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## Synthesis, photophysical and photochemical studies of benzophenone based novel monomeric and polymeric photoinitiators

Demet Karaca Balta<sup>a</sup>, Özlem Karahan<sup>b</sup>, Duygu Avcı<sup>b,\*</sup>, Nergis Arsu<sup>a</sup><sup>a</sup> Department of Chemistry, Yildiz Technical University, Davutpasa Campus, 34210 Istanbul, Turkey<sup>b</sup> Department of Chemistry, Bogazici University, 34342 Bebek, Istanbul, Turkey

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## ABSTRACT

Four novel benzophenone-containing photoinitiators (monomers PI-1 and PI-2 and their polymers PPI-1 and PPI-2) were prepared from alkyl  $\alpha$ -hydroxymethacrylates. PI-1 was synthesized from reaction of *tert*-butyl  $\alpha$ -bromomethacrylate and 4-hydroxybenzophenone followed by cleavage of *tert*-butyl groups using trifluoroacetic acid. PI-2 was synthesized from reaction of ethyl  $\alpha$ -bromomethacrylate and 3-benzoylbenzoic acid. Thermal polymerization of PI-1 and PI-2 was performed using 2,2'-azobis(isobutyronitrile). PI-1 and PPI-1 show UV absorption (289 and 294 nm) which are red-shifted compared to benzophenone (252 nm), PI-2 (255 nm) and PPI-2 (252 nm). All of the photoinitiators give phosphorescence emissions from their  $n-\pi^*$  states. The photopolymerizations of triethylene glycol dimethacrylate, 2-hydroxyethyl methacrylate and hexanediol diacrylate initiated by PI-1, PI-2, PPI-1, PPI-2 and benzophenone were studied by photo-differential scanning calorimeter using *N,N*-dimethyl-*p*-toluidine as coinitiator. Polymeric photoinitiators were found to have higher efficiencies than benzophenone and monomeric ones. Photopolymerization results are also compared to that of an alkyl  $\alpha$ -hydroxymethacrylate-based photoinitiator previously reported by us; and the influence of monomer structure on polymerization efficiency is discussed.

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## 1. Introduction

Polymeric photoinitiators (PPIs) with pendant or in-chain active groups are of increasing interest due to their advantages in comparison with their corresponding low molecular weight analogs [1–4]. Some of these advantages are low odoring, non-yellowing and non-toxic properties due to reduced migration of both unreacted photoinitiator molecules and photolysis products to the film surface. Also, solubility and compatibility problems observed with low molecular weight analogs are eliminated using polymeric ones. In addition, the efficiency of photoinitiation can be enhanced which results in a reduction of exposure time and increase of productivity.

Many PPIs containing free radical photoinitiator moiety are described in the literature and are classified as type I [5–9] or type II [10–34]. Most of the type II PPIs are based on thioxanthone [10–12], camphorquinone [13,14], benzophenone [15–34], anthraquinone or benzyl moieties and require the presence of a coinitiator (usually an amine) in the formulation to work. Also reported are PPIs which contain both components in the same

macromolecule [11–18,20,24,27,29,30,33]. Some of these materials were found to have higher photoinitiation performance than PPIs with externally supplied coinitiator amines; probably because no diffusion is required for the excited photoinitiator to react with the coinitiator [16]. On the other hand, in some cases systems with one photoinitiating component (ketone) on the polymer and external small amine coinitiators can perform even better [13].

It is desirable to understand the relationship between the structure and photoinitiating efficiency as much as possible, as any knowledge in this area can obviously guide the effort to design new photoinitiators. Investigating differences in polymerization efficiencies of photoinitiators similar enough to be compared meaningfully, yet contain tailored differences, and their polymers, can yield useful clues.

Recently, we synthesized the first novel RHMA-based monomeric photoinitiator bearing side-chain benzophenone (BP) group, its homopolymer, and copolymer with *N,N*-dimethylaminoethyl methacrylate (Fig. 1) [35]. In the present work, we report synthesis and characterization of new monomeric and polymeric photoinitiators where (i) the BP group is attached to the polymerizable double bond through an ester linkage instead of an ether linkage and (ii) *tert*-butyl group is cleaved to create an acrylic acid derivative (Fig. 2). Their performance as photoinitiators

\* Corresponding author. Tel.: +90 2123596816; fax: +90 2122872467.  
E-mail address: [avcid@boun.edu.tr](mailto:avcid@boun.edu.tr) (D. Avcı).

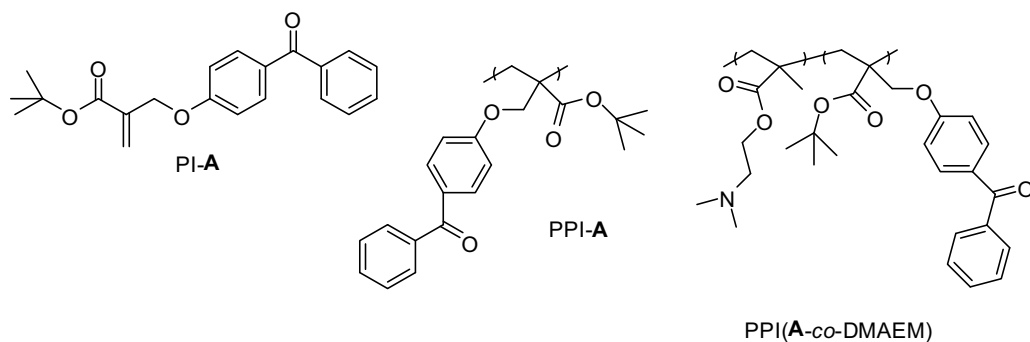


Fig. 1. Structures of previously synthesized photoinitiators.

for polymerizations of triethylene glycol dimethacrylate (TEGDMA), 2-hydroxyethyl methacrylate (HEMA) and hexanediol diacrylate (HDDA) is evaluated using photodifferential scanning calorimeter (photo-DSC).

