Photopolymerization

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N-Heterocyclic Carbene Boranes Accelerate Type I Radical Photopolymerizations and Overcome Oxygen Inhibition[**]

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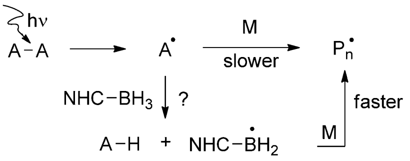
Dedicated to Professor Bernadette Charleux

Radical photopolymerizations are widely used in industry for applications in laser imaging and radiation curing of inks and coatings. In these processes, growth of a crosslinked polymer is triggered by radicals that are generated when a photoinitiator (PI) is activated by light.[1] There are two distinct types of PIs. For Type I PIs, light irradiation directly generates radicals through homolytic bond cleavage and these radicals initiate polymerization. For Type II PIs, light irradiation first excites the initiator, such as benzophenone, to its triplet state species, which in turn abstracts a hydrogen atom from a suitable co-initiator; the co-initiator-derived radicals then initiate the polymerization.

We have recently reported that NHC-boranes are a powerful class of co-initiators for Type II photopolymerizations.[2] Their effectiveness can be attributed to a rapid hydrogen-atom transfer from NHC-boranes to benzophenone in its excited state and to the high nucleophilicity of the generated NHC-boryl radicals, which add rapidly to acrylates.

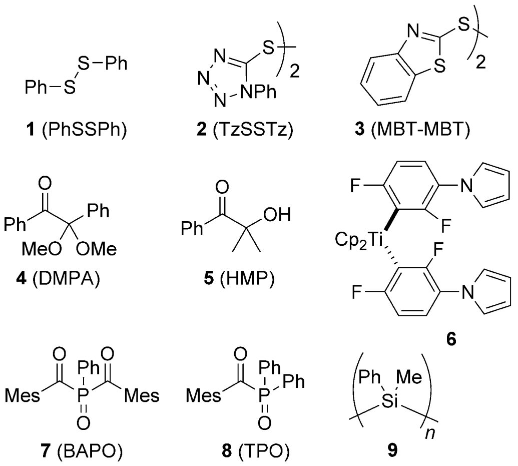
Type I PIs have some advantages over Type II PIs. The excited states of Type I PIs are very short lived, and thus, excited-state quenching by oxygen is much weaker. Additionally, polymerizations using Type I PIs have higher polymerization rates.[1] Some Type II co-initiators are corrosive (amines) or are foul smelling (thiols).

Co-initiators are not used with Type I PIs. Nevertheless, we decided to test NHC-boranes as additives in Type I photopolymerizations because the rate constant for addition of the NHC-boryl radical $\mathbf{10}^{\bullet}$ (see Scheme 3) onto methyl acrylate is larger than those of PI-derived radicals (see the Supporting Information, Table S1). We envisioned that if hydrogen transfer from the NHC-boranes to the Type I PI-derived radicals was sufficiently rapid, then the polymerization efficiency might be improved (Scheme 1).[3] We report herein a general method to enhance the reactivity of known Type I PIs in the photopolymerization of acrylates.



Scheme 1. General principle of the NHC-borane accelerated Type I photopolymerization. A–A is a Type I photoinitiator (structures given in Scheme 2). $A^{\bullet}$ is a radical derived from homolytic cleavage of the photolabile bond in the photoinitiator. M = monomer, NHC = N-heterocyclic carbene.

The PIs that were investigated are shown in Scheme 2: disulfides **1**–**3**, which generate thiyl radicals upon cleavage of the S–S bond;[4] acetophenone derivatives **4** and **5**, which generate carbon-centered benzoyl, 2-hydroxypropyl, or dimethoxybenzyl radicals upon Norrish Type I cleavage;[5] titanocene **6**, which generates aryl and cyclopentadienyl radicals;[5,6] the acylphosphine oxides bisacylphosphine oxide (BAPO; **7**) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO;



Scheme 2. Type I photoinitiators used in this work. Cp = cyclopentadienyl, Mes = mesityl.

