



# Photoinitiability of triblock copolymer PDMS-*b*-(PMAEBB-*co*-PDMAEMA)<sub>2</sub> as a macro-photoinitiator prepared via RAFT polymerization

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## ABSTRACT

In this study, we prepared a novel triblock copolymer, PDMS-*b*-(PMAEBB-*co*-PDMAEMA)<sub>2</sub> (*tri*-PI) bearing side-chain benzophenone (BP) and coinitiator amine, as a macro-photoinitiator via reversible addition-fragmentation chain transfer (RAFT) copolymerization of the polymerizable photoinitiator 2-(methacryloyloxy)ethyl-2-benzoylbenzoate (MAEBB) and the unsaturated coinitiator amine 2-(dimethylamino)ethyl methacrylate (DMAEMA) with a bifunctional polydimethylsiloxane (PDMS) macro-chain transfer agent (macro-CTA). The structure of synthesized copolymer was confirmed by Fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (<sup>1</sup>H NMR), differential scanning calorimetry (DSC), and gel permeation chromatography (GPC). The effects of the photoinitiator/coinitiator ratio, concentration, and photoinitiator systems on the photopolymerization kinetics of tri(propylene glycol) diacrylate (TPGDA) were investigated by real-time FT-IR. The mobility of the *tri*-PI chain segments was proven by X-ray photoelectron spectroscopy (XPS), and the surface morphology of TPGDA curing coatings was studied by scanning electron microscopy (SEM). Results showed that *tri*-PI strongly suppressed the effect of oxygen inhibition on the photopolymerization system. *Tri*-PI was also used in the curing of UV-curable waterborne polyurethane acrylate (UV-WPUA) resin to determine its versatility.

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## 1. Introduction

The photoinitiated polymerization continuously expands the occupancy in the industry, because of its excellent characteristics, such as cost effectiveness, high efficiency, energy conservation, and being friendly to environment. This technique is widely applied not only in conventional areas such as coatings, inks, and adhesives but also in high-tech domains including optoelectronics, stereolithography, and nanotechnology [1–4]. Given its high quantum efficiency and reactivity, free radical photopolymerization has attracted considerable attention in the research area of photoinitiated polymerization and UV-curing industrial applications. Photoinitiators mainly affect the polymerization rate in radical photopolymerization [5]. Therefore, photoinitiators play a major

role in photopolymerization despite their low volume in a free radical photopolymerizable formulation.

In the free radical photopolymerization, small molecular photoinitiators are mostly added in the formulation. However, it leads to many undesirable effects on UV-curing materials because of their inherent disadvantages, such as odor, yellowing, migration, and poor compatibility [6]. To overcome these disadvantages, many macro-photoinitiators have been prepared. [7] The unique properties of macromolecular chains endow macro-photoinitiators with good compatibility in formulations and limited migration in materials, which favor the synthesis of environmental friendly products.

In general, macro-photoinitiators are classified as cleavage (Norrish I) and H-abstraction type (Norrish II) [8–10]. Generally, the Norrish II macro-photoinitiators are based on thioxanthone [11–14], camphorquinone [15–17], anthraquinone [18], or BP [19–22] moieties. BP-based polymerizable photoinitiators are widely used in photopolymerization because of their relatively low cost and high photoinitiation efficiency that can be enhanced with the addition of a coinitiator (usually an amine) in the for-

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mulation [23]. Several previous studies have developed such a macro-photoinitiator system. Yin et al. [24–27] reported a number of polymerizable photoinitiators possessing both BP groups and hydrogen-donating sites. Arsu et al. [28–30] also synthesized various macro-photoinitiators by using BP-based polymerizable photoinitiators.

The interaction between the BP group and coinitiator amine, which involves an electron and proton transfer process, is crucial in the generation of active radicals in an H-abstraction type photoinitiator system. Most macro-photoinitiators based on a BP/coinitiator amine system are synthesized by conventional radical copolymerization. However, it is regarded as a means that lack of control of polymer structure including molecular weight distribution and copolymer composition, thus resulting in a difficult control of the proportion of BP and coinitiator amine in the macro-photoinitiator structure. There are still few reports about such effect on photopolymerization. Recently, controlled/living radical polymerization (CRP) methods have been developed primarily to overcome the above mentioned difficulties [31,32]. Poly et al. [33] prepared polymers with a xanthate chain-end functional group and a terminal monomer unit derived from *N*-vinylcarbazole via RAFT polymerization and demonstrated that such compounds can be considered as efficient and versatile macro-photoinitiators because of their capacity to initiate both free radical and radical-promoted cationic polymerizations under UV irradiation. Enlightened by this work, the CRP methods show a promising potential for the design of tailor-made macro-photoinitiators that is able to tune the final UV-curing product performance.

Although free radical photopolymerization has been widely developed for various industrial applications in the past decades, several limitations hinder further development of this process. A major drawback of free radical polymerization is related to the well-known oxygen inhibition [34]. Reactive species, such as initiating and propagating radicals, are easily quenched by O<sub>2</sub> to yield highly stable peroxy radicals that cannot participate in further photopolymerization initiation reactions, resulting in the loss of photoinitiation efficiency [35,36]. Therefore, many strategies have been developed to suppress oxygen inhibition. Recent studies have focused on utilizing the low surface energy of fluorine and siloxane as the main driving force for the enrichment of photoinitiator at the material surface to reduce O<sub>2</sub> inhibition [22,37]. Nie et al. [38] synthesized a novel photoinitiator with fluorinated species, which would migrate towards the air interface to overcome oxygen inhibition. Similarly, polysiloxane-based photoinitiator featuring backbone flexibility and low surface energy is a potential candidate that exhibits excellent resistance of surface oxygen inhibition. By using polysiloxane-based macro-photoinitiators, Sun et al. [39–42] successfully prepared gradient materials.

