

Synthesis and Characterization of 4-(2-hydroxyphenoxy) phthalic nitrile

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Abstract. 4-(2-hydroxyphenoxy) phthalic nitrile was prepared by the nucleophilic substitution reaction of catechol and 4-nitro phthalic nitrile in DMF with the existence of N₂ and K₂CO₃. The optimal reaction conditions were obtained as follows: the mole ratio of catechol, K₂CO₃ and 4-nitro phthalic nitrile is 2:1:1, with the quality of the solute concentration of 0.222g/mL and reaction temperature 80°C. Consequently, the yield of final product reached 87.64%, and the structure of the 4-(2-hydroxyphenoxy) phthalic nitrile was characterized by IR, ¹H NMR and DSC.

1. Introduction

With the development of aerospace industry, the high-temperature resistant resin matrix composites have attracted a lot of attentions owing to their promising applications in aerospace manufacturing. Among the wide range of high-temperature resistant resin matrix composites, nitrile resin matrix composites, which possess excellent mechanical property, high-temperature resistance, abrasion resistance, flame resistance and high char yield, are widely applied in the preparation of new-style equipment [1-2]. Therefore, many researchers [3-11] have focused on their research of phthalic nitrile. Besides, a lot of researches [12-15] showed that phenol hydroxyl could improve the self-catalyzed property of phthalic nitrile monomer. However, at present, many researches about this resin monomer are mainly at the stage of laboratory research. One important reason is the lack of basic data for extensive industrial application. In this paper, we used the catechol and 4-nitro phthalic nitrile to synthesize 4-(2-hydroxyphenoxy) phthalic nitrile, and the structure was characterized by ¹H-NMR and FTIR. DSC was used to confirm self-catalyzed polymerization behavior. And synthesis process has been carefully investigated, in order to provide basic data for massive industrial production.

2. Experiment

2.1. Materials

Catechol (AR) was obtained from Chinese Medicine Group Co. Ltd. Potassium carbonate (AR) by grinding was calcinated for 5 hours in the muffle furnace after 500°C. 4-Nitro phthalic nitrile (AR) was bought from Shanghai XIYA Chemical. Co. Ltd. N, N-Dimethyl formamide (DMF, AR) and dimethyl sulfoxide (DMSO, AR) were obtained from Tianjin HengXing Chemical Reagent Co. Ltd, and dried for at least a month with activated A4 molecular sieve.



2.2. Characterization

Solution proton nuclear magnetic resonance (^1H NMR) spectra were recorded on an Agilent DD2 400-MR spectrometer using DMSO- d_6 and CDCl_3 as solvents with respect to tetramethylsilane as the internal standard.

For APN and HPN, Fourier transform infrared spectra (FTIR) were recorded with a PerkinElmer Spectrum TWO spectrometer in the solid state as KBr pellets. FTIR spectra of curing APN and HPN were also recorded every 2 min on the same instrument through the infrared reflectance mode with a heating furnace at a heating rate of 2°C min^{-1} .

DSC diagrams were recorded on a Mettler–Toledo DSC1 STAR System (Zurich, Switzerland) at different heating rates under nitrogen at a flow rate of 40 mL min^{-1} .

2.3. Synthesis of 4-(2-hydroxyphenoxy) phthalic nitrile

In the first stage, catechol (2.20g, 0.02mol), K_2CO_3 (1.38g, 0.01mol) and DMF (15mL) were added to a 50 mL two-necked flask to form a uniform solution by magnetic stirring at 80°C for 4h with the protection of nitrogen. In the following stage, 4-nitro phthalic nitrile was added into the mixture when the solution cooled down to ambient temperature, and kept stirring at 80°C for 5h. Next, the reaction liquid was filtered after the reaction stopped and its volume was measured with measuring cylinder. Then, 12mL filtrate was dissolved into 60mL water, and extracted 3 times with 30mL ethyl acetate each time. Finally, ethyl acetate was evaporated and 4-(2-hydroxyphenoxy) phthalic nitrile was separated from the mixture through the silica gel column, and the volume ratio of eluent (petroleum ether/ethyl acetate) is 1/0.24. The as-obtained 4-(2-hydroxyphenoxy) phthalic nitrile was dried in vacuum at 70°C for 3 days. In the last stage, final product was weighed with analytical balance to calculate the product yield.

