Facile Preparation of a Macromolecular Benzophenone Photoinitiator

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Abstract. Photoinitiators play important roles in the preparation of photo-cured resins. Macromolecular as well as reactive photoinitiators have attracted much attention both in industry and in academia due to the disadvantages of conventional small molecular photoinitiators such as volatility and mobility. A macromolecular benzophenone photoinitiator was designed and efficiently synthesized in this study. Hydroxyl-containing Michler’s ketone was firstly synthesized in 82% yield, followed by reacting with toluene di-isocyanate (TDI) to prepare polyurethanetype macromolecular benzophenone photoinitiator.

1. Introduction
Photo-cured resins have found wide applications in many areas such as coatings, oil inks, and dental materials due to their unique advantages (e.g., rapid curing, energy-saving, environmental-friendliness, and adaptability to large-scale manufacturing)[1-4]. However, conventional photo-cured resins are usually produced by small molecular photoinitiators which are gradually restricted due to their negative effect on the environment and the polymer products. In recent years, researchers are seeking to design and synthesize macromolecular and polymeric photoinitiators to solve the problems [5-9]. Herein, we designed and synthesized a hydroxyl-containing Michler’s ketone, followed by forming a polyurethane-type macromolecular photoinitiator.

2. Experimental

2.1 Instruments and reagents
Bruker AV 400 MHz nuclear magnetic resonance meter (CDCl₃ as solvent, TMS as internal standard). The FTIR spectra were recorded via the KBr pellet method by using a Bruker V70 FTIR spectrophotometer.

4-Methyl benzophenone, 40% aqueous HBr, 30% H₂O₂, urea, diethanolamine, toluene diisocyanate (TDI), dibutylin dilaurate (DBTDL), ethylenediamine tetraacetic acid (EDTA) were all AR grade and used as received without treatment.

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2.2 Synthesis of urea hydrogen peroxide (UHP)
Into a 250 mL of three-necked flask were added 30% hydrogen peroxide (95 mL, 0.85 mol), urea (60.0 g, 1 mol) and EDTA (1.6 g, 5.5 mmol). The mixture was stirred at room temperature for 30 min, filtered, and the filtrate was cooled at 0 °C for 5 h. The resulting precipitate was filtered, and the filtered cake was collected and dried at 40-45 °C to obtain UHP product as white crystals (32.1 g, 40%).

2.3 Synthesis of 4-bromomethyl benzophenone (1)
4-Methyl benzophenone (1.25 g, 6.4 mmol) and UHP (1.2 g, 12.8 mmol) were dissolved in dichloromethane (30 mL) and were heated to reflux. Under irradiation of a 100-watt bulb, aqueous HBr (1.4 mL, 6.9 mmol) was added dropwise within about 20 min, followed by refluxing for additional 40 min. The reaction mixture was cooled, and water was added, separated, and the organic layer was dried with anhydrous Na₂SO₄, filtered, and finally concentrated in vacuo to afford a white solid, which was recrystallized in anhydrous ethanol to give pure 4-bromomethyl benzophenone (1.60 g, 91%). M.p. 109-110 °C. IR: ν (cm⁻¹) 3040, 1668, 1610, 1463, 1419, 852, 599. ¹H NMR (CDCl₃): δ 7.80-7.77 (m, 4H), 7.60-7.58 (m, 1H), 7.51-7.47 (m, 4H), 4.53 (s, 2H).

2.4 Synthesis of 4-[di(hydroxyethyl)aminomethyl] benzophenone (2)
4-bromomethyl benzophenone (0.28 g, 1 mmol) was dissolved in dichloromethane (20 mL), followed by adding sodium hydroxide (0.2 g, 5 mmol) and diethanol amine (0.21g, 2 mmol). The mixture was stirred at room temperature for 10 h, until which TLC results indicated that the reactant 4-bromomethyl benzophenone was almost completely consumed. To the resulting mixture was poured water (20 mL) and the mixture was stirred vigorously for 10 min. The organic layer was separated, dried with anhydrous sodium sulfate, filtered, and the filtrate was concentrated in vacuo to afford the crude product. Further purification on silica gel chromatography with petroleum ether/ethyl acetate (5 : 1, v : v) as eluant gave pure oily product. (0.25 g, 82%). ¹H NMR (CDCl₃): δ 7.74-7.72 (m, 4H), 7.57-7.53 (m, 1H), 7.46-7.41 (m, 4H), 3.78 (s, 2H), 3.64 (t, 4H, J = 5.2 Hz), 3.51 (s, br, 2H), 2.71 (t, 4H, J = 5.2 Hz). ¹³C-NMR (CDCl₃): δ 196.5, 143.6, 137.6, 136.6, 132.4, 130.3, 130.0, 128.9, 128.3, 59.6, 58.9, 55.8.

