellitic) dianhydride obtained has good thermal resistance. From the course of the DTG curve in Fig. 4 it may be stated that the initial thermal decomposition of the tested compound occurs in air at temperature not lower than 340° C. The mass decrement reaches 5% of the sample mass after its heating to 385° C. The highest mass loss rate occurs at 450° C. Based on our previous studies it may be stated that a new acid dianhydride was obtained which contains a large polar group in a molecule ensuring its exceptionally good solubility in many organic solvents and low molecular epoxy resins. This feature together with its relatively low melting point and high thermal resistance make it possible to apply the new dianhydride in synthesis of thermal-resistant polyesterimides and as a hardening agent for epoxy resins.

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