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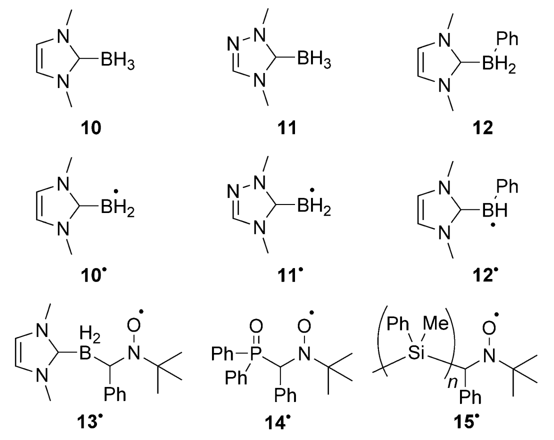
8), which generate phosphinoyl radicals upon cleavage of C–P bonds;[7] and polyphenylmethylsilane (**9**), which generates silyl radicals through Si–Si bond cleavage.[8] NHC-boranes **10**–**12** were selected as additives (Scheme 3).



Scheme 3. Structures of NHC-borane additives (top), derived boryl radicals (middle) and spin-trapped radicals (bottom) used in this work.

We carried out two kinds of photopolymerizations. In open systems, 20 μm thick films were deposited on a BaF_2 pellet and irradiated using a polychromatic light source. Oxygen from the air can diffuse into the photosensitive formulation during this process, and therefore strong inhibition of the photopolymerization under such conditions is common.[9] Alternatively, in laminated systems the 20 μm thick photosensitive formulation was sandwiched between two polypropylene films to ensure that no oxygen can enter the polymerization medium, except the amount that is initially dissolved in the monomer.

We tested diphenyldisulfide **1** first because our previous work had shown that phenylthiyl radicals efficiently abstract hydrogen atoms from **10**.[10] Disulfide **1** was dissolved (1% w/w) in a bulk formulation of trimethylolpropane triacrylate (TMPTA). The double-bond content was followed by real-time FTIR spectroscopy at room temperature (Figure 1a, curve A);[9] no polymerization was observed.

No polymerization was observed when **1** was replaced with **10** (2% w/w). However, when both **1** and **10** were added, polymerization was observed (Figure 1a, compare curves A and B to curve C). In situ IR monitoring of the B–H vibrational band showed that approximately half of the B–H bonds were consumed during polymerization (Figure 1b). Next, a solution of disulfide **2** and **10** was irradiated in the presence of α-phenyl-*N*-*tert*-butyl nitrone (PhCH=N(O)*t*Bu; PBN) in an ESR-spin trap cavity. The only signals observed were those of the adduct of radical **10•** and PBN (**13•**;[11] Figure 1c, $a_N = 15.4$; $a_H = 2.1$ and $a_B = 4.3$ G for **10•**). Similar ESR spectra were obtained two minutes after light irradiation was stopped. Using the same experimental setup, in the absence of **10**, only the thiyl-derived nitroxide was observed (see the Supporting Information, Figure S5).