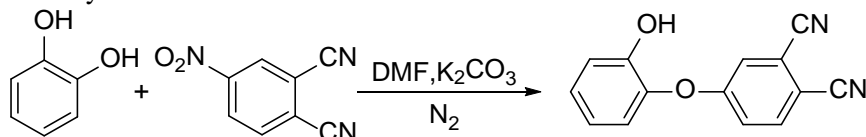


Figure 1. Synthesis of 4-(2-hydroxyphenoxy) phthalic nitrile

3. Results and discussion

3.1. The optimal time of reaction

Different reaction conditions, especially different temperatures, always leads to different reaction time. During this reaction, a moderate condition can result in a relatively short reaction time. To acquire maximum yield of 4-(2-hydroxyphenoxy) phthalic nitrile, the optimal reaction time should be adopted. The product and reactants of the reaction are all sorts of aromatic ramification, which own the hallmark of the obvious sample points by TLC in the UV camera analyzer, and can be beneficial to determine the optimal reaction time.

During the reaction, 0.1 mL reaction media was transformed to the centrifuge tube with pipette every 0.5 h after the 4-nitro phthalic nitrile was added. Subsequently, 200 times diluted reaction media was obtained by diluting the pristine reaction media with ethyl acetate. A certain amount of the diluent was put on the thin-layer plate by capillary glass and plate was put into the UV camera analyzer to compare the color of the product at every time point. The deepest color represent the optimal reaction time. The optimal reaction times at each temperature are shown in Table 1.

Table 1. The optimal reaction times at each temperature

| Temperature/ $^\circ\text{C}$ | 40 | 50 | 80 |
|-------------------------------|----|----|----|
| Reaction time/h | 14 | 12 | 5 |

An apparent decrease of the reaction time can be observed from 50 °C to 80 °C. Temperature plays a vital role in nitro nucleophilic substitution. Wang et al [16], found that the nitro nucleophilic substitution is limited when the temperature is lower than 60 °C. Thus, the effects caused by other factors can be carefully investigated at the optimal reaction time in different temperatures.

3.2. The effect of temperature on production yield

To research the effect of temperature on production yield, all the reactions shared the same reaction condition. The moles ratio of catechol, K_2CO_3 and 4-nitro phthalic nitrile is 2:1:1 (the moles amount of catechol is 0.02), and solvent was DMSO. The first step took 4 hours, after adding 4-nitro phthalic nitrile, and the reaction time was determined by different temperatures (14 h at 40 °C, 12 h at 50 °C, and 5 h at 80 °C).

Table 2. The effect of temperature on yield

| Temperature/°C | 40 | 50 | 80 |
|----------------|-------|-------|-------|
| Yield/% | 65.22 | 70.31 | 72.04 |

As is shown in table 2, the yield increase with the increase of the reaction temperature. The yields between 50 °C and 80 °C only show negligible difference, but the reaction cost more time at 50 °C. Though there are more by-products at 80 °C, they did not affect the purification of the target product in the post-treatment process. Thus, 80 °C is chosen as the optimal temperature.

3.3. The effect of the moles ratio among different ingredients on the yield

According to the above experimental results, the condition (80 °C, 4h+5h) was fixed to research the effect of the moles ratio among different ingredients on the yield. The experimental condition is as follows: The reaction temperature is 80 °C for 5 h, and the solvent is DMSO (15 ml), the moles amount of 4-nitro phthalic nitrile is 0.01. The moles ratios of catechol, K_2CO_3 and 4-nitro phthalic nitrile are shown in table 3.

