



Development and Optimization of Producing 3,3', 4,4'-benzophenonetetracarboxylic dianhydride

ANTON SERGEYEVICH YEGOROV*, **ALYONA IGOREVNA WOZNIAK**,
VITALY SERGEYEVICH IVANOV, **ELENA ALEKSANDROVNA AVERINA** and
OLGA ANATOLEVNA ZHDANOVICH

Federal State Unitary Enterprise «State Scientific Research Institute of
Chemical Reagents and High Purity Chemical Substances» (FSUE "IREA")
107076, Bogorodsky val, 3. Moscow. Russia.

*Corresponding author E-mail: egorov@irea.org.ru

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ABSTRACT

This paper includes a series of experiments conducted in order to develop a laboratory method for producing 3,3', 4,4'-benzophenonetetracarboxylic dianhydride and selection of the optimum conditions, allowing to obtain the greatest yield. 3,3', 4,4'-benzophenonetetracarboxylic dianhydride is used for the preparation of polyimides with high thermal stability, chemical resistance as well as high strength and high Young's modulus. Benzophenonetetracarboxylic dianhydride was prepared by multistep route: Friedel-Crafts alkylation of o-xylene to obtain 3,3', 4,4'- tetramethyl benzophenone followed by liquid phase oxidation to benzophenonetetracarboxylic acid and dehydration.

Keywords: 3,3', 4,4'-benzophenonetetracarboxylic dianhydride, dianhydrides, polyimides, alkylation, heat resistant polymers, monomer.

INTRODUCTION

It is necessary to improve polymers due to the extensive use of polymeric materials in terms of maintaining their properties during heating, increase of the heat, thermal and radiation stability of the polymers and polymeric materials. Heat resistance of polymers and polymeric materials determines their

shape stability, including deformation stability when heated.

Polyimides are the class of thermally stable polymers, generally with rigid aromatic backbone chains. The most common method for producing aromatic polyimide is the reaction of dianhydrides of aromatic tetracarboxylic acids with aromatic

diamines. This reaction is carried out both by a two-stage or a single-stage method¹. The most common is the two-stage method. A soluble prepolymer is obtained at the first stage, of which films, fibers, coatings and other products can be formed. This reaction consists in the acylation of diamine with tetracarboxylic dianhydride in a polar solvent to form a polyamic acid (PAA) according to the equation shown in Figure 1.

The second stage of the reaction consists in dehydrocyclization of polyamic acid (PAA) (imidization) (see Figure 2) to form the end-product - the aromatic polyimide (PI) - and carried out by thermal or chemical methods².

In this paper, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (Figure 3) has been selected as a target, which further can be used to obtain the polyimide. The dianhydride is a powder of white or slightly grayish color, which is resistant to air moisture at room temperature; melting point is 225-228°C³.

The literature contains information about methods for preparation the appropriate dianhydride by anhydridization of corresponding tetra-carboxylic acid, obtained by oxidation of 3,3',4,4'-tetraalkylbenzophenone (mostly 3,3',4,4'-tetramethyl benzophenone), as shown in Figure 4.

The first oxidation method consists in treatment with nitric acid of tetrasubstituted benzophenone⁴⁻⁶. The yields of 70-75% of theoretical value (for acid) are achieved by this method.

The second method consists in a liquid-phase catalytic oxidation of tetraalkyl benzophenone with air in the acetic acid using a metal halide catalysts (Co-Br, Co-Mn-Br, Co-Mn-Mo-Br) in the medium, providing the activation of the catalyst (protonic acids and halogen- substituted aliphatic acids)^{7,8}. The yields of 79-96% of theoretical value (for acid) are achieved by second method.

The most economically feasible and available raw materials used to obtain 3,3',4,4'-tetraalkyl benzophenone are in particular o-xylene, formaldehyde and acetaldehyde. H₂SO₄ or more expensive metal-containing catalysts are usually used as the catalysts (see Figure 5). All sources of these raw materials are widely available.