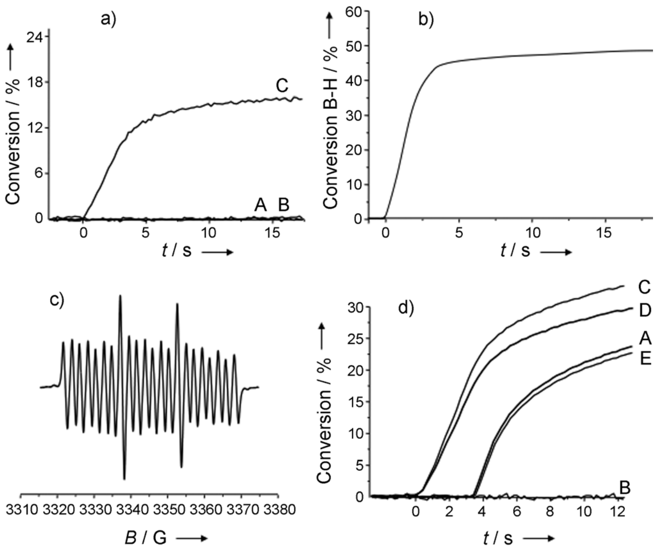


Figure 1. Photopolymerization of TMPTA. a) Under air for different PIs: (Curve A) **1** (1% w/w); (Curve B) **10** (2% w/w); (Curve C) **1**/**10** (1%:2% w/w). b) B–H conversion for the polymerization of TMPTA; (**2**/**10** (1%:2% w/w)). c) ESR spin trapping (PBN) spectra for the formation of **10•** (**2**/**10**) under light irradiation ([PBN] = 0.01 M, [**10**] = [**2**] = 0.05 M). d) The use of different PIs in the laminated system: (Curve A) **1** (1% w/w); (Curve B) **10** (2% w/w); (Curve C) **1**/**10** (1%:2% w/w); (Curve D) **1**/**12** (1%:3.3% w/w); (Curve E) **1**/Ph_3P-BH_3 (1%:5% w/w).

In the laminated system, **10** alone did not initiate polymerization (Figure 1d, curve B). Disulfide **1** alone was able to initiate polymerization, albeit inefficiently (Figure 1d, curve A), and the polymerization was initially strongly inhibited because of the presence of dissolved oxygen (Figure 1d, curve A). Conversely, when **10** and **1** were used together, the polymerization started immediately and the monomer conversion was much better (Figure 1d, curve C). When triphenylphosphine borane (Ph_3P–BH_3) was used in place of **10**, the same result as that of using **1** alone was observed (Figure 1d, compare curves A and E). The use of the other two disulfides (**2** and **3**) led to similar results (see the Supporting Information, Figure S1), as did the use of a different acrylate (ethoxylated pentaerythritol tetraacrylate, EPT) either under air in an open system or in a laminated system (see the Supporting Information, Figure S1).

We next examined the efficiency of the photopolymerization reaction under aerobic conditions wherein other photocleavable initiators were used in the presence or the absence of NHC-borane additives (Figure 2 and see the Supporting Information, Figure S2). When **10** was included, the conversion of the reactions using **4** (Figure 2a, curve B) and **7** (Figure 2b, curve B) were almost doubled in comparison to the conversions of the reactions in the absence of **10**. The addition of **10** led to a corresponding four-fold increase in conversion for the reactions in which titanocene initiator **6** (Figure 2c, curve B), HMP, and TPO were used (see the Supporting Information, Figure S2). Importantly, even the use of silicon-based initiator **9** led to efficient photopolymerization in the presence of **10** or **11** (Figure 2d, curves B and C).

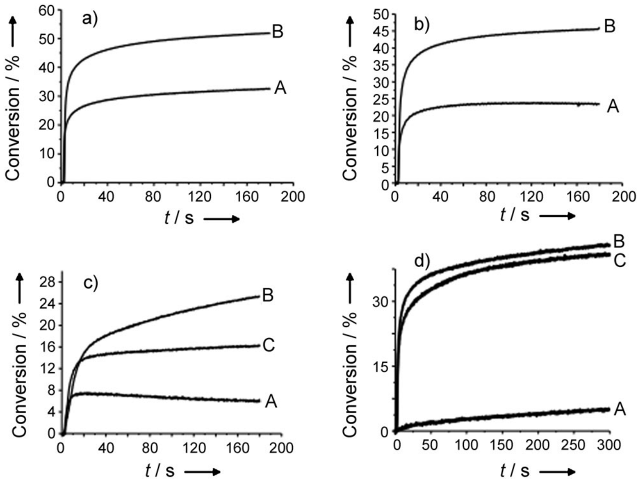
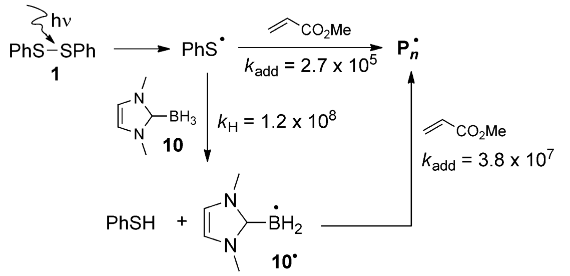


