Tetramethylammonium Tetraorganylborates as Coinitiators with 5,7-Diiodo-3-butoxy-6-fluorone in Visible Light Polymerization of Acrylates[1]

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Introduction

Upon oxidation, tetraorganylborate anions have been shown to be very useful as free-radical sources (eq 1).

$$R_4B^- - 1e^- \rightarrow R_3B + R^\bullet \qquad (1)$$

In an initial application, Schuster *et al.*[2] reported the cyanine dye−tetraorganylborate salts could be used as visible light initiators for the polymerization of acrylates. The mechanism of the initiation step[2,3] involves alkyl radical formation as a result of photoinduced electron transfer from a borate anion to the singlet excited state of the cyanine dye cation, followed by addition of the alkyl radical formed to the carbon−carbon double bond of the acrylate. Several have patented related photoinitiating systems which include various visible light and IR absorbing dyes in combination with a variety of borates.[4] However, there have been almost no studies of structural relationships in borates with more than one alkyl ligand on boron. Most of the reports have been confined to triarylalkyl- or tetraarylborate systems.[2,5]

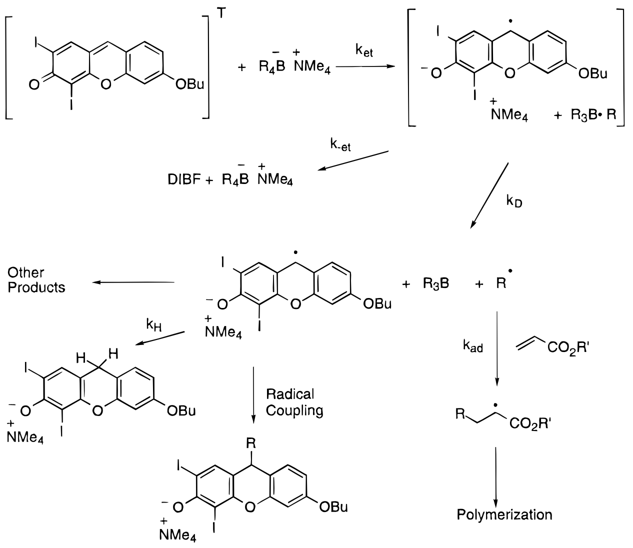
In this paper, we have compared the reactivity of several tetraalkylammonium tetraalkyl-, trialkylaryl-, dialkyldiaryl-, and alkyltriarylborates as coinitiators with 5,7-diiodo-3-butoxy-6-fluorone (DIBF, $\lambda_{max} = 470$ nm in CH_3CN) in the photopolymerization of a standard acrylate composition.[6] Dialkyldiphenylborates have been found to be of good reactivity, solubility, and better stability in a selected acrylic formulation and will likely be the coinitiators of choice in future applications. Tetramethylammonium tetraalkyl- and trialkylarylborates were unstable when mixed with the previously studied formulation and caused rapid polymerization during dissolution in the dark.[6] Therefore, in order to carry out the studies without a complicating thermal polymerization, a borate and DIBF were first dissolved in *N*,*N*-dimethylacrylamide (DMAA) and then mixed with the less reactive 1,6-hexanediol diacrylate.

Experimental Section

1,6-Hexanediol diacrylate was obtained from Monomer-Polymer & Dajac Laboratories Inc.; DMAA was obtained from Aldrich. DIBF was previously synthesized in this laboratory.[7] Lithium trialkylphenyl-, alkyltriphenyl-, and dialkyldiphenylborates were prepared by addition of phenyllithium to obtained *in situ* trialkyl-, alkyldichloro-, and dialkylchloroboranes, respectively.[8] Tetraalkylborates were prepared by addition of the alkyllithium (or Grignard) to $BF_3 \cdot Et_2O$. The resulting salts were metathesized with tetramethylammonium chloride. The tetramethylammonium tetraorganylborates, except tetrabenzylborate, have been previously characterized.[6]

Tetramethylammonium tetrabenzylborate was prepared via the addition of 4 equiv of BnMgCl to $BF_3 \cdot Et_2O$ in 89% yield; mp 232−234 °C dec (from acetone). ^1H NMR (DMSO-d_6, 200 MHz) δ 7.00 (t, $J = 7.8$ Hz, 8H), 6.87 (d, $J = 7.6$ Hz, 8H), 6.77 (t, $J = 7$ Hz, 4H), 3.05 (s, 12H), 1.36 (q, $J = 5.3$ Hz, 8H). ^{13}C NMR (DMSO-d_6, 50 MHz) δ 152.7, 129.0, 126.6, 120.5, 54.52 (t, $J = 4$ Hz), 34.89 (q, $J = 38$ Hz). ^{11}B NMR (DMSO, 128 MHz) δ −30.14 (referenced to $B(OMe)_3$ as the internal standard). Anal. Calcd for $C_{32}H_{40}BN$: C, 85.51; H, 8.97; N, 3.12. Found: C, 85.41; H, 8.95; N, 3.17.

