The Synthesis and Characterization of Tetrakis [(p – amino phenoxy) methyl] methane

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Abstract. In order to solve the shortcomings of the cured epoxy resin poor toughness, this paper proceeded from the structural design of curing agent to synthesize a special curing agent tetrakis [(p-aminophenoxy) methyl] methane which containing both Benzene ring and amino group. A Symmetric compound of tetrakis [(p-acetamidophenoxy) methyl] methane was prepared by using simple and easy to get pentaerythritoltetrasylate and acetaminophen for raw materials, after Williamson etherification reaction intermediates for synthesis of a symmetrical structure of the compound tetrakis [(p-acetamido phenoxy) methyl] methane, then hydrolysed under acidic conditions it can be tetrakis [(p-amino phenoxy) methyl] methane. The influence of reaction time, reaction temperature and reactant ratio to production yield of tetrakis [(p - acetamidophenoxy) methyl] methane was studied by orthogonal experiment of three factors and three levels, and get the optimal process parameters: the reaction time: 16 h, the reaction temperature: 170 °C, reactant ratio, 1:5. The Structure of tetrakis [(p - acetamidophenoxy) methyl] methane and tetrakis [(p-amino phenoxy) methyl] methane were characterized by infrared and 1H-NMR.

1. Introduction

Pentaerythritol and its derivatives is a compound with symmetrical structure, this special structure makes these compounds to construct complex molecules and supramolecular compounds starting point, in particular, it offers attractive Intermolecular interaction of multiple sites that can be connected to form compounds in complex networks of the Association Center1-3. Pentaerythritol and its derivatives have a wide range of applications in biology and medicine, materials science and catalysts. Pentaerythritol tetra phenyl ether is a pentaerythritol as the core of the four-arm compound, thanks to the special structure of such compounds, more and more researchers introduce special functional groups from the molecular design and synthesis series of different physical and chemical properties of macromolecules to meet the needs of industrial applications4,5 . In order to solve the poor toughness of epoxy resin cured products, this paper, from the design of curing agent structure, synthesizes a special curing agent tetrakis [(p-aminophenoxy) methyl] methane which containing both benzene ring and amino group6,7. Through check out large literature, the synthesis method of tetrakis [(p-aminophenoxy) methyl] methane has had reported, p-nitro phenol and pentaerythritol tetra benzene sulfonate were first
reacted under basic conditions to give tetrakis \([p{-}nitrophenoxy] \) methyl methane, and then tetrakis \([p{-}nitrophenox y] \) methyl methane is catalytically hydrogenated to give tetrakis \([p{-}aminophen oxy] \) methyl methane, but from the aspect of safety, economy, simplicity of operation, this synthesis is not so satisfactory \(^8{10}\). Therefore, in this paper, acetaminophen is used instead of p-nitro phenol and pentaerythritol tetra benzene sulfonate to obtain tetrakis \([p{-}acetamidophen oxy] \) methyl methane, and then hydrolysed under the condition of raced to get tetrakis \([p{-}aminophen oxy] \) methyl methane\(^{11,12}\). This method is more simple and safe than the former, while the synthesis of intermediate tetrakis \([p{-}acetamidophen ox y] \) methyl methane is particularly important. In this paper, orthogonal experiments were carried out to study the optimum conditions for the preparation of tetrakis \([p{-}acetamidophen oxy] \) methyl methane with pentaerythritol tetra benzenesulfonate and acetaminopen\(^{13,14}\).

2. Experimental

2.1 Reagents and Instruments

Pentaerythritol, Sino pharm Group Chemical Reagent Co., Ltd., chemical pure; benzene sulfonyl chloride, Tianjin Daomao Chemical Reagent Factory, Analytical pure; Pyridine, Tianjin Daomao Chemical Reagent Factory, Analytical Pure; Acetaminophen, Shanghai Aladdin Limited Liability Company, chemical pure; ethanol, Tianjin Kemei Ou Chemical Reagent Co., Ltd., analytical pure; sodium hydroxide, Tianjin Bodt Chemical Co., Ltd., analytical pure.

