

# The 'onium butyltriphenylborates as novel donor–acceptor initiators for free radical photopolymerization

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**Novel donor–acceptor initiators, 'onium butyltriphenylborates, containing both an 'onium cation (electron-accepting radical generator) and a butyltriphenylborate anion (electron-donating radical generator) within the same molecule, are synthesized and investigated for the photopolymerization of an acrylic monomer mixture.**

In order to obtain an efficient free radical generating system for many areas of photosensitive materials research, a more efficient initiator or initiator system (*i.e.* a combination of sensitizer and initiator) which generates free radicals for polymerization is required. Many such initiators or initiator systems have been investigated.<sup>1</sup>

Most well known initiator systems are based on photoinduced electron-transfer reactions and are either electron-donating sensitizer/electron-accepting initiators (*e.g.* 'onium salts)<sup>2,3</sup> or electron-accepting sensitizer/electron-donating initiators (*e.g.* borates or amines).<sup>3,4</sup>

The above initiator systems generate the free radical after a photo-induced electron-transfer from the electron-donating sensitizer to the electron-accepting initiator (or from electron-donating initiator to electron-accepting sensitizer) by light irradiation. The free radical comes from decomposition of the initiator and produces polymerization.

The cation radical (or anion radical) of a sensitizer produced by the reaction is usually inert to free radical polymerization. However, if one utilizes the inert cation radical (or anion radical) of the sensitizer, generating an active free radical for radical polymerization, the quantum efficiencies of the radical generation will be increased, and furthermore, the resulting polymerization will be extremely efficient.

Herein we report the discovery that the 'onium butyltriphenylborates containing both an 'onium cation (electron-accepting radical generator) and a borate anion (electron-donating radical generator) within the same molecule are novel donor–acceptor initiators for extremely efficient free radical photopolymerization.

The novel donor–acceptor initiators diphenyliodonium butyltriphenylborate **1** or dimethylphenacylsulfonium butyltriphenylborate **2** were prepared by the reactions of diphenyliodonium chloride or dimethylphenacylsulfonium bromide with lithium butyltriphenylborate,<sup>5</sup> respectively.‡ Both the 'onium borates were characterized by spectroscopic data and elemental analyses.§

The absorption spectra of **1** in CH<sub>2</sub>Cl<sub>2</sub> and MeCN are shown in Fig. 1. For comparison, the absorption spectra of tetrabutylammonium butyltriphenylborate **3**, an electron-donating initiator, and diphenyliodonium hexafluorophosphate **4**, an electron-accepting initiator, in CH<sub>2</sub>Cl<sub>2</sub> are also presented.

Compound **1** in CH<sub>2</sub>Cl<sub>2</sub> exhibits a weak absorption in the 320–400 nm region, while **3** and **4** in CH<sub>2</sub>Cl<sub>2</sub> do not exhibit absorption in the same region. The weak absorption is not observed in MeCN which is a polar solvent. It is important that the enhanced absorptivity of **1** in CH<sub>2</sub>Cl<sub>2</sub> is reproducible and is quite clearly unique to **1** in the non-polar solvent.

We attribute the weak absorption observed for **1** in CH<sub>2</sub>Cl<sub>2</sub> to an ion-pair charge transfer transition from the butyltri-

phenylborate anion to the diphenyliodonium cation. Also the spectrum of **2** in CH<sub>2</sub>Cl<sub>2</sub> showed a slightly greater absorptivity in the 270–350 nm region, in contrast to **3** and dimethylphenacylsulfonium tetrafluoroborate **5** which do not exhibit transitions in the same region. However, both 'onium borates **1** and **2** exist primarily as ion-pairs in CH<sub>2</sub>Cl<sub>2</sub> and as free ions in MeCN.

In order to reveal the capability of the 'onium borates as free radical polymerization initiators, we carried out the photopolymerization of tetrahydrofurfuryl acrylate (THFA). 4,4'-Bis(dimethylamino)benzophenone (MK), 2-chlorothioxanthone (CTX) and 3,3'-carbonylbis(7-diethylaminocoumarin) (KCD) were used as the sensitizers. The photopolymerization was monitored in IR spectroscopy.<sup>6</sup> To obtain the percentage of double bond conversion ( $\gamma$ ), the initiator, sensitizer, THFA and solvent were placed in a sealed KBr cell. The sample was irradiated with light (365 nm) from a high pressure mercury lamp passed through a band pass filter. The IR spectra were taken before and after the irradiation and the absorbances corresponding to an acrylic bending mode at 810 cm<sup>-1</sup> were used for the calculations of  $\gamma$  [eqn. (1)], where  $A_0$  and  $A_t$