Scheme 1. Mechanism of Photoinitiation with DIBF/Borate



The formulations studied were prepared from 1,6-hexanediol diacrylate, DMAA (8.77% w/w), DIBF (9.6 × 10^{-6} mol, ca. 0.09% w/w), and tetramethylammonium tetraorganylborate (1.92 × 10^{-5} mol). A drop of formulated mixture was placed between rectangular NaCl plates using a 15 μm Teflon spacer and polymerized with a 75 W dental lamp (0.73 W/cm^2). Double-bond conversion was monitored by following the disappearance of the peak at 811 cm^{-1} (acrylic C=C bond) in the FTIR absorbance spectrum.[9]

Oxidation potentials of the borates were measured by square wave voltammetry[10] on a BAS-100 instrument using 0.1 M $Ag^+/AgNO_3$ solution in acetonitrile as the reference electrode. The measurements were carried out under argon in a 0.1 M solution of tetrabutylammonium tetrafluoroborate in acetonitrile. The electrode was calibrated with ferrocene using its known reduction value (0.06 V)[11] and converted to those relative to SCE by addition of 0.337 V.

Nanosecond laser flash photolysis experiments were performed using the apparatus previously described.[12] Laser irradiation at 470 nm from an optical parametric oscillator (OPO) pumped by the third harmonic (355 nm) of the Q-switched Nd:YAG laser was used for excitation. The rates of DIBF triplet decay and DIBF radical anion formation (as the result of electron transfer from the borates studied) were measured for 2 × 10^{-5} M solutions of DIBF in acetonitrile.

Results and Discussion

The mechanism for photoinitiation with DIBF/tetraalkylammonium alkyltriarylborate has been previously suggested (Scheme 1).[12] Electron transfer from the borate anion to the triplet excited state of DIBF leads to the formation of DIBF radical anion ($DIBF^{\bullet -}$, $\lambda_{max} = 420$ nm) and the boranyl radical which rapidly and irreversibly decomposes producing an alkyl radical. The latter is the most likely initiator of the polymerization of acrylates. DIBF triplet decay rates and the rates of the formation of the DIBF radical anion were measured for each of the tetraorganylborates studied. It was found that the radical anion, $DIBF^{\bullet -}$ forms with the same rate as the triplet-state decays, as shown in Figure 1 for tetramethylammonium tetrabutylborate. This indicates that electron transfer is the only quench-

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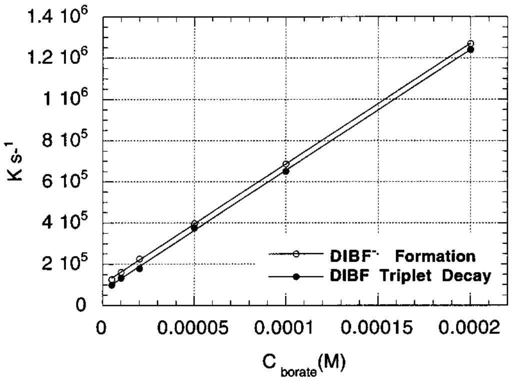

Figure 1. Rates of DIBF triplet decay and DIBF radical anion formation as a function of *n*-Bu_4B NMe_4 concentration.

Table 1. Oxidation Potentials of Borates and Rate Constants for Electron Transfer from the Borates to the Triplet State of DIBF

borate	E_{ox} (V vs SCE)	K_{et} (M^{-1} s^{-1})
n-$BuBPh_3NMe_4$	0.824	6.70×10^7
(c-C_5H_9)BPh_3NMe_4	0.720	7.86×10^8
n-$Bu_2BPh_2NMe_4$	0.481	5.90×10^8
(c-C_5H_9)$_2BPh_2NMe_4$	0.321	4.16×10^9
n-Bu_4BNMe_4	0.298	5.84×10^9
(c-C_5H_9)$_3BPhNMe_4$	0.268	6.15×10^9
($PhCH_2$)$_4BNMe_4$	0.263	4.34×10^9

ing process of DIBF triplet, and the electron transfer rate constants are equal to those of triplet quenching. The electron transfer rate constants obtained for the borates of interest are listed in Table 1.