Table 3. The effect of the moles ratio among ingredients on the yield

| the moles ratio among ingredients | 1.0:1:1 | 1.5:1:1 | 2:1:1 |
|-----------------------------------|---------|---------|-------|
| Yield/% | 44.36 | 59.34 | 72.04 |

Table 3 shows the effect of the moles ratio among ingredients on the yield of final product, and the yield increases with the increase of the moles ratio. The increment of catechol can increase the concentration of negative ions, which can promote the nucleophilic substitution as well as the final yield. Although the increased catechol in original reaction liquid can be redundant in final liquid, the redundant catechol can be recycled during the post-treatments. Thus, the optimal moles ratio among catechol, K_2CO_3 and 4-nitro phthalic nitrile is 2:1:1.

3.4. The effect of solvent on the yield

As dipolar aprotic solvents, DMF and DMSO can promote the nucleophilic. The negative poles of polar groups of DMF and DMSO are both related to O^- (C^+-O^- of DMF and S^+-O^- of DMSO) and have no steric hindrance. However, the steric hindrance of positive poles of DMF and DMSO is bigger than that of negative poles. Consequently, the nucleophilic ability of the anions is enhanced by the preferential solvation.

The nucleophilic ability of reagent with negative charge is better than that of conjugate acid counterparts. Therefore, the K^+ of K_2CO_3 substituted the H^+ of the hydroxyl in the catechol. The stable anions were produced with the effect of the dipolar aprotic solvent. The 4-(2-hydroxyphenoxy) phthalic nitrile was obtained by nucleophilic substitution in the stable anions and 4-nitro phthalic nitrile.

According to the research results above, to study the effect of solvent on the yield, the reaction condition is optimal when the moles ratio between different ingredients is 2:1:1, with the reaction temperature 80 °C. The effects of different solvents on the yield are shown in table 4.

Table 4. The effect of solvent to the yield

| solvent | DMF | DMSO |
|---------|-------|-------|
| Yield/% | 80.82 | 72.04 |

It can be easily found that, when utilizing DMF as solvent, the yield is 8% higher than that of DMSO. This is because the electronic ability of $-\text{NH}_2$ of DMF is better than that of $-\text{CH}_3$ of DMSO, and the increase of electronic ability impairs the solvation between the positive poles of polar groups and anions, and enhances the nucleophilic ability of anions. Thus, DMF was selected as solvent to research the effect of volume of solvent on the yield.

3.5. The effect of solvent amount on yield

In the final stage, the effect of solvent amount on yield was carefully investigated. Four dissimilar solvent amounts, 17.7 mL, 15.0 mL, 13.3 mL and 11.8 mL (corresponding to 0.222 g/mL, 0.262 g/mL, 0.295 g/mL, 0.333 g/mL), were utilized.

Table 5. The effect of solvent amount on yield

| solvent amount/mL | 17.7 | 15.0 | 13.3 | 11.8 |
|-------------------|-------|-------|-------|-------|
| Yield/% | 87.64 | 80.82 | 68.93 | 66.32 |

According to table 5, more the dosage of solvent is, the higher final yield is. When the mass concentration is 0.222 g/ml, the yield reaches to its peak 87.64%. DMF and water are miscible, so, the DMF solution dissolves a bit products. In the post-processing, water was added to precipitate the products. If the DMF amount is increased, more of the products are dissolved, and the yield decreases. So, 0.222 g/ml is chosen to be the optimal mass concentration.

3.6. Analysis of products

The products were characterized by ^1H -NMR and FTIR.