$$\gamma = (A_0 - A_t)/A_0 \quad (1)$$

are the absorbances corresponding at 810 cm<sup>-1</sup> before and after the irradiation, respectively. The rate of polymerization ( $R_p$ ) was obtained from the slope ( $\Delta\gamma/\Delta t$ ) of the linear part of the time– $\gamma$  curve measured by this setup [eqn. (2)]. The values of  $R_p$  were measured below a  $\gamma$  of 10%. [THFA]<sub>0</sub> is the THFA concentration before the light exposure.

$$R_p = [\text{THFA}]_0 (\Delta\gamma/\Delta t) \quad (2)$$

The relative rates of polymerization, calculated using eqns.(1) and (2), are summarized in Table 1. The 'onium borates **1** or **2** clearly show much higher performances as initiators for the polymerization of THFA than **3**, **4** or **5** with any of the sensitizers.

The most pronounced difference was observed with the results of  $R_p$  in CH<sub>2</sub>Cl<sub>2</sub>. The  $R_p$  in CH<sub>2</sub>Cl<sub>2</sub> increased about

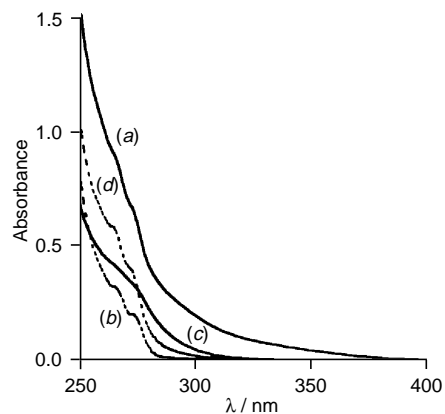


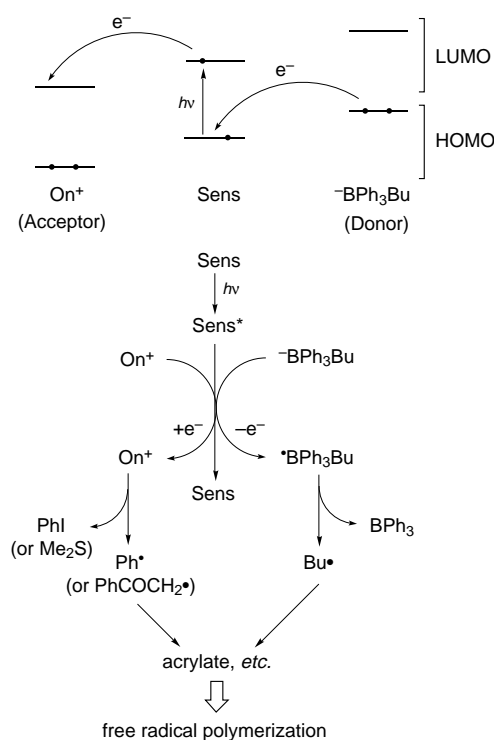
Fig. 1 UV–VIS absorption spectra of (a) **1**, (b) **3**, (c) **4** in CH<sub>2</sub>Cl<sub>2</sub> and (d) **1** in MeCN. Solution concentrations = 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>.

**Table 1** Rate of photopolymerization of THFA with various sensitizers and initiators in MeCN<sup>a</sup>

Run	Sensitizer <sup>b</sup>	Initiator	$R_p$ <sup>c</sup> /mol dm <sup>-3</sup> s <sup>-1</sup>
1	MK	<b>1</b>	5.1 (16) <sup>d</sup>
2		<b>2</b>	4.6 (15) <sup>d</sup>
3		<b>3</b>	0.58 (0.69) <sup>d</sup>
4		<b>4</b>	0.21 (0.26) <sup>d</sup>
5		<b>5</b>	0.062
6	CTX	<b>1</b>	15
7		<b>2</b>	11
8		<b>3</b>	4.0
9		<b>4</b>	2.2
10		<b>5</b>	0.26
11	KCD	<b>1</b>	0.29
12		<b>2</b>	0.26

<sup>a</sup> Radiant power of the light emission at 365 nm was 1.6 mW cm<sup>-2</sup>; [THFA]<sub>0</sub> = 9.18 × 10<sup>-1</sup> mol dm<sup>-3</sup>; [Initiator]<sub>0</sub> = 1.43 × 10<sup>-2</sup> mol dm<sup>-3</sup>.

