

## Structure-reactivity relationships of novel monomeric photoinitiators



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## ABSTRACT

Two different groups of methacrylates containing Type I or Type II photoinitiating moieties were synthesized and evaluated for use in UV curing applications. The first, a novel group of monomeric photoinitiators (MPIs) were synthesized by reactions of *tert*-butyl  $\alpha$ -bromomethacrylate (TBBr) with 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959), 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184) and 4-hydroxyacetophenone to give monomers MPI1, MPI3 and MPI4 respectively; and conversion of MPI1 to MPI2 by cleavage of *tert*-butyl ester groups with trifluoroacetic acid. The second group of photoinitiators were synthesized by reaction of 2-isocyanatoethyl methacrylate (IEM) with Irgacure 2959 (MPI5) and 4-hydroxybenzophenone (MPI6). All these MPIs' absorption range in the UV region was found to be similar to their nonmonomeric analogs. Their photoinitiating abilities in the polymerizations of hexane-1,6-diol diacrylate (HDDA), 2-hydroxyethyl methacrylate (HEMA) and trimethylolpropane triacrylate (TMPTA) were studied using photodifferential scanning calorimeter and the kinetic parameters were correlated with the structures of the photoinitiating systems. Photoinitiating activities of investigated Type I photoinitiators, including small molecule commercial analogs, during polymerizations of HDDA and TMPTA are very slightly influenced by MPIs structure. However, the MPI structure is found to be important for the curing of HEMA, and some of the synthesized MPIs have better efficiency than commercial ones tested. The MPIs based on Irgacure 2959, Irgacure 184 and benzophenone (BP), with similar or increased photoinitiating activity compared to their commercial precursors, appear to be promising photoinitiators. An extra advantage of MPIs is their incorporation into the final formulations, reducing undesired migration of small molecules.

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## 1. Introduction

Photopolymerization has been the subject of growing interest in polymer science and technology due to a wide range of application areas in coatings, adhesives, inks, printing plates, dental materials and microelectronics [1–3]. Photoinitiators, which produce radicals upon absorption of light by either (i) direct fragmentation via bond cleavage, or (ii) a bimolecular reaction where the excited molecule abstracts a hydrogen atom from another molecule, or (iii) the excited molecule transferring its energy to another molecule; to produce radicals and initiate polymerization of monomers, play an important role in these processes. The following requirements are desirable for

photoinitiators: high absorptivity in the spectral region of lamp emission, good solubility in the formulation, high quantum yield, high photoreactivity, low odor, low toxicity, no yellowing due to the presence of migrating residues in the polymer, and good storage stability [4]. Small molecular weight commercial photoinitiators do not exhibit all of these properties. Therefore, in recent years, the development of monomeric (MPI) [5–12] and polymeric photoinitiators (PPIs) [13–25] which do, has become an important issue.

Monomeric and polymeric photoinitiators which contain free radical photoinitiating groups generate radicals by photofragmentation (Type I) or hydrogen abstraction (Type II). We previously synthesized a series of BP-containing monomeric and polymeric photoinitiators based on highly polymerizable alkyl  $\alpha$ -hydroxy methacrylate (RHMA's) [7,10,11]. In the present work, we have attached both Type I and Type II photoinitiators to two different

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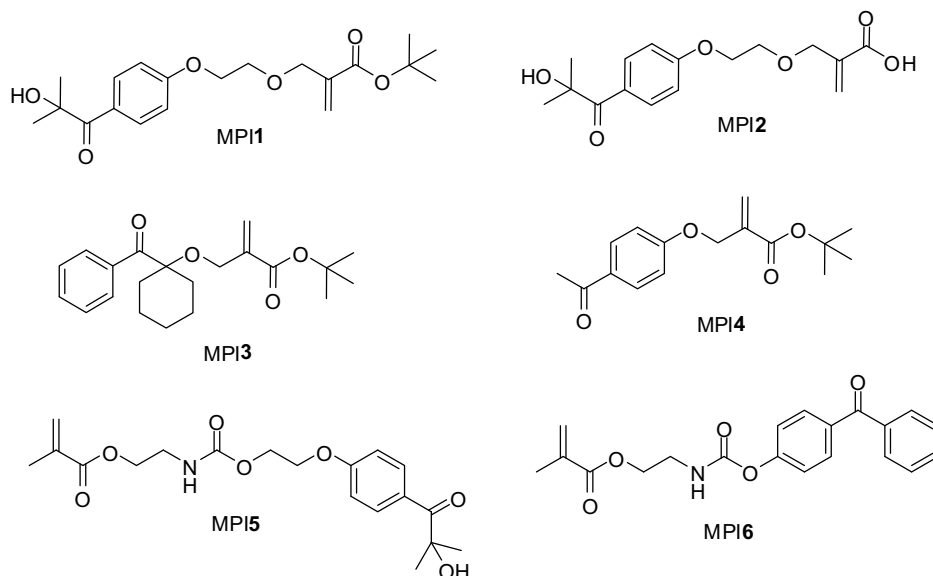


