Relative Activity of Possible Initiating Species Produced from Photolysis of Tetraphenyl and Triphenylbutyl Borates As Measured by Fluorescence Probe Techniques

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ABSTRACT: Fluorescence probe techniques (FPT) have been used to obtain curing profiles for the polymerization of a model monomer, triethylene glycol diacrylate (TEGDA). A number of new chromophore ammonium salt triphenylbutyl and tetraphenylborates differing only in the structure of the ammonium salt moiety have been used as photoinitiators. The borates were chosen for study so that a comparison of their initiation efficiency would reveal information about the relative activity of possible initiating species produced upon borate photodecomposition. The results support our previous postulate that an α-aminoalkyl radical formed immediately after unimolecular decomposition from the tetraphenylborates is the most effective initiating species and that α−aminoalkyl radicals significantly increase the photoinitiator efficiency of triphenylbutylborates as well. The importance of other radicals to the initiation step is also discussed.

Introduction

The photochemistry of tetrasubstituted borate salts has attracted substantial recent research interest.[2−8] Triphenylbutylborates have been studied most extensively, and the butyl radical formed when they are oxidized has been found to be the dominant initiating species for radical polymerization.[3,7−10] Interestingly, tetraphenylborates paired with a similar cationic partner have been observed to have similar initiating efficiencies.[11−13] Tetraphenylborates, when oxidized, are often prone to back electron transfer. Since phenyl radicals are produced from tetraphenylborates upon oxidation inefficiently, if at all, we have surmised that other initiating species must account for the efficiency of tetraarylborate salts. In our most recent work α-aminoalkyl, phenyl, and *p*-benzoylbenzyl radicals were trapped by methyl methacrylate when benzophenonemethylenetributylammonium triphenylbutylborate was photolyzed in its presence in solution.[14]

Fluorescence probe techniques (FPT) have been recently introduced to measure and compare photoinitiator efficiencies.[12,13,15,16] FPT allow one to measure the polymerization kinetics from relative conversion data collected during the polymerization of systems that are similar. These methods are particularly useful for the evaluation of initiators that are similar in structure and for optimizing their performance. The possibility of collecting data over short time intervals (<1 s) makes the analysis simple and accurate. Several borates differing in the ammonium salt but possessing benzophenone and acetonaphthone chromophores have been chosen for the current work.

Experimental Section

Absorption spectra were recorded on a Hewlett-Packard diode array spectrometer.

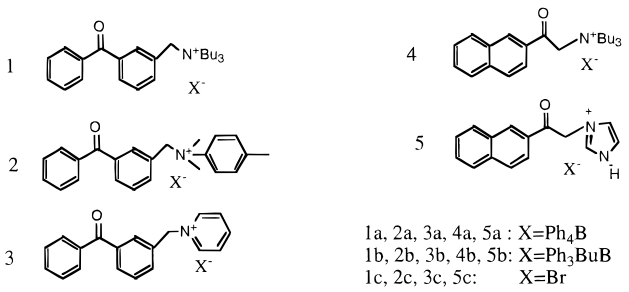

Figure 1. Structures of ammonium borates of this study.

Triethylene glycol diacrylate (TEGDA) was obtained from Sartomer and used without further purification. Ten different borates and bromides (**1a**,**b**,**c**, **2b**,**c**, **3a**, **4a**,**b**, **5a**,**b**, Figure 1) were used for the kinetic measurements. Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone, Ciba Specialty Chemicals) was used to standardize the FTP method. Compounds **2a**, **3c**, and **5c** were found to be insoluble in TEGDA. Compound **3b** and compounds containing the imidazolium moiety (as in **5**) in combination with the benzophenone chromophore could not be synthesized. Synthetic procedure for compounds **1a**,**b**,**c**,[8] **2a**,**b**,**c**,[17] **3a**,**c**,[14] and **4a**,**b**[18] have been described previously. The synthesis of **5a**,**b**,**c** is described below.

Synthesis of 5c. To a solution of 2-bromoacetonaphthone (2.42 g, 9.71 mmol) in diethyl ether (40 mL) was added imidazole (1.0 g, 14.68 mmol) in chloroform (10 mL), and the mixture was stirred at room temperature overnight. A white precipitate was formed, filtered, and washed with ether. Recrystallization from ethanol yielded white crystals of **5c** (43% yield): mp 163−164 °C. ^{1}H NMR (CD_3OD, δ): 8.61 (m, 1H), 8.26 (s, 1H), 7.93 (m, 4H), 7.54 (m, 2H), 7.27 (d, J = 10.6 Hz, 2H), 4.92 (s, 2H).). Anal. Calcd for $C_{15}H_{13}BrN_2O$: C, 56.82; H, 4.10; N, 8.83; Br, 25.20. Found: C, 57.15; H, 4.09; N, 8.95, Br, 24.98.

