

PREPARATION AND PURIFICATION OF A FLAME-RETARDANT POLYPHENYLPHOSPHONATE CONTAINING 4,4'-DIHYDROXYBENZOPHENONE

Graziele Vefago Boaventura Possenti¹, ✉, Aline Vieira de Souza², Rodrigo Battisti¹, Juliani Conti Martins Domingui², Lucas Domingui¹, Cintia Soares², Humberto Gracher Riella²

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Abstract. A polyphenylphosphonate containing 4,4'-dihydroxybenzophenone was synthesized as a flame retardant. However, impurities were detected and may compromise its properties and thermal stability. Thus, a purification route based on water and hexane extraction with reflux was proposed. Results showed success in removing impurities, especially P–Cl groups, without damaging the polymer.

Keywords: polyphenylphosphonate, flame retardant, purification, aqueous extraction, organic extraction.

1. Introduction

An increasing emphasis on the issue of polymer synthesis, as well as its application in several areas, has been observed in recent years. On the other hand, polymers present residual solvents, unreacted monomers and other impurities derived from their synthesis. The presence of such impurities can be problematic with regard to the application, making its purification necessary.¹ Flame-retardants are among polymers that have been synthesized recently. Although they do not completely eliminate combustion, these retardants interfere with the physical and chemical mechanism of combustion and improve the fire resistance of a polymer material.^{2,3}

Phosphorus-containing flame-retardants have good fire resistance and low toxicity when compared to halogen-containing flame-retardants, so they are

considered to be very efficient in many polymers and have been used in this field.⁴ Compounds containing P–C bonds are preferred as flame-retardants because they promote the formation of charcoal, high fireproof efficiency at low phosphorus concentration, thermal stability and easy synthesis.^{5,6} The action of these compounds may occur in the vapor phase by a radical mechanism to disrupt exothermic processes and suppress combustion. In this case, it is likely that the PO, P and P₂ species react with the H and OH radicals to form HPO.⁷ On the other hand, they can also act in the condensed phase. The compounds incorporated in polymeric materials act as acid precursors and the atoms participate in the formation of coal. Soon, a protective layer is formed to prevent further burning.⁸

Several phosphorus-containing compounds have been synthesized and used to improve flame retardancy in polymers, such as triphenyl phosphate (TPP),⁹ resorcinol bis(diphenyl phosphate) (RDP),¹⁰ bisphenol A bis(diphenyl phosphate) (BDP),¹¹ poly(9-oxa-10-(2,5-dihydroxyphenyl)phospha-phenanthrene-10-oxide) phenylphosphonate (WLA-3),¹² and phosphorus oxychloride (POCl₃).¹³ Kricheldorf *et al.*¹⁴ investigated the synthesis *via* a silyl method of flame-retardant polyphosphonates from monomers of phenylphosphonic dichloride with silylated biphenyldiol or diphenols. They concluded that the molecular weights of polyphosphonates synthesized *via* the silyl method are not higher than those prepared under optimum conditions by the conventional interfacial method or thermal condensation of the corresponding free phenols. Nevertheless, the silyl method has the advantage of a great versatility for the preparation of copolyesters from various acid chlorides. Domingui¹⁵ also focused on the synthesis of a polymer containing phosphorus with flame retardant properties. The author used the interfacial polycondensation as the synthesis methodology to obtain a polyphenylphosphonate containing 4,4'-dihydroxybenzophenone. However, unidentified signals or bands not characteristic of

¹ Federal Institute of Education, Science and Technology of Santa Catarina (IFSC), campus Criciúma, Rodovia SC 443 km1, nº 845, Vila Rica, Criciúma, Santa Catarina, Brazil, 88813-600

² Chemical Engineering Department, Federal University of Santa Catarina (UFSC), campus Trindade, Florianópolis, Santa Catarina, Brazil, 88040-900

✉ graziele.vefago@ifsc.edu.br

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polyphenylphosphonate were observed in the NMR and FTIR spectra, respectively. This indicates the presence of impurities from excess sub-products or reagents during the polymerization process.^{15,16}

