



# Synthesis and characterization of organo-soluble and photosensitive benzocyclobutene-terminated imides

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## ABSTRACT

Three kinds of benzocyclobutene (BCB)-terminated imide monomers have been synthesized by the imidization and Heck reaction. The obtained BCB monomers exhibit good solubility in a wide range of organic solvents at room temperature. The BCB monomers show an exothermal curing behavior in the range of 220–270 °C. The curing kinetic parameters, the apparent activation energy ( $E_a$ ), the frequency factor ( $A$ ) and the reaction order ( $n$ ), are obtained by non-isothermal DSC method. The cured BCB resins exhibit good thermal stability ( $T_{d5} > 435$  °C), high glass transition temperature ( $T_g > 300$  °C) and low dielectric constant. Moreover, high quality negative patterns of the BCB films are obtained after the photolithography.

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## 1. Introduction

Polyimides (PIs) have been extensively used in micro-electronic manufacturing as interlayer dielectrics (ILDs), passivation layers and stress buffers based on their excellent physical and chemical properties [1,2]. The rigid imide and phenyl structure give PIs with high modulus, high glass transition temperature ( $T_g$ ) and high thermal stability. However, most of them have an inferior solubility in common organic solvent for the rigidity of the molecular chains and the strong inter/intra-chain interaction. Although many efforts have been made to improve the solubility of PIs, e.g., by incorporating the flexible units ( $-\text{O}-$ ,  $-\text{C}(\text{CF}_3)_2-$ ), bulky pendant groups or asymmetric moieties into the PI backbone [3–11], the mainly used PIs are only soluble in aprotic polar solvents, such as DMF and DMAc. In the field of electronic packaging, the PI film is typically prepared by spin-casting the solution of poly(amic acid)s onto Si/metal substrate, followed by the thermal dehydration/ring-closure reaction. Due to the release of water

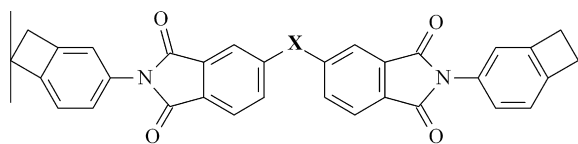
molecules, the polyimide film suffers from severe shrinkage in the thermal imidization process [12].

On the other hand, benzocyclobutene (BCB)-functionalized thermosets are emerging as a new generation of high-performance materials for microelectronic applications due to the versatile reaction chemistry of BCB group and other excellent properties [13–16]. At high temperature, the strained four-membered ring on BCB starts to open to produce a reactive *o*-quinodimethane intermediate, which could react with dienophile to form a Diels–Alder adduct or undergo a dimerization/polymerization. No catalyst is required and no byproduct is produced during the curing process. Compared to the conventional BCB monomers, photosensitive BCBs have attracted much attention for the simplification of the patterning process by avoiding the use of photoresists [17–19].

Since 1980s, Tan and Zhang et al. have developed a series of bisBCB-terminated imides via imidization between 4-aminobenzocyclobutene and various tetracarboxylic dianhydrides (Scheme 1) [20–23]. After curing, the BCB resin ( $\text{X} = -\text{C}(\text{CF}_3)_2-$  in Scheme 1) exhibited high glass transition temperature ( $\sim 280$  °C) and high thermal decomposition temperature ( $T_d > 400$  °C) due to the presence of

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X: O, C=O, C(CF<sub>3</sub>)<sub>2</sub>,....

**Scheme 1.** BCB monomers synthesized by Tan et al.

the imide structure. But most of the synthesized BCB imide monomers (X = —O—, C=O, etc.) were insoluble even in DMF, which largely limited their applications. Herein, we provided a new series of organo-soluble, photosensitive BCB imides (Scheme 2). The incorporation of reactive allyl group into the molecular structure not only increased the solubility of the BCB monomers, but also provided the monomers with photosensitivity by reacting with azide photo-crosslinking agent.

## 2. Experimental section

### 2.1. Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA, 99%, J&K Chemical Ltd.), 4,4'-oxydiphthalic anhydride (ODPA, 97%, Aladdin Reagent Co., Ltd.), 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA, 98%, Adamas Reagent Co., Ltd.) and allylamine (AL, 98%, Langchem Co., Ltd.) were used as received. 4-Bromobenzocyclobutene (97%) was purchased from Chemtarget Technologies Co., Ltd. Palladium acetate, tris(2-methylphenyl)phosphine and 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (BAC-M) were purchased from TCI (Shanghai) Development Co., Ltd. and used as received. Triethylamine, N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) were freshly distilled over calcium hydride in nitrogen before use. Acetic acid, petroleum ether, anhydrous methanol, tetrahydrofuran, dichloromethane and mesitylene (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) were used as received. The negative-imaging developer (RFX-2277) was purchased from Suzhou Ruihong Electronic Chemical Co., Ltd.

