Green Synthesis and Application of New Antioxidant 3052

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Abstract. A new synthetic antioxidant, 4-methyl-2-tert-butyl-6-(4-methyl-3-tert-butyl-2-hydroxybenzyl)phenyl acrylate (3052) was developed. Using solid phosgene as green acyl chloride reagent, DMF as initiator, acrylic acid and 2246 bisphenol as raw materials, two-component synthesis of antioxidant 4-methyl-2-tert-butyl-6-(4-methyl-3-tert-Butyl-2-hydroxybenzyl)phenyl ester. The experimental results show that under the optimized reaction conditions, the yield of 4-methyl-2-tert-butyl-6-(4-methyl-3-tert-butyl-2-hydroxybenzyl) phenyl ester is 85.6%. The purity is greater than 98%. The synthesis method has mild reaction conditions, short reaction time and high yield, and is 4-methyl-2-tert-butyl-6-(4-methyl-3-tert-butyl-2-hydroxybenzyl)phenyl ester. The synthesis of 3052 antioxidants provides a new approach.

1. Introduction

ABS resin is a copolymer of acrylonitrile (A)-butadiene (B)-styrene (C). It is a significant polymer material with high strength, good toughness and easy processing. The antioxidant as a kind of chemical auxiliaries plays an important role in the performance and quality improvement of ABS products in the production process of ABS resin [1-3]. When antioxidant is only present in a small amount in the ABS resin, it can delay or inhibit the oxidation process of the ABS resin, solving the problems of fading, yellowing, hardening, cracking, etc. Besides, it could maintain the mechanical properties, such as impact strength and elongation of the material, prevent ABS resin ages and prolong the service life of ABS resin. Therefore, antioxidants are also known as "anti-aging agents". There are many kinds of antioxidants, including phenols, phosphites, amines.

With the rapid development of the plastics industry, especially the continuous development and utilization of various new functional plastics, the global antioxidant industry is developing towards high molecular weight, multi-functionality and reactivity [4-6].

Bisphenol monoester antioxidant is a new variety of antioxidants. ABS resin with the antioxidant bisphenol monoester can significantly enhance the thermal oxidation resistance of the material. The bisphenol monoester antioxidant is synthesized by reacting bisphenol with an acid chloride under certain conditions to synthesize the target product. The industrialization process involves the acid chloride compound being volatile, irritating and difficult to store. So, the price is relatively expensive, which restricts the application of the bisphenol monoester antioxidant. The traditional methods for synthesizing acid chloride include phosphorus pentachloride method, phosphorus trichloride method, thionyl chloride method, carbon tetrachloride method, phosgene method, etc. After a large number of experimental studies and literature review, the experiment result is a method for preparing acryloyl chloride by a solid phosgene method [7-9].
There are two methods for preparing the antioxidant. In the first method, an organic acid and phosphorus oxychloride are synthesized into an acid chloride, and then an antioxidant is prepared from an acid chloride and a bisphenol. Or bisphenol, organic acid, phosphorus oxychloride and a reaction auxiliary are placed in a reaction vessel, heated and stirred for preparation of the antioxidant [10-11]. One obvious disadvantage is that the total product yield is low, but there are many by-products. The other method is a bisphenol monoester antioxidant prepared by using bisphenol, acid chloride and an organic base as raw materials. The acid chloride is volatile, irritating and difficult to store. It will absorb moisture when exposed to air, and produce a series of exhaust gas as well as waste liquid such as SO2 and H3PO4 in the course of use. Overall, acid chloride could seriously pollute the environment and has high requirements for equipment, it is not appropriate for industrial production. Therefore, the search for new synthetic methods or acylating reagents has good economic and social benefits.

2. Experimental part

2.1 Materials and reagents

Triethylamine, ethanol, dichloromethane, acrylic acid, the above drugs are of analytical grade (Tianjin Damao Chemical Reagent Company), bisphenol 2246 (Hubei Xinningtai Chemical Co., Ltd.), bis(trichloromethyl) carbonate (Shandong Botao Group Co., Ltd.)

2.2 Laboratory apparatus

DF-101S collector type constant temperature heating magnetic stirrer (Gongyi City Yuhua Instrument Co., Ltd.), AVATAR360 infrared spectrometer (KBr tablet, Nicolet), GC-9790II (Zhejiang Fuli Analytical Instrument Co., Ltd.), Varian-Mercury400 Superconducting nuclear magnetic resonance instrument (Bruker), CP-3800/SATURN2200 GC-MS (Varian).

2.3 Resolve resolution

In this paper, the cheaper and stable solid phosgene and acrylic acid are used as raw materials, and DMF is used as an initiator to synthesize an acid chloride reagent in one step. The acid chlorinating reagent is directly used for structural modification of bisphenol to monosubstituted bisphenol, and the synthetic route is as follows:

\[
\text{CH}_2=\text{CHCOOH} + \text{BTC} \rightarrow \text{CH}_2=\text{CHOCl}
\]

2.3.1 Synthesis of acryloyl chloride

A constant pressure dropping funnel and a spherical condenser were placed on a 250 mL dry three-necked flask, and a drying tube was attached to a spherical condenser. Acrylic acid (6.80 g, 0.05 mol) and solid phosgene (5.45 g, 0.0185 mol) were added to the flask. DMF (10 mL, 0.125 mol) was slowly added dropwise. After the dropwise addition was completed, the reaction was further stirred for 3 hours to obtain a colorless transparent liquid as acryloyl chloride. The yield was 80.8%, and the content of the product was 98% by gas chromatography.