The Rehm–Weller equation[13] for photoinduced electron transfer suggests a dependence of the free energy change (ΔG_{et}) on the oxidation potentials of borates (E_{ox}):

$$\Delta G_{et} = E_{ox}(D/D^{\bullet +}) - E_{red}(A^{\bullet -}/A) - E^{T} - Ze^2/\epsilon a \qquad (2)$$

where DIBF triplet energy[12] $E^T = 2.3$e V, $E_{red} = -0.9$ V (vs SCE in CH_3CN); $Ze^2/\epsilon a$ is the Coulombic energy, which is the free energy gained by bringing the radical ions formed to an encounter distance a in a solvent with dielectric constant ϵ. Since oxidation of the borate anion is irreversible, the oxidation potentials of the borates could not be precisely measured by electrochemical techniques.[14] However, the peak potentials obtained by either cyclic or square wave voltammetry usually follow the same trend as those measured by kinetic methods.[2,14] Therefore, these can be used for the comparison of the borates. The measured oxidation potentials of the tetramethylammonium tetraorganylborates are compiled in Table 1.

As was previously reported for the alkyltriphenylborates,[2,3] the rates of alkyl radical formation, as the result of the boranyl radical degradation, are directly related to the known stabilities of the alkyl radicals formed. Since the decay of the boranyl radical is found to be very fast and irreversible, the rate of back electron transfer (k_{-et}) is negligible.[2] Therefore, the efficiencies of alkyl radical formation and, hence, initiation of polymerization depend on the rate of electron transfer from the borate anion to the triplet state of DIBF.

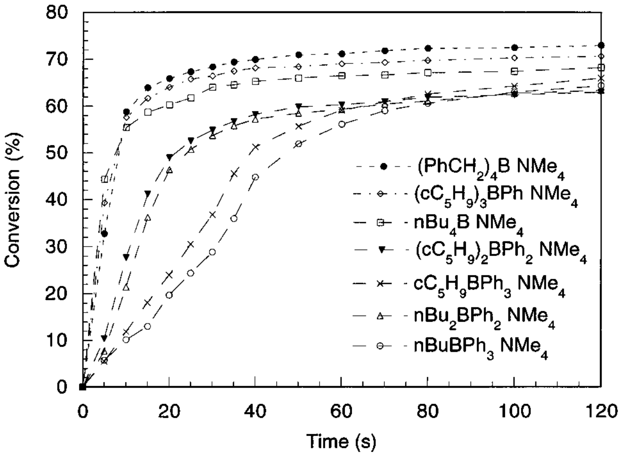

Figure 2. Visible light polymerization of the acrylic formulation with DIBF and tetramethylammonium tetraorganylborates as initiators.

The ease of oxidation of the borates is seen from their oxidation potentials. The tendency is that the more stable radical that can be formed, the easier it is to oxidize the borate. Secondary alkyl radicals are more stable than primary, and cyclopentyltriphenylborate was found to be more reactive than *n*-butyltriphenylborate. The same trend is followed for tetraalkyl-, trialkylaryl-, and dialkyldiarylborates. Thus, dicyclopentyldiphenylborate has a less electropositive peak potential and faster electron transfer rate than dibutyldiphenylborate. Rates of the initiation of photopolymerization follow the same trend under conditions where the borate concentration, relative to the concentration of the dye, is low enough so that a trend can be distinguished (Figure 2).

It has been noted that replacement of aryl(phenyl) ligands on boron by alkyl ligands makes the borates less stable and easier to oxidize. We find there is a marked difference between the rates of photoinitiation of polymerization under the conditions described above when the dialkyldiphenylborates, as opposed to the alkyltriarylborates, are used as coinitiators. Thus, dibutyl- and dicyclopentyldiphenylborates definitely show faster initiation of polymerization than butyl- and cyclopentyltriphenylborates, respectively (Figure 2). Tricyclopentylphenyl- and tetraalkylborates are even more reactive. However, there is not much difference between tetrabenzyl-, tricyclopentylphenyl-, and tetrabutylborates. Even though the rate of electron transfer for tricyclopentylphenylborate is the highest, they show similar excellent reactivity as coinitiators.

Conclusions

The comparative analysis of the borate salts as coinitiators with DIBF shows that the number of alkyl groups per boron determines reactivity. There is not much difference in the reactivity of tetraalkyl- and trialkylarylborates as coinitiators: they are very fast radical producers. However, they are much less stable in the formulations than are dialkyldiarylborates. Dialkyldiphenylborates, on the other hand, initiate polymerization much more rapidly than do alkyltriarylborates. Since they are considerably more stable in formulations than trialkylaryl- and tetraalkylborates and easy to synthesize from a variety of available alkenes, dialkyldiarylborates are likely to be preferred over the slower, less soluble[15] alkyltriarylborates.

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(1) Contribution No. 273 from the Center for Photochemical Sciences.

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(15) Tetraorganylborates become more soluble with the increase of the number of alkyl groups per boron and with more methylenes in the alkyl ligands. The solubility in the monomer can also be improved by altering the ammonium counterion, as in ref 6.

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