There are data of the use of low temperature methods of synthesis of 3,3',4,4'-benzophenonetetracarboxylic dianhydride^{9,10}. However, the use of such compounds as sodium hypochlorite⁹, and the need for use of a complex synthesis scheme, a large amount of initial reagents and expensive palladium and nickel compounds

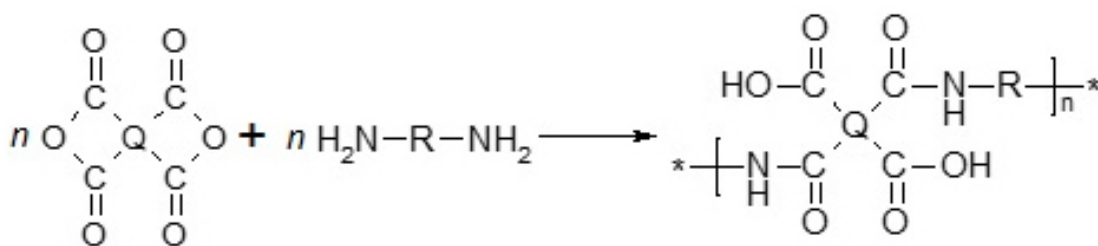


Fig. 1: The scheme of obtaining polyamide acid

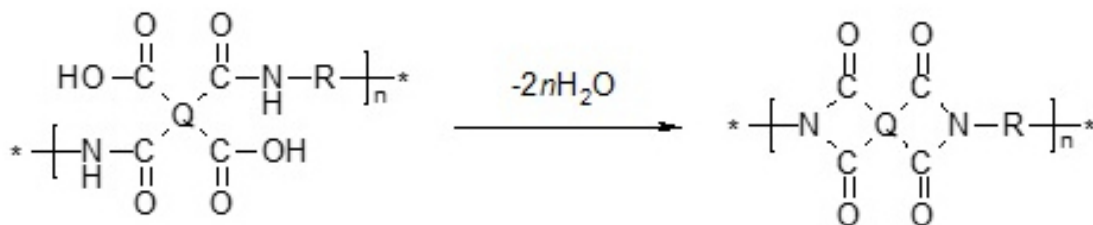


Fig. 2: Scheme of obtaining polyimide from polyamide acid

still limits the ability of the widespread use of these synthesis methods.

According to the patent⁶ the process of oxidation of 3,3', 4,4'-tetramethylbenzophenone is carried out with nitric acid in the temperature range from 150 to 250°C, and the dehydration to obtain benzophenonetetracarboxylic dianhydride at a temperature of 280 - 320°C for 10 hours. Synthesis of the starting aromatic hydrocarbon is carried out by condensation of *o*-xylene with acetaldehyde in the

presence of H₂SO₄, under relatively mild conditions (T = 10 - 50°C, P = 0.6-0.8 MPa), according to the scheme which is similar to that shown in Figure 4. The condensation of *o*-xylene may be carried out using formaldehyde. Selection of formaldehyde or acetaldehyde is determined by availability, as well as fire and explosion hazard of these reagents.

In laboratory conditions, 3,3', 4,4'-tetramethylbenzophenone is prepared by aluminum trichloride catalyzed Friedel-Crafts reaction. The method with alkylation of *o*-xylene with carbon tetrachloride followed by treatment with alkali has been chosen to develop a laboratory technique (see Figure 6)¹¹.

The selected method for the preparation is shown in Figure 7.

Experimental part

Preparation of 3,3', 4,4'-benzophenonetetracarboxylic acid is carried out in four stages. A series

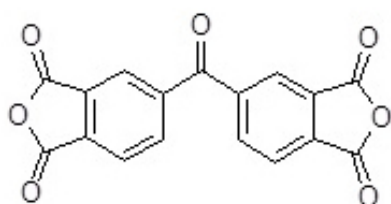


Fig. 3: The structural formula of 3,3', 4,4'-benzophenonetetracarboxylic dianhydride