2.3.2 Synthesis of Antioxidant 3052

Cooling the acryloyl chloride synthesized in 2.3.1 to room temperature. Firstly, adding 500 mL of dichloromethane, adding the acid triethylamine (10 mL, 0.125 mol), and stirring well. Then adding 2246 bisphenol (5.1 g, 0.07 mol). Mixing with 25 mL of dichloromethane, the process of addition lasted about 1 hour. After the addition was completed, the reaction was further stirred for 2 hours. After completion of the reaction, the reaction mixture was cooled to room temperature, and the precipitate was filtered, and the filtrate was evaporated to remove methylene chloride to give a crude
product of antioxidant 3052. Recrystallization from 95% ethanol, filtration and drying gave a white powder as the desired product antioxidant 3052. The yield was 85.6%, and the purity of the product was over 98% by liquid chromatography, and the product was characterized by melting point and \textit{1H-NMR}.

3. Results and discussion

3.1 The single-factor experiment of synthesis of acryloyl chloride

The process was optimized by a single-factor experiment, and the conditions of different solid phosgene initiator, feed molar ratio and reaction time were optimized.

3.1.1 Effect of different solid phosgene initiators on the yield of acryloyl chloride

The effect of different solid phosgene initiators triethylamine, pyridine and DMF on the yield of acryloyl chloride was investigated under the conditions of acid chloride reaction time of 3 hours and \( n \) (acrylic acid) : \( n \) (solid phosgene BTC) =1:0.37. The experimental results are shown in Table 1.

| Initiator       | Triethylamine | Pyridine | DMF  |
|-----------------|---------------|----------|------|
| Yield /%        | 60.2          | 69.8     | 75.9 |

The experimental results in Table 1 indicate that the acryloyl chloride process solid phosgene needs to be able to participate in the reaction under the action of a nucleophile. (Such as Triethylamine, pyridine and DMF etc.) Under the same conditions, DMF is used as the initiator, and the yield of acryloyl chloride is high. Therefore, it is suitable to select DMF as the solid phosgene initiator.

3.1.2 Effect of molar ratio of different materials on the yield of acryloyl chloride

The choice of DMF as the initiator, the acid chloride reaction time is the same as above, the amount of solid phosgene has a great influence on the reaction yield. The effect of the molar ratio of acrylic acid to solid phosgene on the yield of the target product was investigated. The experimental results are shown in Table 2.

| Mole ratio | 1: 0.3 | 1: 0.33 | 1: 0.36 | 1: 0.39 | 1: 0.42 |
|------------|--------|---------|---------|---------|---------|
| Yield /%   | 59.10  | 69.40   | 75.43   | 67.80   | 63.50   |

Note: The molar ratio is the ratio of the amount of acrylic acid to solid phosgene; the yield is in terms of acrylic acid.

The experimental results in Table 2 show that during the synthesis of acryloyl chloride, the yield of acryloyl chloride increases first and then decreases along with the increase of the amount of solid phosgene, and the molar ratio of acrylic acid to solid phosgene is 1:0.37, which is the point that the maximum yield is reached. This is because a slight excess of solid phosgene is beneficial to the reaction to proceed more fully, the yield increases. However, when the solid phosgene is excessively large, the excess solid phosgene will decompose more phosgene and increase the exhaust gas emissions. As a result, a molar ratio of acrylic acid to solid phosgene of 1:0.37 is most suitable.

3.1.3 Effect of Different Reaction Time on the Yield of Acryloyl Chloride

Under the conditions of the initiator and material molar ratio under the above-optimized conditions, the effect of the acid chloride reaction time on the yield of acryloyl chloride was investigated. The experimental results are shown in Table 3.

| Reaction time /h | 2    | 3    | 4    | 5    | 6    |
|------------------|------|------|------|------|------|
| Yield /%         | 57.2 | 73.8 | 71.3 | 72.1 | 70.5 |
It can be seen from Table 3 that the yield of acryloyl chloride tends to be balanced immediately after an increase in the acid chloride reaction time. Therefore, it is reasonable to select the acid chloride reaction time of 3 hours.

3.1.4 Analysis of acryloyl chloride by gas chromatography

The acryloyl chloride product obtained in the experiment was tested by gas chromatography internal standard method, as shown in Figure 1.

Reagents: ethyl acetate; aniline; N, N-Dimethylformamide; acryloyl chloride. Using the best synthetic process conditions: Column: 5% OV-17 glass packed column (3mm × 2m); Sampler temperature: 250 °C; Detector temperature: 210 °C; Temperature programmed: initial temperature 80 °C for 3 min, 10 min temperature to 220 °C for 5 min; detector: flame ionization detector; carrier gas is nitrogen.