<sup>b</sup> [Sensitizer] corresponds to the amount required for 50% transmittance at 365 nm. <sup>c</sup> Rate of polymerization. <sup>d</sup> In CH<sub>2</sub>Cl<sub>2</sub>.



**Scheme 1**

three-fold over the  $R_p$  in MeCN (runs 1 and 2) with the 'onium borate initiators. The reason is that both the 'onium borates exist primarily as ion-pairs in CH<sub>2</sub>Cl<sub>2</sub> and as free ions in MeCN. The photo-induced electron-transfer reaction between the sensitizer and the 'onium borate in CH<sub>2</sub>Cl<sub>2</sub> occurs more efficiently than does the reaction in MeCN. CTX is a more effective sensitizer than MK or KCD. The photopolymerization with KCD and **3**, **4** or **5** were too poor to measure  $R_p$  using this apparatus.

Our postulated reaction mechanism for the sensitizer and the 'onium borate in MeCN is depicted in Scheme 1. Thus, the sensitizer absorbs light at 365 nm which initially generates the excited state of the sensitizer (Sens\*). Next, Sens\* accepts an electron from a butyltriphenylborate in the 'onium borate, and at the same time, donates an electron to an 'onium cation in the 'onium borate. Consequently, the produced butyltriphenylboranyl radical and 'onium radical decompose to form the butyl radical and phenyl (or phenacyl) radical. These radicals initiate polymerization in the presence of a suitable monomer (e.g. THFA). This is also supported by the analysis of the products from the photolysis of the 'onium borates. Conversely, the reaction in CH<sub>2</sub>Cl<sub>2</sub> would occur as the ion-pair complex of 'onium borates.

Thus, we have demonstrated not only that the 'onium borates are efficient donor-acceptor initiators for free radical photopolymerization but also the generating procedure for the free radicals.

## Footnotes

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‡ *General procedure:* A 100 ml round-bottom flask equipped with a Teflon-covered magnetic stirring bar was charged with diphenyliodonium chloride or dimethylphenacylsulfonium bromide (20 mmol) dissolved in water (10 ml). To the flask, lithium butyltriphenylborate (20 mmol) was added with stirring. Diphenyliodonium butyltriphenylborate **1** or dimethylphenacylsulfonium butyltriphenylborate **2** rapidly precipitated. Compound **1** or **2** was collected by filtration and recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>-heptane (1:4). The yields were 43% for **1** and 87% for **2**, respectively.

§ Satisfactory elemental analyses have been obtained. *Selected spectroscopic data for 1:*  $\delta_H$  [270 MHz; (CD<sub>3</sub>)<sub>2</sub>SO; Me<sub>4</sub>Si] 0.68–1.00 (m, 7 H, PrCH<sub>2</sub>B<sup>-</sup>), 1.11–1.27 (m, 2 H, CH<sub>2</sub>B<sup>-</sup>), 6.68–6.78 (m, 3 H, *p*-PhB<sup>-</sup>), 6.84–6.94 (m, 6 H, *m*-PhB<sup>-</sup>), 7.14–7.24 (m, 6 H, *o*-PhB<sup>-</sup>), 7.47–7.57 (m, 4 H, *o*-PhI<sup>+</sup>), 7.60–7.70 (m, 2 H, *p*-PhI<sup>+</sup>), 8.17–8.27 (m, 4 H, *m*-PhI<sup>+</sup>); For **2:**  $\delta_H$  [270 MHz; (CD<sub>3</sub>)<sub>2</sub>SO; Me<sub>4</sub>Si] 0.68–1.00 (m, 7 H, PrCH<sub>2</sub>B<sup>-</sup>), 1.11–1.27 (m, 2 H, CH<sub>2</sub>B<sup>-</sup>), 2.94 (s, 6 H, Me<sub>2</sub>S<sup>+</sup>), 5.40 (s, 2 H, COCH<sub>2</sub>S<sup>+</sup>), 6.68–6.78 (m, 3 H, *p*-PhB<sup>-</sup>), 6.84–6.94 (m, 6 H, *m*-PhB<sup>-</sup>), 7.14–7.24 (m, 6 H, *o*-PhB<sup>-</sup>), 7.58–7.68 (m, 2 H, *m*-PhCO), 7.73–7.83 (m, 1 H, *p*-PhCO), 7.97–8.07 (m, 2 H, *o*-PhCO).

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