Considering the advantages of CRP technology and the specific characteristics of PDMS, we introduced the polymerizable photoinitiator 2-(methacryloyloxy)ethyl-2-benzoylbenzoate (MAEBB) and the unsaturated coinitiator amine DMAEMA into the macromolecular chain via RAFT polymerization by using a bifunctional PDMS macro-CTA. We obtained the well-defined triblock copolymer PDMS-*b*-(PMAEBB-*co*-PDMAEMA)<sub>2</sub> (*tri*-PI) as a macro-photoinitiator, in which BP/amine acts as the photoinitiator system and the PDMS segment endows the capability to reduce oxygen inhibition. The photopolymerization kinetics of TPGDA initiated by *tri*-PI was discussed in detail with real-time FT-IR. The effect of *tri*-PI on the oxygen inhibition in radical photopolymerization was also investigated by XPS and SEM. In addition, the physical and mechanical properties of UV-WPUA coatings were studied to evaluate the versatility of *tri*-PI in UV-curing industrial application.

## 2. Experiment

### 2.1. Materials

4-Dimethylaminoipyridine [DMAP, 99%, Aladdin Industrial Corporation (AIC), USA], *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, AIC), BP (99%, AIC), 2-benzoylbenzoic acid (98%, J&K Scientific Ltd., China), TPGDA (90%, J&K Scientific Ltd.), dihydroxy-terminated poly(dimethylsiloxane) (HO-PMDS-OH, 5000 g/mol, PDI = 1.28, Hangzhou Silong Chem-Tech, China), UV-WPUA (Sartomer, USA) were used as received. 2-Hydroxyethyl methacrylate (HEMA, 99%, AIC) and DMAEMA (99%, AIC) were purified by a neutral alumina column prior to use. 2,2'-Azobisisobutyronitrile (AIBN, 98%, AIC) was used after recrystallization by ethanol. All other reagents were purchased commercially as analytically pure grade and used as received without further purification.

### 2.2. Measurement

Elemental analyses were performed in a N<sub>2</sub> atmosphere using Elementar Vario EL CHNS equipment, and the contents of C, H, and S elements in the product were determined. Electron ionization-mass spectrometry (EI-MS) experiments were performed with an EI-mass spectrometer (DSQ, Thermo, America). FT-IR spectra were obtained between 4000 and 500 cm<sup>-1</sup> for 32 scans at 4 cm<sup>-1</sup> resolution in KBr pellets using a Nicolet Magna 360 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker spectrometer (400 MHz) with CDCl<sub>3</sub> as a solvent at 25 °C. DSC measurements were performed on a DSC Q10 apparatus from TA Instruments and run at equal heating and cooling rates of 10 °C/min in inert atmosphere. The polymer samples were first scanned from room temperature to 150 °C and then cooled down to -150 °C. This temperature was held for 5 min so as to allow the system to attain thermal equilibrium before the second heating scan. The first heating ramp of each sample was discarded in this work. The glass transition temperature (*T*<sub>g</sub>) values were determined as the midpoint between the onset and the end of a step transition. GPC measurement was performed by using a Viscotek VE112 instrument equipped with a VF7510 pump, a VF1122 variable wavelength detector, and a M302 refractive index detector with THF as the eluent at a rate of 1.0 mL/min at 40 °C. The injection volume was 20 μL, and the concentration was 5–10 mg/mL. Calibration was performed by using narrow-molecular-weight polystyrene standards (PDI < 1.1), ranging from 2 × 10<sup>3</sup> to 6 × 10<sup>4</sup> g/mol. UV absorption spectra of samples were obtained with a Shimadzu UV-450 spectrophotometer. SEM was conducted with a Hitachi S-4800 electron microscope with an accelerating voltage of 20.0 kV, and the samples were sputtered with gold before scanning. XPS measurements were performed on a Kratos ESCA spectrometer Axis Ultra DLD with an Al KαX source (150 W, 15 kV) at a take-off angle of 45° from the surface normal. The hemispherical energy analyzer was operated in the CAE mode with a 700 × 300 mm selected area aperture. Survey spectra were collected at constant pass energy of 160 eV with a scan step size of 1.0 eV. High-resolution spectra were collected with pass energy of 40 eV. Static water contact angle (WCA) was measured on a JY-PHB contact angle apparatus from Chengde Jinhe Instrument Manufacturing Co. Ltd. (China). The pencil hardness, flexibility, and adhesion of the UV-curing coatings were measured in accordance with the Chinese National Standard Test Methods of GB6739-86, GB1732-79 and GB9286-98, respectively.

### 2.3. Synthesis of bifunctional PDMS macro-CTA

The bifunctional PDMS macro-CTA was prepared by a simple DCC/DMAP esterification method. First, the RAFT agent precursor *S*-1-dodecyl-*S'*-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate

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