3.2 The synthetic single-factor experiment of antioxidant 3052

The process was optimized by a single-factor experiment, and the conditions of different material molar ratio, reaction temperature and reaction time were optimized.

3.2.1 Effect of molar ratio of different materials on the yield of antioxidant 3052

Methylene chloride was added at a ratio of material to liquid of 1:5.3. The molar ratio (2246: acryloyl chloride) was 1:0.9, 1:1, 1:1.1, 1:1.2 at a fixed reaction temperature of 30 °C and a reaction time of 2 hours. The synthesis of 3052 was carried out at 1:1.3, and the yield was calculated. The experimental results are shown in Table 4.

| Mole ratio | 1:0.9 | 1:1 | 1:1.1 | 1:1.2 | 1:1.3 |
|------------|-------|-----|-------|-------|-------|
| Yield /%   | 44.5  | 71.8| 78.5  | 69.3  | 62.4  |

The experimental results show that when the reaction temperature and reaction time are constant, the yield of antioxidant 3052 increases first and then decreases along with the increase of molar ratio. The reason is that as the molar ratio increases, the degree of esterification of the system increases, and
the yield of the antioxidant 3052 increases accordingly. When the molar ratio reaches 1:1.1, the yield of the antioxidant 3052 reaches the highest value of 78.5%. The molar ratio continues to increase, the amount of HCl produced in the system increases, and the system changes from alkaline to acidic, affecting the degree of esterification.

3.2.2 Effect of different reaction temperatures on the yield of antioxidant 3052

The reaction temperature was set to 20 °C, 25 °C, 30 °C, 35 °C under the conditions of a fixed reaction time of 2 hours and a molar ratio of (2246: acryloyl chloride) 1:1.1. At 40 °C, synthesis of antioxidant 3052 was carried out, and the yield was calculated. The experimental results are shown in Table 5.

| Drop temperature / °C | 20  | 25  | 30  | 35  | 40  |
|-----------------------|-----|-----|-----|-----|-----|
| Yield /%              | 58.4| 64.3| 69.3| 72.3| 76.5|

The experimental results show that along with the increase of reaction temperature, the overall trend of antioxidant 3052 is increasing. As for the reason, the esterification reaction is a reverse reaction of the neutralization reaction which requires endotherm. Therefore, as the reaction temperature increases, the degree of esterification of the antioxidant 2246 increases, the conversion rate and yield of the antioxidant 3052 also increase. Since the boiling point of methylene chloride is 40 °C, we are currently exploring only 40 °C.

3.2.3 Effect of different reaction time on the yield of antioxidant 3052

The reaction time was set to 1.0 hour, 1.5 hours, 2.0 hours, 2.5 hours at a fixed reaction temperature of 40 °C and a molar ratio of (2246: acryloyl chloride) 1:1.1 at a solid-liquid ratio of 1:5.3. At 3.0 hours, synthetic antioxidant 3052 was carried out, and the yield was calculated. The experimental results are shown in Table 6.

| Reaction time /h | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|------------------|-----|-----|-----|-----|-----|
| Yield /%         | 65.2| 78.1| 82.5| 76.4| 70.9|

The experimental results show that along with the increase of reaction time, the yield of antioxidant 3052 increases first and then decreases. When the reaction time is 2 hours, the yield of 3052 is 82.5%. After that, the reaction time continues to increase, and the yield of antioxidant 3052 gradually decreases. The reason is that in the course of the reaction, along with many side reactions, the yield of side reactions and impurities increases with time.

3.2.4 $^1H$ NMR spectrum of antioxidant 3052

The nuclear magnetic resonance spectrum of the experimental product was tested, and the test results are shown in Figure 2. According to Figure 2, we can see: $^1H$ NMR (400 MHz, Chloroform-d) δ 7.09 (d, J = 2.2 Hz, 1H), 7.02 (d, J = 2.2 Hz, 1H), 6.81 (d, J = 2.2 Hz, 1H), 6.72 – 6.61 (m, 2H), 6.40 (dd, J = 17.3, 10.5 Hz, 1H), 6.13 – 6.03 (m, 1H), 5.26 (brs, 1H), 3.63 (d, J = 5.2 Hz, 2H), 2.27 (s, 3H), 2.20 (s, 3H), 1.37 (s, 9H), 1.34 (s, 9H). The product was confirmed to be an antioxidant 3052.
figure 2: $^1$H NMR spectrum of antioxidant 3052

4. Conclusion

(1) In this paper, acryloyl chloride was prepared by the one-step synthesis of solid phosgene with low temperature and room temperature and acrylic acid as raw material under the action of initiator DMF. The optimal synthesis conditions were as follows: reaction time was 3 hours, n (acrylic acid): n (Solid phosgene) = 1: 0.37, the initiator was DMF.

(2) The acryloyl chloride was directly applied to the bisphenol antioxidant 2246 to obtain a novel antioxidant 3052. The optimal synthesis conditions were as follows: reaction time was 2 hours, n (antioxidant 2246): n (acryloyl chloride) = 1: 1.1, the reaction temperature was 40 °C.

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