Purification of products is necessary to remove contaminants that may interfere with the application of the material, which will consequently lead to a decrease in the final cost of the product. Thus, the purification strategies to be employed must be satisfactory, fast, high yield, and robust. The key to successful and efficient purification is to select the most appropriate technique, optimize its performance to meet the requirements, and combine them in a logical way to maximize productivity and reduce the number of steps required.¹⁷ In addition, according to Wilkie and Morgan,¹⁸ the impurities present in polymers in general, more specifically in flame retardant polymers, can influence their thermal degradation characteristics, being recognized as a critical variable by manufacturers. Still according to the authors, it is sufficient to state, at this point, that the consequences of these impurities are generally those of promoting the overall degradation and can give rise to the slow thermal degradation and related deterioration in the properties of the polymer, often experienced when in use, and exposed to service temperatures well below their normal rapid degradation temperatures. Researches have been focused on the purification of reaction products and sub-products. Zagklis and Paraskeva,¹⁹ for example, optimized a solvent extraction process to purify phenolic compounds, followed by fractionation with membrane filtration and adsorption/desorption. Zeng *et al.*²⁰ improved Soxhlet extraction for purification of polybrominated diphenyl ethers (PBDEs). Iliescu *et al.*²¹ purified a polyphosphonate with washing in distilled water and by the dissolution/precipitation method.

One of the basic operations of separation of materials is extraction. Extraction is a method of chemical separation, which can be applied in different ways. The principle of extraction is to remove substances that may negatively influence the sample. In addition, it is used to concentrate solutions and transport compounds between different solvents. Among some types of extraction, liquid-liquid extraction is highlighted. Liquid-liquid extraction is based on the displacement of a solute from one solvent to another according to the solubility equilibrium, in which the solvents are immiscible. This equilibrium solubility depends directly on the temperature and pressure of the system.²² Thus, purification favors the application of the product, besides creating reuse or recycling opportunities of sub-products with some added value. Furthermore, Domingui¹⁵ indicated the presence of impurities from by-products or reagents in excess of the polymerization process of the flame-retardant polymer and highlighted the need for its purification.

In this context, the present work aims to propose a purification route for a polyphenylphosphonate containing 4,4'-dihydroxybenzophenone synthesized for flame retardant applications.

2. Experimental

2.1. Materials

The materials used in the synthesis and purification route of the polyphenylphosphonate polymer were: phenylphosphonic dichloride (PPDC), 4,4'-dihydroxybenzophenone (DHBP) and benzyltriphenylphosphonium chloride (BTPC), supplied by Sigma Aldrich (USA). Dichloromethane (DCM), tetrahydrofuran (THF) hexane and sodium hydroxide, supplied by Vetec, Neon and Dynamic (Brazil), respectively, and distilled water. All reagents were of analytical grade and were used without any prior purification.

2.2. Methods

2.2.1. Synthesis of the polyphenylphosphonate

To obtain the polyphenylphosphonate (PPP), an optimized version of the method presented by Domingui¹⁵ was applied (Fig. 1). For this, a jacketed glass reactor of 200 mL was used. The system was maintained at reflux, at controlled temperature and in agitation to control the reaction. Initially, a 1.0 mol/L NaOH solution and a 0.1 mol/L BTPC solution dissolved in DCM were prepared. The solutions were added to the reactor and stirred for 30 ± 1 min at 277 K to yield a biphasic mixture. Subsequently, a solution of DHBP (0.007 mol/L) dissolved in DCM and 0.0114 mol of PPDC, were simultaneously added to the reactor. The resulting solution was kept under stirring for 4 h at the temperature of 277 ± 0.1 K. After this reaction period, the synthesized polymer was precipitated with cold hexane and water. For evaporation of solvent residues, the synthesized polymer was oven dried at 333 ± 1 K.