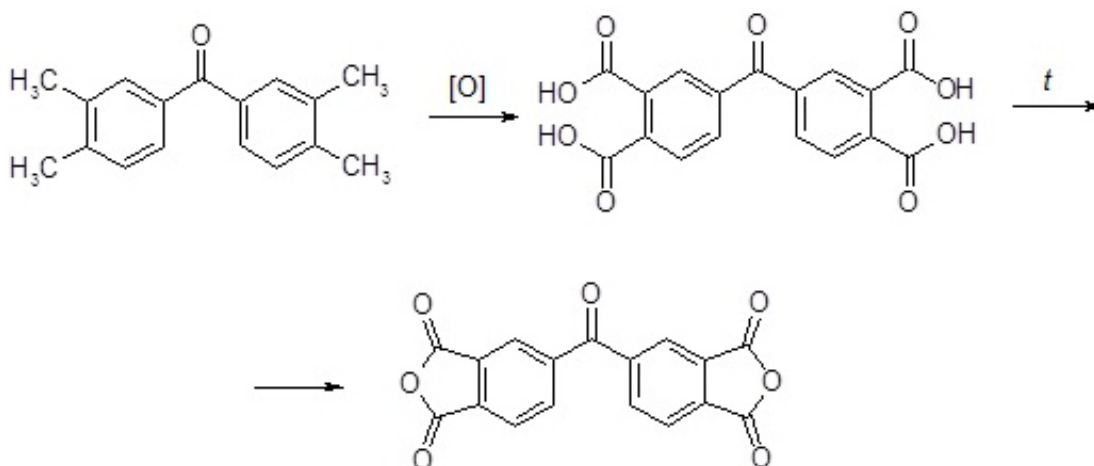


Fig. 4: Preparation of 3,3', 4,4'-benzophenonetetracarboxylic dianhydride by the oxidation of 3,3', 4,4'-tetramethyl benzophenone

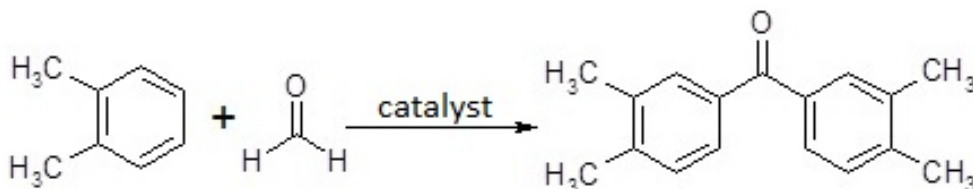


Fig. 5: Scheme of obtaining 3,3', 4,4'-tetramethyl benzophenone

of optimization experiments were conducted for each of successive reactions.

also purchased from Vekton and calcined before use. Toluene, o-xylene, pyridine, heptane, diphenyl oxide were purchased from Component-Reaktiv.

MATERIALS

Carbon tetrachloride, aluminum chloride, sodium hydroxide, potassium permanganate were purchased from Vekton. Magnesium sulfate was

Analytical techniques

The resulting products and their purity were identified by NMR spectroscopy, elemental analysis and mass spectroscopy. NMR spectra were

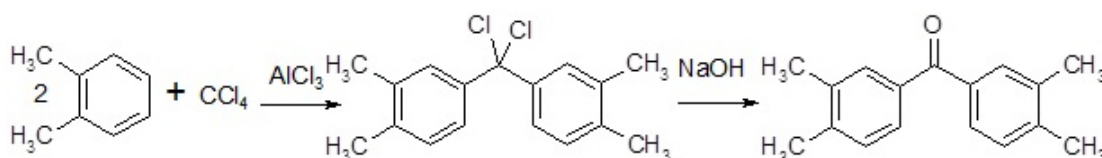


Fig. 6: Preparation of 3,3', 4,4'-tetramethyl-benzophenone by Friedel-Crafts alkylation followed by treatment with alkali [11]

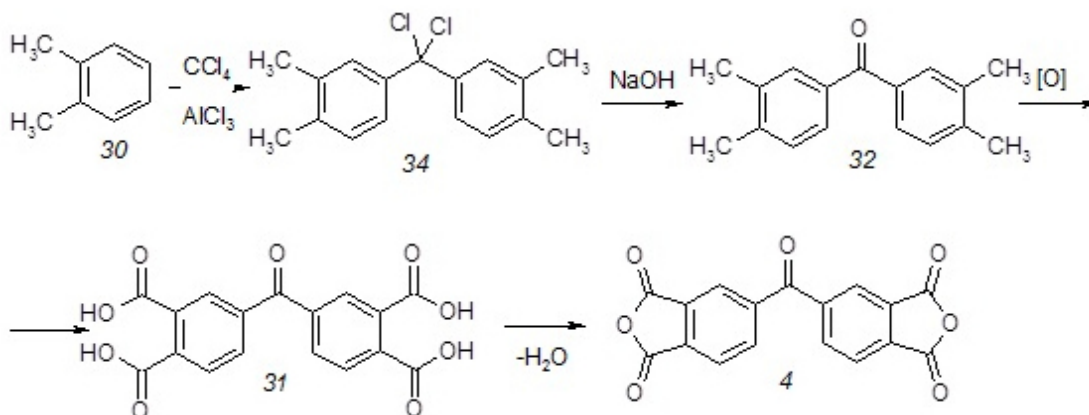


Fig. 7: The selected method for the preparation of 3,3', 4,4'-benzophenonetetracarboxylic acid