### 2.2. Synthesis of allylamine end capped monomers (monomer 2 in Scheme 2)

A typical synthesis is given for BTDA-AL [24]:

For the synthesis of allylamine end capped 3,3',4,4'-benzophenonetetracarboxylic dianhydride, BTDA-AL, 3.22 g (0.01 mol) of BTDA and 40 mL of acetic acid were added into a 100-mL three-necked flask equipped with a condenser, a mechanical stirrer and a nitrogen inlet. After BTDA dissolved in acetic acid, 1.3 g (0.023 mol) of allylamine was added dropwise. The mixture was refluxed for 90 min under nitrogen atmosphere, then cooled to room temperature and poured into cold water. The precipitated BTDA-AL was collected through vacuum filtration, then dissolved in a minimum of acetone and precipitated one more time in cold water. After the filtration, 3.39 g of white powder was obtained in 85% yield after drying at 120 °C for 24 h under vacuum.

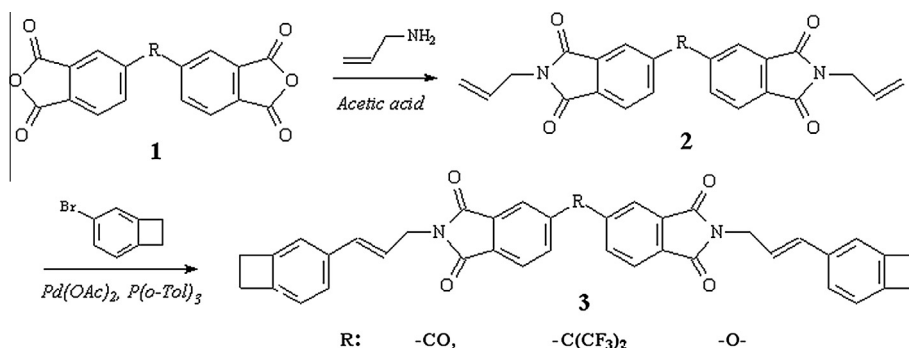
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 4.34 (d, 4H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 5.89 (m, 2H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 5.28 (dd, 4H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 8.03–8.18 (m, 6H, aromatic protons). FTIR (KBr): 1776 and 1706 cm<sup>-1</sup> (ν<sub>C=O</sub>), 1388 cm<sup>-1</sup> (ν<sub>C—N</sub>), 735 cm<sup>-1</sup> (τ<sub>C=O</sub>), 1655 cm<sup>-1</sup> (ν<sub>C=C</sub>, allylic double bond). mp: 153 °C.

6FDA-AL: 2.25 g (0.005 mol) of 6FDA, 0.62 g (0.01 mol) of allylamine and 40 mL of acetic acid were used. 1.47 g of 6FDA-AL imide was obtained as a white powder in 58% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 4.32 (d, 4H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 5.87 (m, 2H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 5.26 (dd, 4H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 7.78–7.94 (m, 6H, aromatic protons). FTIR (KBr): 1776 and 1709 cm<sup>-1</sup> (ν<sub>C=O</sub>), 1392 cm<sup>-1</sup> (ν<sub>C—N</sub>), 1254 and 1145 cm<sup>-1</sup> (ν<sub>C—F</sub>), 723 cm<sup>-1</sup> (τ<sub>C=O</sub>), 1648 cm<sup>-1</sup> (ν<sub>C=C</sub>, allylic double bond). mp: 152 °C.

ODPA-AL: 3.15 g (0.01 mol) of ODPA, 1.25 g (0.022 mol) of allylamine and 40 mL of acetic acid were used. 2.32 g of ODPA-AL imide was obtained as a light yellow powder in 60% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 4.31 (d, 4H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 5.89 (m, 2H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 5.24 (dd, 4H, N—CH<sub>2</sub>—CH=CH<sub>2</sub>), 7.37–7.91 (m, 6H, aromatic protons). FTIR (KBr): 1771 and 1702 cm<sup>-1</sup> (ν<sub>C=O</sub>), 1387 cm<sup>-1</sup> (ν<sub>C—N</sub>), 729 cm<sup>-1</sup> (τ<sub>C=O</sub>), 1642 cm<sup>-1</sup> (ν<sub>C=C</sub>, allylic double bond). mp: 136 °C.



**Scheme 2.** Synthetic route of BCB-terminated imide monomers.

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