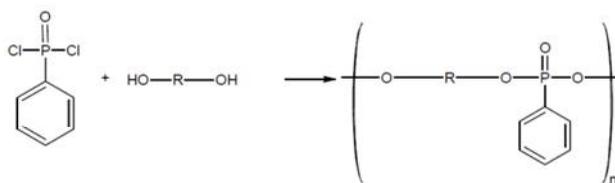


Fig. 1. Generic reaction to obtain a phosphorous polymer

2.2.2. Solubility test

The solubility test was performed with the objective of identifying the solvent in which each reagent is soluble. It is thus possible to define what is present in

each liquid phase resulting from the synthesis. For this purpose, 0.50 ± 0.01 g of epy reagent was used and solubilized in 5.0 ± 0.1 mL of solvent.

2.2.3. Purification of the polyphenylphosphonate

For purification of the polyphenylphosphonate (PPP), a two-step purification route was applied. In the first step, the polymer was subjected to an aqueous extraction and in the second step it was subjected to an organic extraction. Fig. 2 shows a flowchart of the analytical route applied in the purification of PPP.

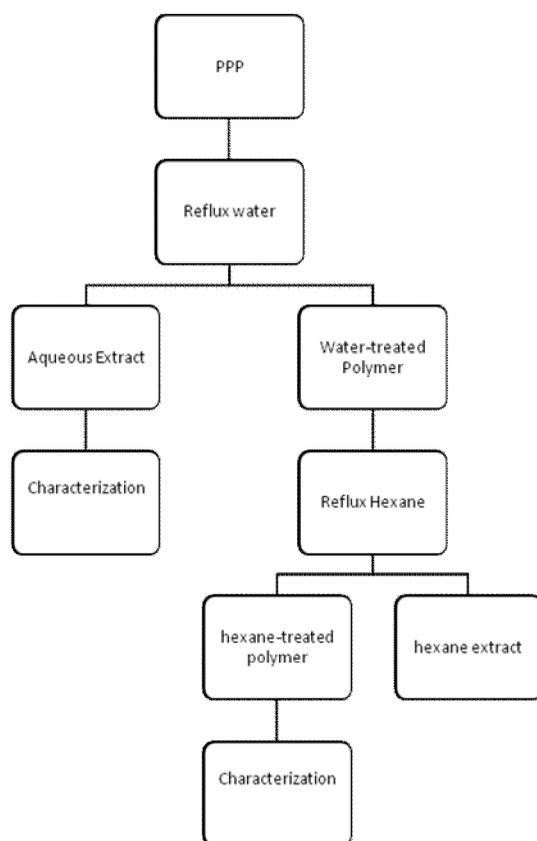


Fig. 2. Organization of the analytical route applied in the purification and characterization of PPP

Initially, in the first step of the purification route, 1.50 ± 0.01 g of the polymer was refluxed in distilled water. For this, the sample was added to a 250 mL flat bottom flask, with 100 mL of distilled water, coupled to a condenser that is maintained at the temperature of 288 ± 1 K. The extraction system was heated to the temperature of 343 ± 1 K for 50 ± 1 min after the reflux began. The sample was then removed from the reflux flask and taken to the oven for drying at the temperature of 333 ± 1 K. In the second step, the polymer resulting from the aqueous extraction process was refluxed in

hexane. For this, the sample was transferred to a 250 mL flat bottom flask and 100 mL hexane was added. The flask was coupled to a condenser maintained at the temperature of 288 ± 1 K. The extraction set was heated to the temperature of 333 ± 1 K. After the beginning of reflux, the system was maintained for 50 ± 1 min under heating and stirring and after this process, the polymer was removed from the flask, washed with a little distilled water at room temperature and dried in an oven at 333 ± 1 K.

