



# A facile approach to catechol containing UV dismantlable adhesives



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## ABSTRACT

We report a facile synthetic approach to a new type of catechol containing UV dismantlable adhesive. A series of linear polymers containing pendent catechol moieties and main chain *o*-nitrobenzyl ester groups were synthesized by the Passerini multicomponent polymerization (MCP) of a di-*o*-nitrobenzaldehyde, 1,6-diisocyanohexane, 3-(3,4-dihydroxyphenyl) propionic acid, and undecanoic acid. The content of the catechol moieties was adjusted by varying the molar ratio of 3-(3,4-dihydroxyphenyl) propionic acid to undecanoic acid. The thermal properties of these polymers were investigated, they are stable up to 250 °C, and the glass transition temperatures ( $T_g$ ) are in the range of 17–70 °C. Increasing the catechol content will increase the  $T_g$  and slightly decrease the thermal stability. The pendent catechol groups and the *in situ* formed *o*-nitrobenzyl ester linkages in the polymer main chain endow the polymer with dual functions, substrate adhesiveness and UV degradation. The UV degradation process was monitored by  $^1\text{H}$  NMR, GPC, UV–Vis and FTIR. Lap shear strength tests revealed that the adhesion performance of these polymers could be tuned by varying the catechol contents. UV irradiation could cleave the polymer chains, thus decreasing the adhesion strength.

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## 1. Introduction

Adhesives are such materials that can hold different substrates together. Every year, quantities of adhesives are produced worldwide to meet different demands in industry, medicine and daily use. In fact, human beings have used natural glues such as starch or hydrolyzed collagen long before, many of which are still being used today [1]. However, with the development of adhesion technology, more and more attentions have been paid to synthetic adhesives. Because of the ease to finely tune the chemical compositions of synthetic polymers, which is a major factor influencing the adhesion strength, scientists can design better adhesives for different purposes. One such good example is the mimicry of bio-adhesives inspired by marine mussels [2–18]. These organisms are able to attach themselves firmly to the underwater surface by secreting adhesive proteins containing unique amino acid 3,4-dihydroxyphenylalanine (DOPA) [19,20]. Studies have revealed that DOPA moieties have extensive interactions with virtually any substrates via metal chelation, oxidation and Michael adduct formation etc [21–23]. Though the incorporation of DOPA or its

derivatives into polymers as new functional materials has been pursued for many years, the synthetic pathway is rather complicated, often requiring complex synthetic routes and protection–deprotection procedures [2–5].

On the other hand, facile debonding ability after use is another aspect of adhesive research. This emerging area promises smart adhesives with great industrial potentials not only in terms of saving energy but also recycling materials. As can be expected, dismantlable adhesives require external stimuli, such as heat [24–34], light [35–37] and electrostatic interactions [38] to achieve the on-demand disassembly. Among them, photo irradiation is particularly attractive, because of its temporal and spatial control [39–43], which ensures precise and selective removal of adhesives. Ideally, this method provides an opportunity for easy operation and minimal damage to the substrates. A common strategy toward light responsiveness is the incorporation of *o*-nitrobenzyl ester groups in polymers [44–46]. This photolabile structure undergoes photocleavage and generates an *o*-nitrosobenzaldehyde and a carboxylic acid upon UV irradiation [47,48], which in turn changes the material properties.

However, it remains difficult to simultaneously introduce catechol moieties and *o*-nitrobenzyl ester groups into polymer through conventional synthetic procedures. An intriguing methodology is the use of multicomponent reactions (MCRs) [49–54]. Unlike

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traditional two component reactions, the fundamental superiority of MCRs is the simultaneous incorporation of more than two starting materials into a single product, providing a chance to circumvent the aforementioned problems.

Passerini reaction is a typical isocyanide based multicomponent reaction. First reported in 1921 [52], this three component reaction can assemble a carboxylic acid, an isocyanide and an aldehyde into an  $\alpha$ -acyloxy amide in an atom-economic way. Thanks to the mild reaction conditions and functional group tolerance, our group [55–62] and others [63–69] have exploited this reaction in many aspects such as polymerization and post-functionalization. Our recent works demonstrated that the multicomponent polymerization (MCP) of a diisocyanide, a dicarboxylic acid and an *o*-nitrobenzaldehyde was a straightforward way to synthesize photocleavable polymers [59,60]. The key point was the in-situ formed *o*-nitrobenzyl ester linkage in the polymer main chain, this linkage can be cleaved upon UV irradiation. We here report that two functionalities, catechol and *o*-nitrobenzyl ester groups, can be simultaneously incorporated into a linear polymer via the MCP of a di-*o*-nitrobenzaldehyde derivative, 1,6-diisocyanohexane, and 3-(3,4-dihydroxyphenyl) propionic acid (Scheme 1). The facilely obtained polymers show good adhesion and UV debonding abilities, and they are expected to be used as dismantlable adhesives.