Figure 2. Polymerization profiles for TMPTA under air for different photoinitiators. a) (Curve A) **4** (1 % w/w); (Curve B) **4/10** (1 %:2 % w/w). b) (Curve A) **7** (1 % w/w); (Curve B) **7/10** (1 %:2 % w/w). c) (Curve A) **6** (1 % w/w); (Curve B) **6/10** (1 %:2 % w/w); (Curve C) **6/11** (1 %:2 % w/w). d) (Curve A) **9** (1 % w/w); (Curve B) **9/10** (1 %:2 % w/w); (Curve C) **9/11** (1 %:2 % w/w).

ESR spin-trapping experiments were also conducted for the photopolymerization reactions promoted by TPO **8** (generating a phosphorus-centered radical) and polysilane **9** (generating a silicon-centered radical). Irradiation of **8** in the presence of PBN in *tert*-butyl benzene delivered the nitroxide adduct **14**$^\bullet$, which is derived from addition of a phosphinoyl radical to PBN (see the Supporting Information, Figure S3). Similarly, when **9** was irradiated, in the presence of PBN, the silyl-based adduct **15**$^\bullet$ was observed. When both of these reactions were performed in the presence of **10**, only **13**$^\bullet$ was observed.

Taken together, the observations show that the presence of NHC-boranes, species that do not absorb light and are thus not PIs, improves the polymerization profiles of all PIs tested. We believe that the radicals initially formed directly from the PIs rapidly abstract hydrogen atoms from NHC-boranes, to give the corresponding NHC-boryl radicals. These radicals then react with TMPTA, thus initiating the polymerization. The hydrogen atom transfer is fast in all cases because in the presence of NHC-borane, we only observed long-lived (over two minutes) spin adducts derived from the boryl radicals, and never those derived from the PI radicals. The NHC-boranes **10** and **11**, the boryl radicals (**10**$^\bullet$ and **11**$^\bullet$) of which add to acrylate with the highest rate constants,[11,12] are the best initiators.

In the case of thiyl radicals, the rate constants of all the elementary processes have been measured (Scheme 4).[10,13] Irradiation of diphenyldisulfide leads to thiophenyl radicals, which add slowly to methyl acrylate ($k_{\text{add}} = 2.7\times10^5\,\text{M}^{-1}\text{s}^{-1}$), which was chosen as a typical acrylate and is a reaction partner of mismatched polarity in this case. Instead, PhS$^\bullet$ rapidly abstracts a hydrogen atom from **10** ($k_{\text{H}} = 1.2\times10^8\,\text{M}^{-1}\text{s}^{-1}$).[10] Then **10**$^\bullet$ adds to methyl acrylate very rapidly ($k_{\text{add}} = 3.8\times10^7\,\text{M}^{-1}\text{s}^{-1}$).[12] Thus, one slow initiation step is replaced by two extremely fast steps.



Scheme 4. Rate acceleration of photopolymerization induced by NHC-BH$_3$ (**10**) using PhSSPh (**1**) as the PI. Values are in $\text{M}^{-1}\text{s}^{-1}$.

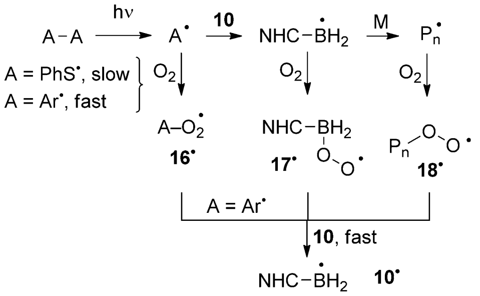
The presence of Ph$_3$P–BH$_3$ does not lead to an improved photopolymerization reaction using **1** because phenylthiyl radicals do not abstract hydrogen atoms from Ph$_3$P–BH$_3$ fast enough ($k_{\text{H}} < 10^6\,\text{M}^{-1}\text{s}^{-1}$ for PhS$^\bullet$/Ph$_3$P-BH$_3$). [10] Finally, the measured conversion of the B–H bonds is consistent with the transformation of more than one B–H bond per NHC-borane, thus suggesting that the boron atoms are also involved in the cross-linking of the final polymer.