2.2.4. Characterization of the extracts resulting from purification

Gravimetric analysis was used to determine total solids. For this, an aliquot of the sample was added in a dry and heavy beaker. The sample was left in the oven at 378 ± 1 K for 24 h. Subsequently it was removed, stored in a desiccator until room temperature, and then weighed, after which the TS concentration was calculated. To determine the conductivity of the aqueous samples, the conductometric method was applied. To carry out the readings, a benchtop conductivity meter (mCA 150, Tecnonon), calibrated with a standard solution of $146.9 \mu\text{S}\cdot\text{cm}^{-1}$ was used. In order to determine the sodium concentration present in the aqueous samples, analyses were carried out. For this, a flame photometer (Analyser, model 910) was used. The determination of chloride concentration was performed by titration using the Mohr method. For titration, a previously prepared and standardized silver nitrate solution (AgNO_3) 0.1 mol/L was used.

2.2.5. Characterization of the purified polymer

MALDI-TOF mass spectrometer. The samples were analyzed on a Bruker MALDI-TOF mass spectrometer (AutoFlex III Smartbean). The method was applied for the purpose of determining the molar mass of polyphenylphosphonate, before and after treatment. Initially, the samples were diluted in tetrahydrofuran (THF). $1 \mu\text{L}$ of the 2,5-dihydroxybenzoic acid matrix (DHB) was applied and crystallized at room temperature in a MALDI target plate (Bruker Daltonics). Next, $3 \mu\text{L}$ of each polyphenylphosphonate sample was applied to the DHB matrix crystallized on the plate. The spectrometer was calibrated with peptide reagent (Bruker) for the range of 1000 to 3500 Da. Mass spectra (MS) by MALDI-TOF were obtained in the positive ion reflection mode, applying a 100 Hz frequency laser, with 80 % of full load, in the detection range of 400–4000 Da.

Fourier Transform Infrared Spectrophotometry (FTIR). A Shimadzu model spectrometer (IR Prestige 21) was used for the FTIR tests, using the KBr technique in the wave number range of $500\text{--}4000 \text{ cm}^{-1}$.

Thermal Analyses. For thermogravimetric analysis (TGA), 10 mg of sample were prepared on an STA (model 443 F3 Jupiter, Netzsch) under N₂ atmosphere (20 mL/min) at the heating rate of 10 K/min. Differential scanning calorimetry (DSC) was performed by using a Perkin Elmer/Jade DSC (Intracooler SP) and Pyris Series Perkin Elmer software. The samples were analyzed in the temperature range of 253–503 K/min cooled to 253 K keeping isotherm for 10 min and heating rate 10 K/min keeping isotherm for 10 min, and N₂ flow rate of 30 mL/min.

3. Results and Discussion

3.1. Solubility Test of the Polyphenylphosphonate and Reagents Used in the Synthesis

From the results presented in Table 1, it is possible to find NaOH and BTPC in the aqueous phase. In addition, the organic phase is composed of two solvents, hexane and dichloromethane, since both are miscible. In the organic phase, it is possible to find the PPDC monomer that did not polymerize. Since the DHBP mono-

mer is insoluble or partially soluble in the solvents present in the synthesis, if an unpolymerized monomer is present, the same may precipitate with the polymer or remain in the system and be removed with the solid phase from the synthesis.

3.2. Purification of the Polyphenylphosphonate

In the first step of the purification, an aqueous extract was obtained. Table 2 shows the results obtained in the analysis of total solids, conductivity, sodium, and chloride in the extract obtained.

From the results, it is possible to affirm that there was removal of impurities in the reflux step in water. The hexane resulting from the second extraction step left a body at the bottom when standing after reflux, and presented 500 mg/L of soluble solids. The solid obtained in the reflux step in hexane was classified as a byproduct of the purification process and characterized. Solubility and FTIR assays were performed to characterize the sub-product. Table 3 shows the solubility test results determined for the sub-product obtained in the reflux step in hexane.