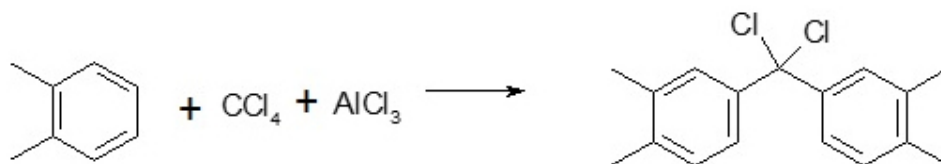


Fig. 8: Preparation of 3,3', 4,4'-diphenyl dimethyl dichloromethane

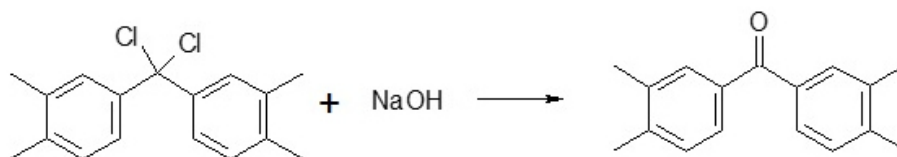


Fig. 9: Preparation of 3,3', 4,4'-tetramethyl benzophenone

recorded on Bruker Avance III HD with an operating frequency of 300 MHz. DMSO-d₆ was used as the solvent and tetramethylsilane as internal standard. Elemental analysis was recorded on CHNS-analyzer

(EuroVector, Euro EA 3000 model). Mass spectra were obtained using chromatography-spectrometry system "Chromatec Kristall 5000.2" with mass-spectrometer detector ISQ Thermo Scientific.

Table 1: The effect of the temperature conditions and the ratio of raw materials to yield of 3,3',4,4'-tetramethyl diphenyl dichloromethane

No	Temperature mode of adding <i>o</i> -xylene solution (initial and final temperature), °C	Aluminum chloride		The molar ratio of the reactantso-xylene: aluminum chloride	Yield, %
		Weight, g	Quantity, mol		
1	-5 – 0	19	0,135	1:1,5	60,0
		12	0,09	1:1	62,0
		8	0,06	1:0,67	85,0
		6	0,045	1:0,5	57,0
2	0 – 5	19	0,135	1:1,5	54,0
		12	0,09	1:1	75,0
		8	0,06	1:0,67	90,0
		6	0,045	1:0,5	64,0
3	5 – 10	19	0,135	1:1,5	47,0
		12	0,09	1:1	49,0
		8	0,06	1:0,67	51,0
		6	0,045	1:0,5	42,0
4	10 – 15	19	0,135	1:1,5	30,0
		12	0,09	1:1	37,0
		8	0,06	1:0,67	45,0
		6	0,045	1:0,5	34,0