2.5 Synthesis of polyurethane type macromolecular photoinitiator (3)
Toluene diisocyanate (TDI) (1.045 g, 6 mmol) was dissolved in DMF (10 mL) at room temperature. Then 4-[di(hydroxyethyl)aminomethyl] benzophenone (0.9 g, 3 mmol) in DMF (10 mL) was added dropwise to the above solution, followed by the addition of a drop of dibutyltin dilaurate (DBTDL). The resulting mixture was stirred at 65 °C for 4 h, cooled, poured slowly into diluted aqueous NH₃, and the precipitate was filtered. The filter cake was washed with distilled water, ethanol, and distilled water again. Finally, the solid product was dried in a vacuum oven at 40 °C for 24 h, and the product mass was 1.43 g.

3. Results and Discussion
3.1 Synthesis, characterization and properties of 4-[di(hydroxyethyl)aminomethyl] benzophenone (2)
First, 4-(bromomethy) benzophenone (1) was easily prepared from 4-methy benzophenone in excellent yield by using light-promoted oxidation and bromination reactions. Under the reaction conditions, Baeyer-Villiger reaction may be a competitive side reaction, but this ester-forming reaction usually requires harsh conditions or very long reaction times, and the presence of phenyl ring further retarded the reaction. For example, only 47% yield of ester was obtained when 4-methy benzophenone
underwent Baeyer-Villiger reaction with the time of as long as 8 days [10]. On the other hand, HBr can be easily converted to bromine radical under UHP and light irradiation, and bromination readily occurred at benzyl site of 4-methy benzophenone to form the product. As a matter of fact, more than 90% yield of 4-(bromomethy) benzophenone (1) was obtained within about 1 h. Then, the synthesis of compound 2 was conducted by 4-bromomethyl benzophenone (1) and diethanol amine in the presence of a strong base (Fig. 1).

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{UHP, aq. HBr, light} & \quad \text{Br} \\
\text{Ph} & \quad \text{O} \\
\end{align*}
\]

Fig. 1 Synthesis of polyurethane type macromolecular photoinitiator (3)

\[^{1}\text{H NMR spectrum of compound} \ \text{2} \ \text{was shown in Fig. 2A. Nine protons at the chemical shifts around 7-8 ppm represented aryl hydrogens; a single peak at 3.78 ppm corresponded to the protons from the benzyl CH}_2; \ \text{two triplet peaks at 3.6 and 2.7 ppm corresponded to the two hydroxyl ethyl protons; a broad peak at 3.5 ppm represented the two hydroxyl active hydrogens. The structure of 2 was further confirmed by}^{13}\text{C NMR spectrum in Fig. 2B.} \]
The intermediate 2 is a functional molecule that contains benzophenone moiety, tertiary amine and hydroxyl groups. The benzophenone part is a hydrogen-trapping photoinitiator, tertiary amine acts as co-photoinitiator, and dihydroxyl groups are hydrophilic and can react with other functional groups. Therefore, compound 2 is expected to be a water-based Michler’s ketone type photoinitiator.

3.2 Preparation of polyurethane type macromolecular photoinitiator (3)

The compound 2 contains two hydroxyl groups that can react with diisocyanates to form polyurethanes under proper conditions. The polyurethane is a useful functional polymer as the macromolecular type II photoinitiator. Furthermore, tertiary amine groups can act as both co-photoinitiators and curing agents for polyurethanes.

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