DF-101S collector temperature heating magnetic stirrer, Gongyi City to China Instrument Co., Ltd.; XT5 micro-melting point detector, Beijing Branch instrument electro-optical instrument factory; Fourier transform infrared spectrometer, Perkin Elmer; nuclear magnetic resonance spectrometer, Germany Bruker.

2.2 Synthetic Principle of Tetrakis \([p{-}aminophen oxy] \) methyl methane

The synthesis of intermediate tetrakis \([p{-}acetyl-amino phenoxy] \) methyl methane is similar to the Williamson ether synthesis reaction principles, the Williamson etherification reaction is the substitution of the hydrogen atom of the hydroxyl group in the alcohol or phenolic molecule by an alkyl or aryl group Etherification or phenolic etherification. The reaction of tetrakis \([p{-}acetamidophen oxy] \) methyl methane is carried out by reacting the phenol with a salt under alkaline conditions to form a phenate anion, salts anion as the nucleophile and the alkyl halide or sulfonate SN2 Nucleophilic substitution reactions occurred. Tetrakis \([p{-}acetyl-amino phenoxy] \) methyl methane was hydrolysed under acidic conditions to give tetrakis \([p{-}aminophen oxy] \) methyl methane, and the total amount of tetrakis the reaction is shown in Figure 1:

![Figure 1. The synthesis equation of Tetrakis \([4{-}acetamidophen oxy] \) methyl methane](image-url)
2.3 Synthesis of Pentaerythritol Tetra benzene Sulfonate

Into a 250ml round-bottomed flask were added 4.36g Pentaerythritol, 20 mL pyridine, 20 ml of benzene sulfonyl chloride was continuously added dropwise while stirring, the dropping rate was controlled and the reaction temperature was controlled below 35 °C, after completion of the dropwise addition, the temperature was raised to 40 °C and the reaction was stirred for 3 h. After the reaction, the product of the three-necked flask was poured into a large beaker containing 30 mL hydrochloric acid, 33 mL ice water and 67 mL methanol mixed solution in a timely manner, stirred and allowed to stand for sedimentation and filtration. Then configure a volume of acetone and ethanol mixed solution to filter crystals obtained from recrystallization, where v (acetone): v (alcohol-free) =1:4, continued to filter, oven drying at 70 °C, get 19.3 g of white powder, yields 85.3%, melting point 99-101 °C.

2.4 Synthesis of Tetrakis [(p- acetamidophenoxy) methyl] methane

In the 250 mL flask three by adding a certain amount of acetaminophen and sodiumhydroxide, ethanol as the solvent of the measured amount of dry, In a 250 mL three-necked flask were added a certain amount of acetaminophen and sodium hydroxide, dry ethanol was measured amount as the solvent. The reaction mixture was stirred and heated for 1h at 60 °C, then add the appropriate amount of pentaerythritol tetra benzenesulfonate, heated to 150 °C above the reaction for a certain time.

2.5 Synthesis of Tetrakis [(p- aminophenoxy) methyl] methane

The prepared tetrakis (p-acetamidophenoxoxy) methyl] methylene crystals were poured into a three-necked flask, 20 ml of glacial acetic acid and 10 ml of 8 mol / L hydrochloric acid were added, the reaction mixture was heated 100 ° C under stirring and refluxing for 10 h. When the reaction is complete, remove device, cooling the solution to room temperature, configure the 10mol/L concentration of NaOH solution, the solution is titrated until the solution is neutral. Stand to precipitation filter and then get tetrakis [(p-amino phenoxy) methyl] methane.

2.6 Tetrakis [(p-acetyl-amino phenoxy) methyl] methane Analysis Method

Melting point testing: XT-5 binocular microscope melting point Tester, according to JJG 701-2 008 "melting point Analyser verification regulation of" determination of melting point.

FT-IR: with potassium bromide Tablet method, Fourier transform infrared spectrometer Perkin Elmer (USA) was tested on, scanning range of 400~4 000 cm⁻¹.

Nuclear testing: using deuterated DMSO as solvent and TMS as internal standard, tested on Agilent 400 MR nuclear magnetic resonance spectrometer analysis.