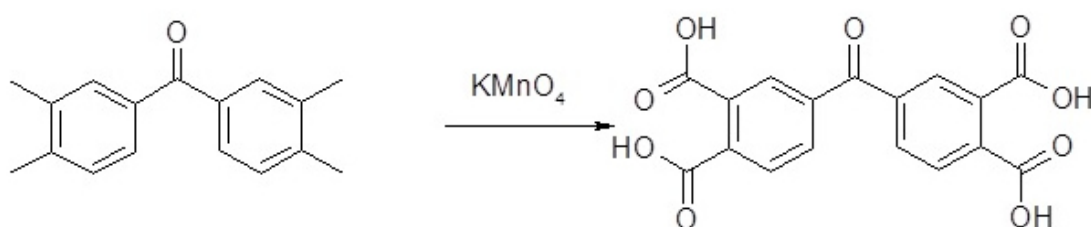


Fig. 10: Preparation of 3,3',4,4'- benzophenonetetracarboxylic acid

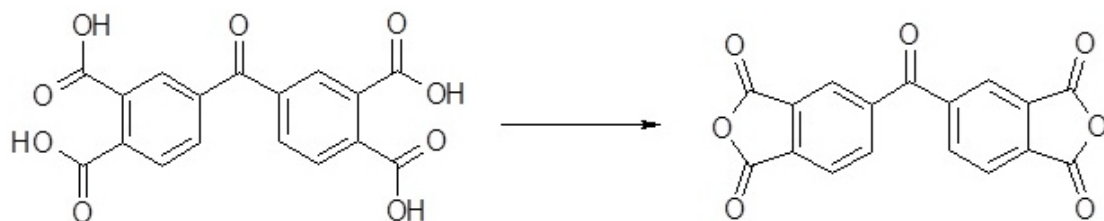


Fig. 11: Preparation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride

Preparation of 3,3',4,4'-tetramethyldiphenyldichloromethane

A three-necked round bottom flask equipped with magnetic stirrer, a reflux condenser, a thermometer and a dropping funnel was filled with anhydrous aluminum chloride and 22 ml (35 g, 0.23 mol) of carbon tetrachloride, then reaction mixture was cooled with vigorous stirring and a solution of 10 g (0.09 mol) of *o*-xylene and 6 ml (9.5 g, 0.06 mol) of carbon tetrachloride was added dropwise in such a way that the temperature of reaction mixture did not rise above a certain value. Upon complete addition 20 ml of distilled water was added to the reaction mixture through the dropping funnel, the organic layer was separated, washed with distilled water (2 × 20 ml) and dried with anhydrous magnesium sulfate. Then, carbon tetrachloride was distilled under vacuum and the product was obtained as colorless oil, which was used in the next stage without further purification. The results are shown in Table 1.

¹H NMR spectrum (DMSO - d₆) (δ, ppm): 7.07-7.25 (m, 6H, H_{Ar}), 2.43 (s, 12H, CH₃).

Table 1 shows that the preparation of 3,3', 4,4'- tetramethylphenyldichloromethane by alkylation of carbon tetrachloride in the presence of anhydrous aluminum chloride should be conducted at a molar

ratio of *o*-xylene: aluminum chloride 1: 0.67 at 0 - 5°C.

Preparation of 3,3',4,4'-tetramethyl benzophenone

A round bottom flask, equipped with magnetic stirrer and reflux condenser was filled with 200 ml of sodium hydroxide solution and 20 g (0.07 mol) of 3,3',4,4'-tetra methyldiphenyldichloromethane. The reaction mixture was heated while stirring. The reaction mixture was cooled to room temperature and extracted from the aqueous phase with toluene (3 × 50ml), the extracts were combined, washed with distilled water (3 × 50 ml) and dried with anhydrous magnesium sulfate. The solvent was distilled off under vacuum to obtain the product as a white powder, which was used in the next step without further purification. The test results are shown in Table 2.

Elemental analysis. Calculated, %: C 85.67; H 7,61. Found, %: C 85,72; H 7,54.

¹H NMR spectrum (DMSO - d₆) (δ, ppm): 7.29-7.51 (m, 6H, H_{Ar}), 2.38 (s, 12H, CH₃).

Table 2 shows that the hydrolysis of 3,3', 4,4'-tetramethyldiphenyl dichloromethane has been carried out with 10% sodium hydroxide solution for 1 hour.

Table 2: The influence of the concentration of hydrolyzing agent, and reaction time on the yield of 3,3', 4,4'-tetramethyl benzophenone

No	Dwell time, hour	The concentration of sodium hydroxide solution, %	Yield, %
1	0,5	2	40,0
		5	63,0
		10	75,0
2	1	2	65,0
		5	90,0
		10	93,0
3	2	2	79,0
		5	87,0
		10	93,0
4	3	2	81,0
		5	87,0
		10	93,0

Preparation of 3,3',4,4'-benzophenone tetracarboxylic acid

A four-necked round bottom flask equipped with mechanical stirrer, a reflux condenser, thermometer and funnel for loading bulk solids was filled with 10.7 g (0.045 mol) of 3,3',4,4'-tetramethylbenzophenone, 64 ml of solvent and 320 ml of water. Then started stirring and heating, the reaction mixture was adjusted to 85°C. At this temperature, potassium permanganate (5 - 7 g) was added through the funnel portionwise. Before adding a further portion of potassium permanganate, a sample (2 ml) should be taken from the reactor via a Pasteur pipette, and visually observed the moment by color change of the mixture from violet to muddy brown, when all added potassium permanganate reacted, and only then the following portion should be added. Oxidation is considered to be finished, if a new portion of potassium permanganate introduced was not oxidized for 1 hour. During the experiment, it was found that 60 g (0.38 mol) of potassium permanganate was necessary to fully oxidize the 3,3',4,4'-tetramethyl benzophenone.