Table 1. Results of the solubility test of the reagents, the polymer and the solvents used in the polyphenylphosphonate synthesis

Reagent	Physical state	Distilled water	Hexane	DCM	THF
PPDC	liquid	miscible	immiscible	miscible	miscible
DHBP	solid	insoluble	insoluble	partially soluble	soluble
BTPC	solid	soluble	insoluble	insoluble	insoluble
NaOH	solid	soluble	insoluble	insoluble	insoluble
PPP	solid	insoluble	insoluble	insoluble	soluble
DCM	liquid	immiscible	miscible	–	miscible
Hexane	liquid	immiscible	–	miscible	miscible

Table 2. Results of the total solids, conductivity, sodium, and chloride tests for the aqueous extract

Analysis	Result
Total solids	500 mg/L
Electric conductivity	165.30 μ S/cm
Sodium	15.87 mg/L
Chlorides	<10 mg/L

Table 3. Results of the solubility test of the sub-product obtained in the reflux stage in hexane compared to results obtained for the solid reagents used in the polymerization reaction

Reagent	Distilled water	Hexane	DCM	THF
Sub-product	insoluble	insoluble	insoluble	soluble
DHBP	insoluble	insoluble	partially soluble	soluble
BTPC	soluble	insoluble	insoluble	insoluble
NaOH	soluble	insoluble	insoluble	insoluble

Analyzing the obtained results, it is possible to note that the byproduct presents characteristics similar to the monomer DHPB. In order to confront the present connections in the sub-product and DHPB, FTIR analysis was performed. As shown in Fig. 3, the presence of DHPB-like bands was evidenced in the sub-product sample.

Bands characteristic of DHPB are found in 1510 and 1446 cm^{-1} , corresponding to the C=C aromatic bond.^{15,23} The band at 1600 cm^{-1} corresponds to the C=O group and the band at 853 cm^{-1} corresponds to the C-H aromatic bond.^{15,24-26} Fig. 4 shows the detailed diagram of the purification route and the parameters that showed positive results are exposed.

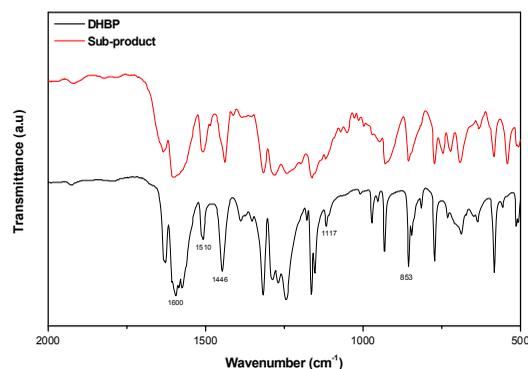


Fig. 3. FTIR spectra for the sub-product and the 4,4'-hydroxybenzophenone monomer

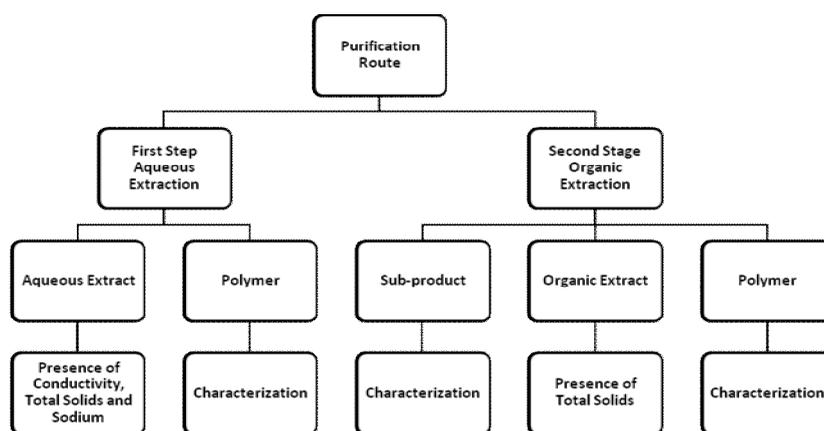


Fig. 4. Detailed diagram of the purification route

3.3. Characterization of the Purified Polymer

3.3.1. MALDI-TOF mass spectrometer

By observing the presented results, it is possible to verify that impurities were removed, since the treatment resulted in a sub-product and the laboratory tests presented soluble solids in the obtained extracts. The MALDI-TOF spectra shown in Figure 5 show the molar masses obtained for the polyphenylphosphonate polymer (or in this case, being classified as an oligomer) before and after being subjected to the purification route. The results showed similar peaks between the purified and in natura sample, that is, the molar masses were conserved during the purification process. Thus, the purification route does not affect the polymer structure, therefore, it is possible to apply the method.