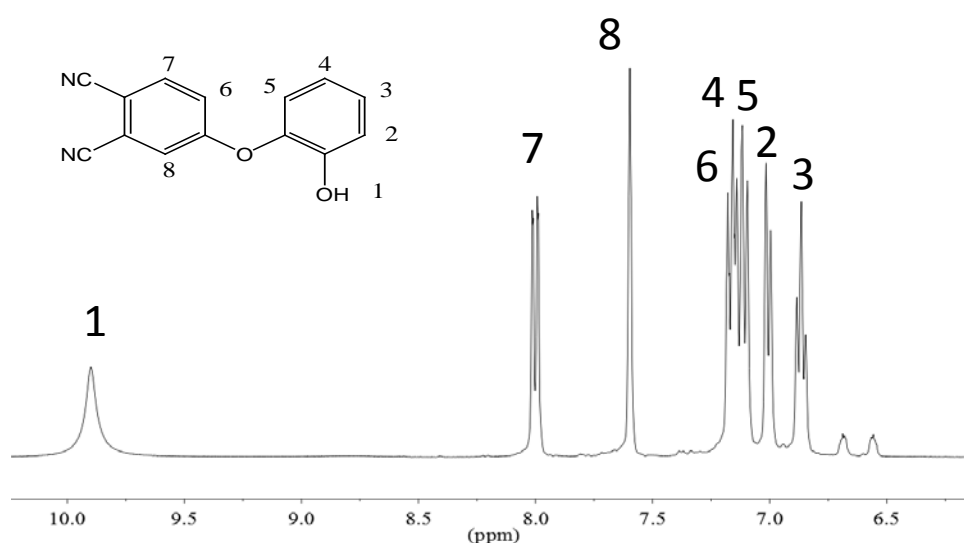


Figure 1. ^1H -NMR spectra of 4-(2-hydroxyphenoxy) phthalic nitrile

Figure 1 shows $^1\text{H-NMR}$ spectra of 4-(2-hydroxyphenoxy) phthalic nitrile. According to the chemical shift values, the phenol hydroxyl protons appeared at 9.90 ppm, the aromatic protons appeared as multiple at 6.87-8.00 ppm. The results indicated the successful synthesis of 4-(2-hydroxyphenoxy) phthalic nitrile.