## 2. Experimental section

### 2.1. Materials

The following chemicals were used as received: 5-hydroxy-2-nitrobenzaldehyde (99%, Beijing Datianfengtuo Chem. Co., Ltd.), bromoethane (A. R., Tianjin Guangfu Fine Chem. Res. Inst.), 1, 12-dibromododecane (98%, Alfa Aesar), 1,6-diisocyanohexane (98%, Alfa Aesar), *tert*-butyl isocyanide (98%, Alfa Aesar), 3-(3,4-dihydroxyphenyl) propionic acid (98+%, Alfa Aesar), undecanoic acid (98%, Alfa Aesar). All other chemicals were purchased from Beijing Chem. Reagent Co. and used as received unless otherwise noted. THF was refluxed with Na and distilled before use.

### 2.2. General measurements and characterization

<sup>1</sup>H NMR (300 MHz) spectra were recorded in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> on a Varian Gemini 300 spectrometer with tetramethylsilane (TMS) as the internal reference for chemical shifts ( $\delta$ , ppm). Molecular weights and polydispersity index (PDI =  $M_w/M_n$ ) of polymers were measured with a gel permeation chromatography (GPC) equipped with a 2414 refractive index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel HT columns (HT2, HT3, HT4). The columns were thermostated at 35 °C and THF was used as an eluent at a flow rate of 1.0 mL/min. Calibration was made against linear polystyrene standards. Thermal gravimetric analysis (TGA) was carried out using a Q600-SDT thermogravimetric analyzer (TA Co., Ltd.) with nitrogen purging rate set at 50 mL/min. Measurements were conducted from room temperature to 600 °C at a heating rate of 10 °C/min. Calorimetric measurement was performed using a Q100 differential scanning calorimeter (TA Co., Ltd.) with nitrogen purging rate set at 50 mL/min. The program was set to finish two cycles in a temperature range of –80 to 200 °C at a heating/cooling rate of 10 °C/min. Data of the endothermic curve were acquired from the second scan for each polymer sample. TA Universal Analysis software was applied for data acquisition and processing in the two measurements.

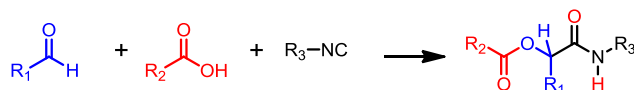
### 2.3. Synthesis of 5-ethoxy-2-nitrobenzaldehyde

5-Hydroxy-2-nitrobenzaldehyde (1.6712 g, 10 mmol), bromoethane (1.6346 g, 15 mmol) and potassium carbonate (1.6583 g, 12 mmol) were dissolved in DMF (20 mL). The reaction mixture was heated at 30 °C for 24 h. The excess bromoethane was evaporated under reduced pressure and the residue was poured into water to precipitate the product. After filtration, simply washing with water for three times offered 5-ethoxy-2-nitrobenzaldehyde as a pale yellow solid in 77% yield.  $T_m = 63$  °C (Fig. S1).

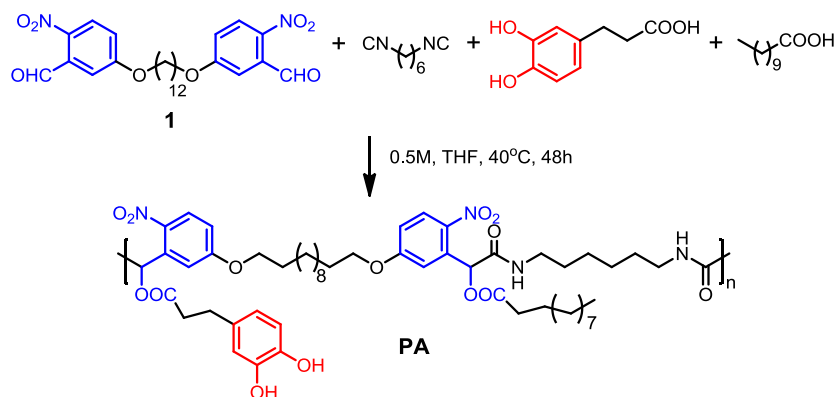
### 2.4. Synthesis of di-*o*-nitrobenzaldehyde derivative monomer **1**

1, 12-dibromo-dodecane (1.6407 g, 5 mmol), 5-hydroxy-2-nitrobenzaldehyde (2.5068 g, 15 mmol), and potassium carbonate

#### (A). Passerini reaction:



#### (B). Dismantlable adhesives synthesized by Passerini reaction:



Scheme 1. Synthetic strategy for the dismantlable adhesives.

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