## 2. Experimental

### 2.1. Materials

Ethyl  $\alpha$ -bromomethacrylate (EBBr) and *tert*-butyl  $\alpha$ -bromomethacrylate (TBBr) were synthesized from the corresponding alkyl  $\alpha$ -hydroxymethacrylates (RHMA) according to literature procedures [36,37]. Trifluoroacetic acid (TFA), 4-hydroxybenzophenone, 3-benzoylbenzoic acid, HEMA, TEGDMA, HDDA, *N,N*-dimethyl-*p*-toluidine, *N*-methyldiethanolamine (MDEA), BP, 2,2'-azobis(isobutyronitrile) (AIBN) and all other reagents and solvents were obtained from Aldrich Chemical Co. and used as received.

### 2.2. Characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken on Varian Gemini (400 MHz) spectrometer. Elemental analyses were obtained from Thermo Electron SpA FlashEA 1112 elemental analyser (CHNS separation column, PTFE; 2 m;  $6 \times 5$  mm). The photopolymerizations were carried out on a TA Instruments Q100 differential photocalorimeter (DPC). Gel permeation chromatography (Viscotek) was carried out with THF solvent using polystyrene standards. UV-vis spectra were taken on a Varian UV-Visible Carry 50 spectrophotometer. Phosphorescence spectra were recorded on a Jobin Yvon-Horiba Fluoromax-P in a cold finger at 77 K. A Nicolet 6700 FT-IR spectrophotometer was used for recording IR spectra.

### 2.3. Synthesis of monomeric photoinitiators

#### 2.3.1. 2-((4-Benzoylphenoxy)methyl)acrylic acid (PI-1)

TFA (0.5 mL) was added dropwise to *tert*-butyl 2-((4-benzoylphenoxy)methyl)acrylate (0.20 g, 0.6 mmol), whose

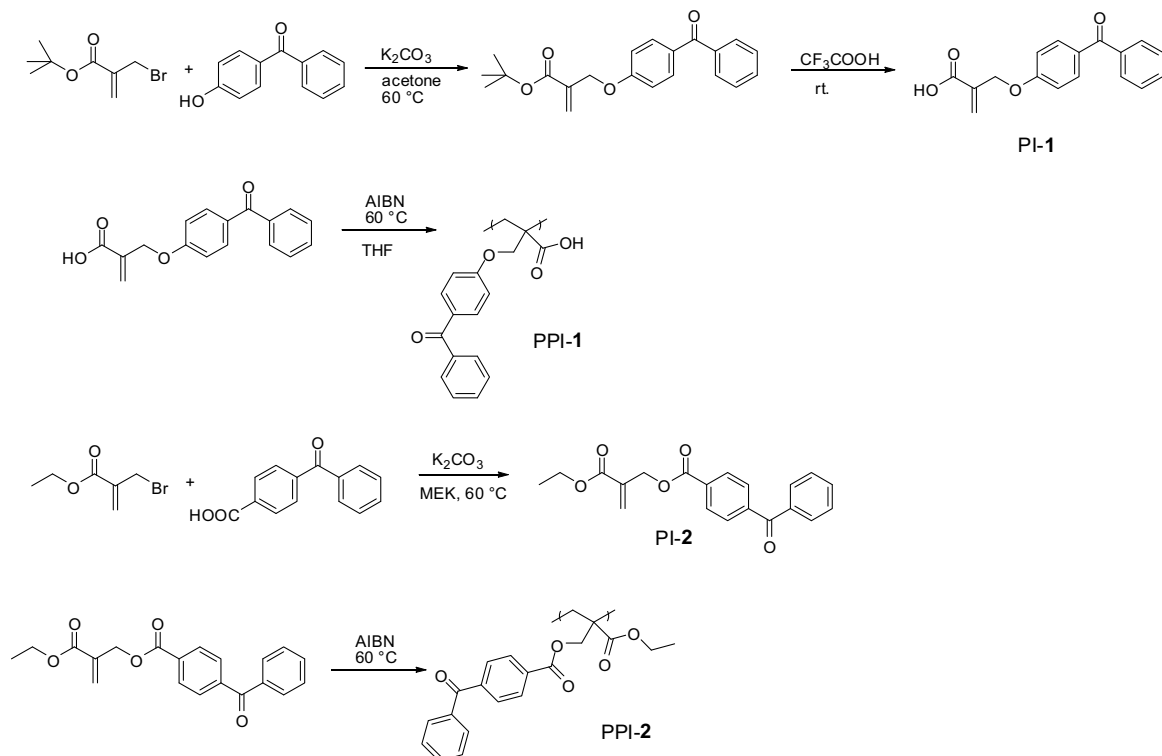


Fig. 2. Synthesis of novel BP-containing photoinitiators.

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