Fig. 1. Structures of synthesized MPIs.

methacrylates (TBBr & IEM) in order to combine the advantages of polymerizability with the advantageous properties of commercial photoinitiators (Fig. 1). We also wanted to investigate the effect of attaching the same photoinitiator to different monomers; the first such investigation to the best of our knowledge. The Type I photoinitiators were Irgacure 2959 and Irgacure 184, and the Type II photoinitiators, BP and acetophenone (AP). In particular, one of the photoinitiators (from TBBr) also has an adhesion promoter carboxylic acid group, which might make it important for metal, glass and hyperbranched polymer surface applications. Monomers

MPI1-MPI4 are novel and MPI5 and MPI6 are mentioned in two different patents [26,27].

## 2. Experimental

### 2.1. Materials

TBBr was synthesized according to literature procedures [28,29]. Irgacure 2959, Irgacure 184, 4-hydroxybenzophenone, 4-hydroxyacetophenone, IEM, HDDA, HEMA, TMPTA, ethyl 4-

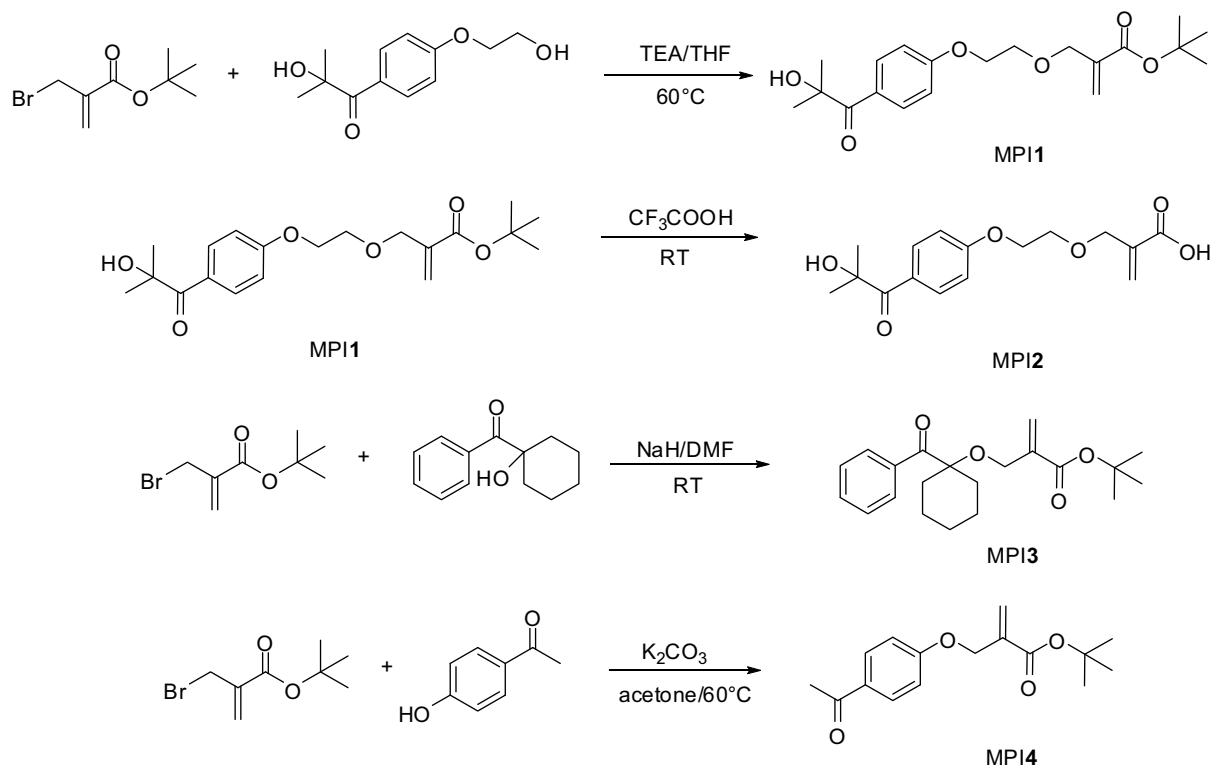


Fig. 2. Synthesis of MPIs from TBBr.

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