3.3.2. Fourier transform infrared spectrophotometry (FTIR)

Fig. 6 shows a comparison between the FTIR spectra of the in natura and purified samples. The results

show that the spectra are similar, not characterizing the decomposition of the polymer molecule and its chemical bonds.

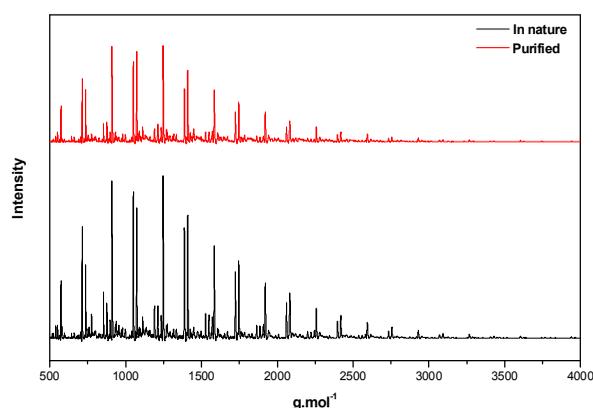


Fig. 5. MALDI-TOF results of the polyphenylphosphonate polymer in natura before and after purification route

The bands characteristic of polyphenylphosphonate are present in the spectra without being altered by the purification, which are located in the regions 1610, 1439,

1239–1320, and 921 cm^{-1} , corresponding to the presence of the C=O, P–C, P=O and P–O–C aromatic groups, respectively.^{23,25,27,28} In addition, it is possible to observe a change in bands of 686 and 583 cm^{-1} , corresponding to the P–Cl bond.^{15,29} Peaks pertaining to samples treated in this region are minimized, which corresponds to the reduction of this grouping in the polymer. Since the P–Cl group represents impurity in the sample, it can be said that the method was effective in removing impurities.

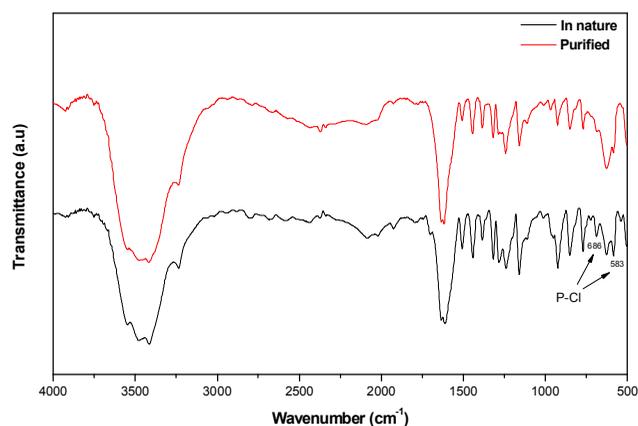


Fig. 6. FTIR results of the polyphenylphosphonate polymer in natura before and after the purification route, in the wave range of 4000–500 cm^{-1}

3.3.3. Thermal analyses

TGA analysis demonstrated that the polyphenylphosphonate polymer sample showed three bands

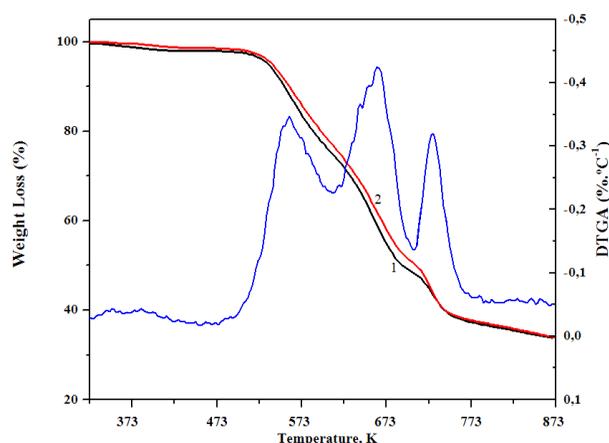


Fig. 7. TGA and DTGA results of the polyphenylphosphonate polymer in nature (1) and after the purification route (2)