To convert the excess of potassium permanganate to manganese oxide (IV) 20 ml of ethanol was added to the reaction mixture and stirred at room temperature until disappearance of the purple color. Manganese oxide (IV) formed during the reaction was filtered off and washed with hot water (6 × 50 ml). Basic filtrate and washing water were combined and water and solvent were evaporated on a rotary evaporator so that the 1/3 of the initial volume of the solution was remained. The resultant filtrate was poured into a glass, cooled to 10°C and under stirring concentrated hydrochloric acid was added until acidic reaction on universal indicator. The acidic solution was left overnight at room temperature. The crystals precipitated was filtered and recrystallized from 10% of hydrochloric acid solution. A pyridine solvent should be used for preparation of 3,3', 4,4'-benzophenonetetracarboxylic acid.

Elemental analysis. Calculated, %: C 56.99; H 2,81. Found, %: C 57,04; H 2,76.

¹H NMR spectrum (DMSO - d₆) (δ, ppm): 11.31 (s, 4H, COOH), 8.59 (d, 2H, H_{Ar}, J = 7.69 Hz), 8.29 (d, 2H, H_{Ar}, J = 7.53 Hz), 8.07 (c, 2H, H_{Ar}).

Mass spectrum m/z (I_{rel}, %): 322 [M - H₄O₂] (32,7), 278 [M - CH₄O₄]

Preparation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride

A two-necked round bottom flask equipped with magnetic stirrer, thermometer and Dean-Stark trap with reflux condenser was filled with 5.8 g (0.016 mol) of 3,3', 4,4'-benzophenonetetracarboxylic acid, 15ml of solvent (forming an azeotrope with water, separating from the water and not reacting with either an acid or anhydride) was added. Reaction mixture was heated while stirring to boiling, and water was removed from the reaction mixture as an azeotrope mixture. The process was continued until the formation of clear, light brown solution in the reaction flask and the separation of ~ 0.6 ml of water. The solution in the reactor was cooled to 50°C and 24 ml of 1,4-dioxane was added. It was cooled to room temperature. The precipitated crystals were filtered, washed with 10 ml of boiling 1,4-dioxane and dried in vacuo.

According to the results it has been found that anhydridization of 3,3',4,4'-benzophenonetetracarboxylic acid requires high temperatures and therefore high boiling solvent. The reaction should be conducted in the diphenyl ether at a temperature of 230°C for 2 hours for the best results.

Elemental analysis. Calculated, %: C 63.37; H 1.88. Found, %: C 63,26; H 1,85.

¹H NMR spectrum (DMSO - d₆) (δ, ppm): 8.96 (2H, dd), 8.35 (2H, d), 8.19 (2H, d).

RESULTS AND DISCUSSIONS

As a result of studies it has been found an optimum ratio of o-xylene and aluminum chloride in the preparation of 3,3',4,4'- tetramethyldiphenyl dichloromethane by alkylation with carbon tetrachloride is 1:0.67 of o-xylene: aluminum chloride at 0-5°C. The yield of 3,3', 4,4'-tetramethyldiphenyl dichloromethane under these conditions attains the value 90%.

Optimal conditions for obtaining 3,3',4,4'-tetramethylbenzophenone with a yield of

93% were determined, the reaction time was 1 hour, the concentration of sodium hydroxide solution was 10%.

From the series of experiments for obtaining 3,3',4,4'-benzophenonetetracarboxylic acid by oxidation of 3,3',4,4'-tetramethylbenzophenone with potassium permanganate follows that to carry out this process with a maximum yield a molar ratio of 3,3',4,4'-tetramethylbenzophenone to potassium permanganate should be 1: 8.4. The maximum yield obtained has been achieved at this ratio and reached 70%.

Preparation of 3,3',4,4'-benzophenonetetracarboxylic acid by anhydridization should be performed using diphenyl ether as a solvent. Maximum yield of dianhydride reaches 70%.

All the products obtained at the intermediate and final stages of the developed method have the purity of not less than 90%.

CONCLUSION

A laboratory procedure for the preparation of intermediate products and 3,3',4,4'-benzophenonetetracarboxylic dianhydride has been developed and optimized. The conditions which allow to achieve yields of more than 70 and up to 95% were chosen at each stage. The available and the least expensive reagents were used in method obtained. The resulting target dianhydride can be used to obtain thermally stable polyimides.

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