3. Analysis and Discussion

3.1 FT-IR Analysis of Tetrakis [(p-acetyl amino phenoxy) methyl] methane

Figure 2 is an infrared spectrum of tetrakis [(p-acetamidophenoxoxy) methyl] methane in which 3 297 cm⁻¹ is attributed to the stretching vibration of NH, and 1 659 cm⁻¹ is attributed to the stretching vibration of C = O, Thereby indicating the presence of the amide bond. 1 609 cm⁻¹ and 1 512 cm⁻¹ attributed to the skeleton vibration absorption peak of the benzene ring proved the presence of benzene ring. 2 959 cm⁻¹, 2 922 cm⁻¹ and 2 868 cm⁻¹, belonging to the telomeric vibration of methyl methylene; 1 232 cm⁻¹ is the characteristic absorption peak of Ar-O; 831 cm⁻¹ P-Substitution of the benzene ring. By comparing the spectra with the groups in the structural formula of tetrakis [(p-acetamidophenoxoxy) methyl] methane, it is basically determined that the functional groups represented by the characteristic peaks on the spectrum are tetrakis [(p-acetamidophenoxoxy Base) methyl] methane.
3.2 Analysis of Nuclear Magnetic Spectrometry of Tetrakis [(p-acetamidophenoxy) methyl] Methane

Figure 3 is a Tetrakis [(p-acetyl-amino phenoxy) methyl] hydrogen nuclear magnetic resonance spectra of methane, molecule solvents using deuterated dimethyl sulfoxide (DMSO), analysis is shown in table 1, The integrated area ratios of absorption peaks 1 to 5 coincide with the number of H at the corresponding positions in the molecular structure of tetrakis [(p-acetamidophenoxy) methyl] methane, and there are 1H NMR (400 MHz, dmso) δ 9.73 (s (P, 1H), 7.41 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 4.17 (s, 2H), 1.96 (s, 3H) which Prove that the resulting material is tetrakis [(p-acetamidophenoxy) methyl] methane.

Table 1. The chemical shifts of H atoms of Tetrakis [(4 - acetamidophenoxy) methyl] methane in 1H-NMR

| Serial | δ     | Number of H | Peak area |
|--------|-------|-------------|-----------|
| 1      | 9.73  | 1           | 0.29      |
| 2      | 7.41  | 2           | 0.59      |
| 3      | 6.87  | 2           | 0.59      |
| 4      | 4.17  | 2           | 0.54      |
| 5      | 1.98  | 3           | 1.00      |

Figure 3. 1H-NMR of Tetrakis [(4 - acetamidophenoxy) methyl] methane
### 3.3 FT-IR Characterization of Tetrakis \([p\text{-aminophenoxy} \text{ methyl}] \text{ methane}\)

![FT-IR Characterization of Tetrakis \([p\text{-aminophenoxy} \text{ methyl}] \text{ methane}\)](image)

**Figure 4.** The infrared figure of Tetrakis \([(4\text{-aminophenoxy}) \text{ methyl}] \text{ methane}\)

The characteristic peaks are shown in the following table:

| Absorb position (cm\(^{-1}\)) | Attribution statement       |
|-------------------------------|-----------------------------|
| 3436, 3352                    | -NH\(_2\)-stretching vibration |
| 1627                          | N-H in-plane bending vibration |
| 1585, 1511                    | Benzene ring C = C stretching vibration |
| 1233                          | Ar-O                        |
| 2934, 2883, 1384              | -CH\(_2\)-stretching vibration |
| 832                           | p-substitution of the benzene ring |

The absorption peak of primary amine NH stretching vibration at 3436, 3352 cm\(^{-1}\), the in-plane bending vibration absorption peak of NH on primary amine at 1627 cm\(^{-1}\); 2934, 2883 and 1384 cm\(^{-1}\) are attributed to the stretching vibration absorption peak of methylene CH, And 1585, 1511 is the skeleton vibration peak of benzene ring, 832 cm\(^{-1}\) is the para substitution of benzene ring, 1233 cm\(^{-1}\) is Ar-O vibration absorption peak. It can be seen that the characteristic peaks of tetrakis [(p-aminophenoxy) methyl] methane can be found in the infrared map.