Significantly, although photopolymerizations using commercial PIs are usually inhibited when conducted in the presence of oxygen, our studies herein show that oxygen has no such effect when NHC-boranes also form part of the reaction mixture. In the laminated systems, oxygen inhibition usually leads to a polymerization delay (see Figure 1 d, curve A) that is equal to the time needed to consume all of the dissolved oxygen. The inhibition problem is more significant for polymerization under air because diffusion of oxygen leads to continuous suppression of polymerization (see Figure 1 a, curve A). In the presence of NHC-boranes, the polymerizations start immediately and give higher conversions (for example in Figure 1 a and Figure 1 d, compare curves A and curves C).

How does oxygen inhibit the polymerization and how is this inhibition negated in the presence of NHC-boranes? As mentioned above, quenching of the excited states of PIs by oxygen is not expected to be important. However, oxygen reacts with and traps the different radicals involved in the polymerization (Scheme 5), including i) radicals formed from the PIs (to give **16**$^\bullet$); ii) NHC-boryl radicals **10**$^\bullet$ (to give **17**$^\bullet$); and iii) the growing radical-bearing polymer chains (to give **18**$^\bullet$).

Initiator-derived radicals, such as thiyl radicals, react slowly with oxygen. However, aryl radicals react rapidly with oxygen to give unproductive peroxyl radicals represented by **16**$^\bullet$. Oxygen can also react rapidly with **10**$^\bullet$ to give boraperoxyl radicals **17**$^\bullet$.[2] We know that **17**$^\bullet$ reacts fast with **10** to regenerate **10**$^\bullet$.[12] This turnover maintains efficient initiation. However, this reaction only partially explains the beneficial effect of **10** because growing polymer chains can also react with oxygen to give **18**$^\bullet$. The inhibition can only disappear if the formation of **18**$^\bullet$ does not also terminate the chemical reaction.

To model the reactivity of both **16**$^\bullet$ and **18**$^\bullet$, we measured the rate constant for hydrogen-atom transfer from **10** to *t*BuOO$^\bullet$ by kinetic ESR spectroscopy. We measured a high



Scheme 5. The reactivity of O_2 in the presence of NHC-boranes. Ar = aryl.

rate constant ($350\,\text{M}^{-1}\text{s}^{-1}$, see the Supporting Information, Figure S4). The electrophilic peroxyl radicals thus react rapidly with the nucleophilic species of matched polarity **10**,[10,14] generating **10**$^{\bullet}$.

On the basis of this model reaction we believe that NHC-borane **10** reacts with all of the oxygen adducts **16**$^{\bullet}$, **17**$^{\bullet}$, and **18**$^{\bullet}$ to regenerate the initiating radical **10**$^{\bullet}$. The mechanism behind the negation of oxygen inhibition in Type II photopolymerization thus remains valid for Type I polymerizations.

In summary, the presence of NHC-boranes significantly improves the efficiency of Type I photopolymerizations mediated by a diverse range of photoinitiators. This striking effect is due to two distinct features of NHC-boranes. First, the latter rapidly transfers hydrogen atoms to the radicals initially formed from the PIs to give highly nucleophilic NHC-boryl radicals, which add rapidly to the monomers. Second, NHC-boranes reacts with all unproductive peroxyl radicals, formed in the presence of oxygen, to give an initiating species, thus negating the oxygen inhibition that would have occurred in the absence of NHC-borane. The formulations containing NHC-boranes and the photoinitiators were stored for days under air, in the dark and at room temperature without decomposition, an attribute that is also important for practical use.

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