4. Conclusions

A novel purification route for the polyphenylphosphonate containing 4,4'-dihydroxybenzophenone was proposed. The method can be applied without damage to

of mass loss (Fig. 7). The determined mass loss temperatures were 558, 662 and 728 K for both samples. By observing the thermogram, it can be seen that the bands of mass loss of the polyphenylphosphonate polymer were not significantly altered by the application of the purification route. However, it can be verified that the purified sample presented slightly better thermal stability than that in nature sample, characterized by the reduction of mass loss. The mass loss derivative (DTGA) represents the degradation temperature peaks, with the maximum degradation in the components being 662 K. The minimum degradation range of the polyphenylphosphonate polymer is above the working range used in the purification route. Thus, the temperature applied would not influence the structure of the molecule.

Fig. 8 shows the DSC thermogram of the polyphenylphosphonate polymer before and after the application of the purification route. The DSC results showed one glass transition temperature for both samples. From the thermogram, it can be seen that the determined glass transition temperatures were about 338 K. This result is very similar to that found by Domingui *et al.*,³⁰ who synthesized a polyphosphate polymer with bisphenol (BHBF) and dichloride of phenylphosphonic (PPDC); the authors identified a vitreous transition temperature for this polymer about 339 K. It can be seen also that the polymer melting temperature is about 475 K for both samples, before and after the purification steps. Thus, it is significant to say that the result obtained after the purification route was satisfactory, not degrading the polymer molecule.

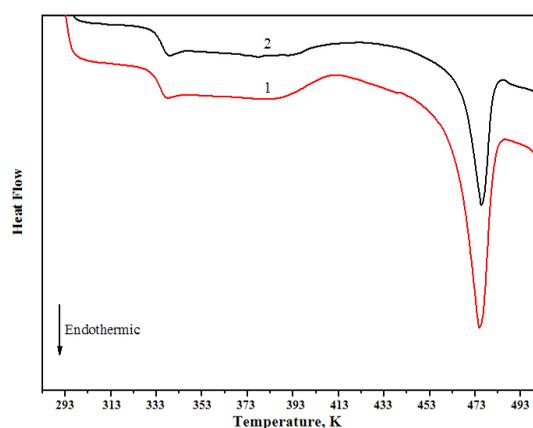


Fig. 8. DSC results of the polyphenylphosphonate polymer in nature (1) and after purification route (2)

the polymer. Removal of impurities is observed through the FTIR, MALDI-TOF, TGA and DSC spectra associated with the conductivity, chlorides, sodium and solids results. The FTIR spectrum clearly shows the reduction of the P–Cl group, an impurity in the final

product of synthesis. In addition, the sub-product from the organic extraction stage has characteristics similar to the 4,4'-dihydroxybenzophenone monomer. The FTIR spectrum presented the bands characteristic of the clusters present in 4,4'-dihydroxybenzophenone. The applied route allowed the purification of the polyphenylphosphonate, without damage to the molecule, besides recovering the DHPB reagent, which contributes to increase in the efficiency of the final product and reduces the environmental impact.

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ПРИГОТУВАННЯ ТА ОЧИЩЕННЯ АНТИПІРЕНУ – ПОЛІФЕНІЛФОСФОНАТУ, ЩО МІСТИТЬ 4,4'-ДИГІДРОКСИБЕНЗОФЕНОН

Анотація. Поліфенілфосфонат, що містить 4,4'-дигідроксибензофенон, синтезований як антипірен. Виявлено домішки, які можуть погіршити його властивості та термостійкість. Запропоновано очищення на основі екстракції води та гексану, внаслідок якого домішки, особливо P-Cl групи, успішно видалені без пошкодження полімеру.

Ключові слова: поліфенілфосфонат, антипірен, очищення, водна екстракція, органічна екстракція.