### 3.4 Nuclear Characterization of Tetrakis \([(p\text{-aminophenoxy}) \text{ methyl}] \text{ methane}\)

Figure 5 shows the NMR spectra of the tetrakis \([(p\text{-aminophenoxy}) \text{ methyl}] \text{ methane molecules, solvent used deuterium generation two methyl Asia sulfone (DMSO), analysis as table 2-9 by shows, absorption peak 1 to 4 of points area ratio and tetrakis \([(p\text{-aminophenoxy}) \text{ methyl}] \text{ methane molecular structure in the corresponding location Shang h of number anastomosis, proved proceeds material for tetrakis \([(p\text{-aminophenoxy}) \text{ methyl}] \text{ methane.} \)

| Serial number | 1    | 2    | 3    | 4    | 5    | 6    |
|---------------|------|------|------|------|------|------|
| Chemical shift| 4.59 | 6.43 | 6.65 | 4.03 | 3.33 | 2.48 |
| Number of H   | 2    | 2    | 2    | 2    | water| DeuteriumDMSO |
| Peak area     | 1.00 | 0.98 | 1.03 | 1.05 |      |      |
3.5 Discussion on Influencing Factors of Synthesis Reaction

Orthogonal experiment is a highly efficient, fast and economical research multi-factor and multi-level design method. As the synthesis of intermediates has a decisive effect on the yield of the final product, the yield of tetrakis (p-acetamidophenoxy) methyl] methane is taken as an index by orthogonal test. The reaction time, Reaction temperature, and reaction product feed ratio of three factors are preferred, the choice of L9 (3^3) for orthogonal experiments, the impact of factors were shown in Table 1.

**Table 4.** The levers of impact factors to the synthesis reaction of Tetrakis [(4 - acetamidophenoxy) methyl] methane

| level | Reaction time /h | Reaction temperature /℃ | n(pentaerythritoltetrasylate):n (acetaminophen) |
|-------|------------------|--------------------------|-----------------------------------------------|
| 1     | 12               | 160                      | 1:4                                           |
| 2     | 16               | 170                      | 1:5                                           |
| 3     | 20               | 180                      | 1:6                                           |

Orthogonal table was shown below:

**Table 5.** The preparation process of Tetrakis [(4 - acetamidophenoxy) methyl] methane by orthogonal design

| Serial number | Reaction time /h | Reaction temperature /℃ | n(pentaerythritoltetrasylate):n (acetaminophen) | Yield/% |
|---------------|------------------|--------------------------|-----------------------------------------------|---------|
| 1             | 12               | 160                      | 1:4                                           | 55.2    |
| 2             | 12               | 170                      | 1:5                                           | 66.3    |
| 3             | 12               | 180                      | 1:6                                           | 64.6    |
| 4             | 16               | 160                      | 1:5                                           | 74.2    |
| 5             | 16               | 170                      | 1:6                                           | 71.8    |
| 6             | 16               | 180                      | 1:4                                           | 57.5    |
| 7             | 20               | 160                      | 1:6                                           | 66.8    |
| 8  | 20  | 170 | 1:4   | 62.3 |
|----|-----|-----|-------|------|
| 9  | 20  | 180 | 1:5   | 63.6 |
| K1 | 186.1 | 196.2 | 175.0 |
| K2 | 203.5 | 200.4 | 204.1 |
| K3 | 192.7 | 185.7 | 203.2 |
| k1 | 62.01 | 65.4  | 58.3  |
| k2 | 67.8  | 66.8  | 68.0  |
| k3 | 64.2  | 61.9  | 67.7  |
| R  | 5.7  | 4.9  | 9.7   |

Primary and secondary order: C>A>B

Excellent level:
- A2
- B2
- C2

Excellent combination: A2 B2 C2

From the above calculation and analysis, we can see that the reaction ratio has the greatest influence on the experiment, which is the main influencing factor and the reaction temperature is not important factor. The optimal level is A2B2C2, that is, the reaction time is 16 h, the reaction temperature is 170 °C, the ratio of reactants was 1:5, and the reaction was carried out according to the optimum synthesis conditions. The yield of the product was 76.2%, which was higher than that of the fourth group, so that the reaction of tetrakis (p-acetamidophenoxy) methyl methane was The optimum reaction time was 16 h, the reaction temperature was 170 °C, and the reaction ratio was 1:5.