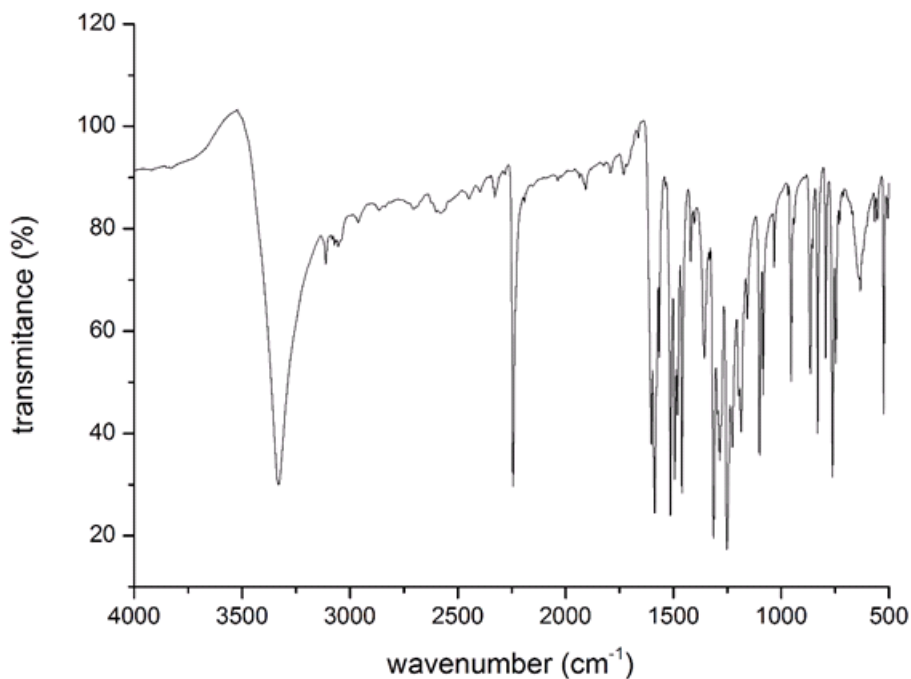


Figure 2. FTIR spectra of 4-(2-hydroxyphenoxy) phthalic nitrile

Figure 2 presents FTIR spectra of 4-(2-hydroxyphenoxy) phthalic nitrile. The peak at 3331 cm^{-1} was characteristic of the phenols, the peak at 2244 cm^{-1} was characteristic of the cyano, the peaks at 1586 cm^{-1} , 1513 cm^{-1} , 1494 cm^{-1} and 1460 cm^{-1} were characteristic of the benzene ring, the peak at 1252 cm^{-1} was characteristic of the asymmetrical vibrations of the aromatic ether, the peaks at 747 cm^{-1} , 762 cm^{-1} , 794 cm^{-1} , 831 cm^{-1} , 864 cm^{-1} and 867 cm^{-1} were characteristic of the out-of-plane C-H stretching. The characterization of FTIR proves the structure of 4-(2-hydroxyphenoxy) phthalic nitrile.

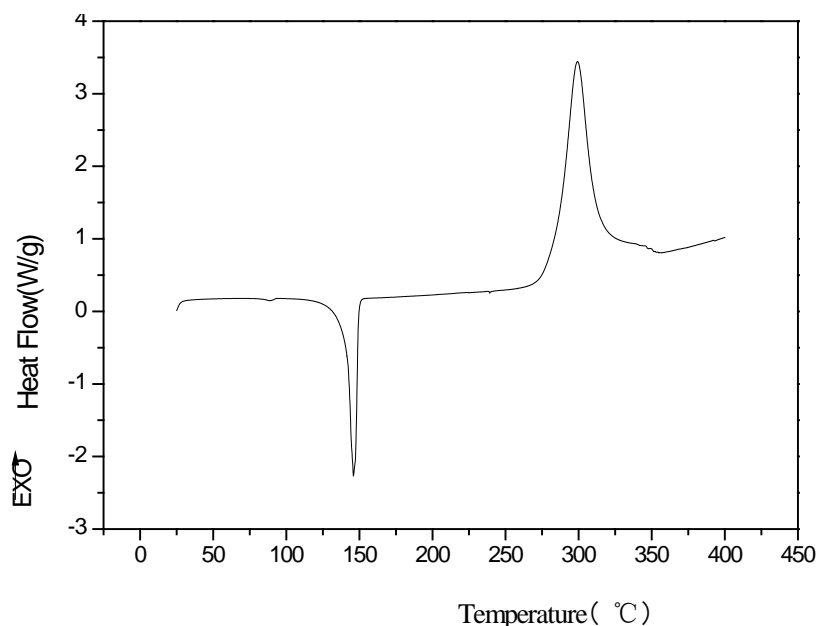


Figure 3. DSC curve of 4-(2-hydroxyphenoxy) phthalic nitrile

Figure 3 shows the nonisothermal DSC thermogram of 4-(2-hydroxyphenoxy) phthalic nitrile. There is a sharp endothermic peak at 146°C, and it is considered to be the melt peak of 4-(2-hydroxyphenoxy) phthalic nitrile. And the products are considered to have high-purity due to the narrow peak. A broad exothermic peak can be observed at 299°C. It is considered to be caused by curing behavior. There is no curing agent in 4-(2-hydroxyphenoxy) phthalic nitrile, so, the result indicates that 4-(2-hydroxyphenoxy) phthalic nitrile has excellent performance of self-catalysis.

4. Conclusion

The final product, after characterized by FTIR and $^1\text{H-NMR}$, can be confirmed to be 4-(2-hydroxyphenoxy) phthalic nitrile. Simultaneously, it shows outstanding self-catalyzed performance according to DSC. After a rigorous study, the optimal reaction condition can be determined: the moles ratio among catechol, K_2CO_3 and 4-nitro phthalic nitrile is 2:1:1, with the quality of the DMF concentration of 0.222 g/mL and reaction temperature 80°C, and the final yield reaches to 87.64%.

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