4. Conclusion

(1) The experiment was carried out by L9 (33) orthogonal experiment. The results showed that the reaction ratio had the greatest effect on the synthesis of tetrakis (p-acetamidophenoxy) methyl methane, and the reaction temperature was unimportant. The optimum conditions for the synthesis of tetrakis [(p-acetamidophenoxy) methyl] methane were as follows: reaction temperature 170 °C, reaction molar ratio 1:5, reaction time 16 h, the yield was 76.2%.

(2) The FT-IR and NMR spectra of the obtained product were verified, and it was proved that the final product was tetrakis (p-aminophenoxy) methyl methane, which indicated that the synthetic route was feasible.

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References

[1] DOMINIC L, THIERRY M, JAMES D W. Molecular Tectonics. Porous hydrogen-bonded networks built from derivatives of pentaerythritoltetraphenyl ether [J]. Organic Chemistry. 2004, 69(6): 1776-1787

[2] WEI Y, SHAO Y. The improved synthesis of pentaerythritolTetramine [J].Energetic Materials, 2002, 10(2): 49-52.

[3] PENG Y L, LUO C, CHEN B G. Synthesis and structure characterization of 1, 3-dibromo-2, 2-bis (bromomethyl) propane [J]. Journal of Wuhan Institute of Technology, 2013, 35(7): 37-42.

[4] TANG X D, ZHANG Q Z, ZHOU Q F. Application of pentaerythritol and its derivatives in the synthesis of dendrimers [J]. Organic Chemistry, 2004, 24(6): 585-590.

[5] ZHANG H C, HaAO a Y, DU G Y, etal. Derivatives of pentaerythritol as the matrix of sugar
families with sugars dendritic molecules and application [J]. Organic Chemistry, 2008(9): 1515-1522.

[6] YANG Y F, TANG G P, CHENG H F, et al. Research progress of toughening epoxy resin [J]. Materials Review, 2010, 24(8): 85-88.

[7] LI J R. Synthesis, curing behavior and properties of a heat resistant curing agent with flexible unit [D]. Beijing University of Chemical Technology, 2013.

[8] DOMINIC L, THIERRY M, ERIC D, et al. Molecular Tectonics. Hydrogen-Bonded Networks Built from Tetra- and Hex anilines [J]. Crystal Growth & Design, 2005, 5(4): 1451-1456.

[9] LI G H. The Position of Different Substituents Star of Synthesis and Properties of Liquid Crystal Compounds [D]. Northeastern University, 2010.

[10] BACKER H J, DIJKEN G. Pentaerythritol thioethers [J]. View Issue, 1932, 51(3): 289-293.

[11] PETER A, HENDERSON and CORRIE T I. Methylene-linked liquid crystal dimers and the twist-bend nematic phase [J]. Liquid Crystals, 2011, 12(38): 1407–1414.

[12] WALTER A J, MICHAEL H. On nitro- and aminophenoxyacetic acids [J]. Chemical Society, 1917, 39(10): 2188-2224.

[13] Ashraf A, ABBAS, ADEL S G, et al. A convenient synthesis of thiamacrocyclic dilactams [J]. Heteroatom Chemistry, 2007, 18(3): 249-254.

[14] Wang M L, LEE Z F. Synthesis of novel multisite phase-transfer catalysts and their applications to the catalyzed reaction of bisphenol a and allyl bromide [J]. Industrial & Engineering Chemistry Research, 2006, 45(14): 4918-4926.

[15] SUNGGAK K, CHUNG K N, YANG S B, et al. Direct synthesis of ethers via zinc chloride mediated etherification of alcohols in dichloromethane [J]. Journal of Organic Chemistry. 1987, 52(17): 3917-3919.