Synthesis of 5b. An aqueous solution of the lithium salt of triphenylbutylborate (1.15 g, 3.76 mmol) was added slowly with stirring to **5c** (1.0 g, 3.15 mmol) in water:methanol (150:15 mL). A slightly stoichiometric excess of the lithium salt of triphenylbutylborate was used to ensure complete conversion. A white solid gradually precipitated, and the resulting mixture was stirred an additional 30 min. The solid

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Table 1. Kinetic Data of TEGDA Radical Photopolymerization in the Presence of Borate Initiators Employed in This Study[a]

borate	slope × 10^{-3} at 375 nm	rel slope at 375 nm	A_{375}	slope × 10^{-3} at 365 nm	rel slope at 365 nm	A_{365}
1a	2.06 ± 0.03	0.881	0.38	2.68 ± 0.12	0.194	0.58
1b	2.34 ± 0.02	1	0.39	3.39 ± 0.09	0.246	0.60
1c	0.622 ± 0.020	0.266	0.41			
2b	1.71 ± 0.01	0.730	0.32			
2c	0.361 ± 0.009	0.154	0.25			
3a	0.380 ± 0.009	0.162	0.36	0.640 ± 0.020	0.046	0.52
4a				6.27 ± 0.09	0.454	1.6
4b				13.8 ± 0.2	1	1.6
5a				0.090 ± 0.010	0.007	0.71
5b				0.380 ± 0.010	0.028	0.71
Irg 651				6.53 ± 0.08	0.473	0.81
BP + TBA				0.467 ± 0.016	0.034	0.55
BP + DMT				0.307 ± 0.020	0.022	0.59
BP + Pyr				*b*	0	0.56

[a] BP = benzophenone, TBA = tri-*n*-butylamine, DMT = dimethyl-*p*-toluidine, Pyr = pyridine. Path length of 0.1 cm was used for absorption measurents. Slopes are given for the inflection point of polymerization curve. The initiator concentration was 7.1 × 10^{-3} M. [b] No reaction.

was filtered, washed with water, and then air-dried overnight. After recrystallization from ethanol **5b** was obtained as a white solid (42% yield): mp 115−117 °C. ^{1}H NMR (CD_3CN, δ): 8.46 (m, 1H), 7.83 (m, 5H), 7.49 (m, 4H), 7.09 (m, 6H, ortho to B), 6.92 (m, 6H, meta to B), 6.78 (m, 3H, para to B), 5.27 (s, 2H), 2.87 (m, 2H), 1.38 (m, 2H), 1.18 (m, 2H), 0.98 (t, J = 6.6 Hz, 3H). Anal. Calcd for $C_{37}H_{37}BN_2O$: C, 82.88; H, 6.90; N, 5.22. Found: C, 82.72; H, 6.88; N, 5.24.

Synthesis of 5a. To a solution of **5c** (0.44 g, 1.39 mmol) in water−methanol (90:10 mL) was added with stirring an aqueous solution of the sodium salt of tetraphenylborate (0.62 g, 1.80 mmol). A white thick precipitate formed immediately. After stirring at room temperature for 30 min, it was diluted with water and filtered. After recrystallization from ethanol white needles of **5a** (62%) were obtained: mp 94−96 °C. ^{1}H NMR (CD_3CN, δ): 7.97 (m, 1H), 7.35 (m, 5H), 7.01 (m, 4H), 6.55 (m, 8H, ortho to B), 6.32 (t, J = 7.4 Hz, 8H, meta to B), 6.16 (t, J = 7.4 Hz, 4H, para to B), 5.09 (s, 2H).). Anal. Calcd for $C_{39}H_{33}BN_2O$: C, 84.21; H, 5.93; N, 5.03. Found: C, 84.15; H, 6.01; N, 4.98.

The mixture for testing consisted of TEGDA, the fluorescent probe DASB [5-(dimethylamino)naphthalene-1-sulfonyl-*n*-butylamide][19] (0.05 wt %), and the initiator [7.1 × 10^{-3} M]. Formulations were prepared by heating the mixture at 50 °C in an ultrasonicator for 1.5 h. UV spectra of all mixtures were obtained following preparation to check the absorbance at the excitation wavelength. Compounds that possessed the same chromophore exhibited similar absorption spectra. Therefore, no normalization for absorbance was needed for data analysis. Polymerization kinetics was measured with a CM 1000 cure monitor. Samples were prepared by placing several drops of mixture between two 1 mm glass slides separated by 0.17 mm glass spacers. The excitation light of the cure monitor was used to cure a small spot within the sample while the ratio of intensities of the probe fluorescence at 485 and 564 nm was monitored as a function of time. The excitation monochromator was set to 375 or 365 nm, and cure profiles were collected under steady-state irradiation conditions. The intensity of the curing light was attenuated to ensure that the polymerization process occurred in the isothermic regime. Cure profiles were recorded in triplicates for each sample. The induction period due to small amounts of oxygen and inhibitors in TEGDA increased with the decrease in the rate of polymerization. To evaluate initiator efficiencies, we used the rate of polymerization rather than induction times. This allowed us to obtain more accurate results. The maximum rate of polymerization was found for each sample by successively fitting 20−40 point portions of the profile to a straight line and finding the highest value of the slope. All experiments were run at room temperature (21−23 °C).

Results and Discussion

All kinetic data and the results of data analysis are summarized in Table 1. Figure 2 compares polymerization rates for compounds **1a**, **1b**, and **1c** in which only the anionic portion of the molecules differs. As expected, triphenylbutylborate **1b** exhibits the highest polymerization rate. However, the polymerization rate found with initiator **1a** does not differ significantly from that observed for polymerizations initiated with **1b** as seen from the calculated slopes of the polymerization curves. Taking into account that the rate of initiation is approximately proportional[12] to ([Rp]^2), it can be concluded that triphenylbutylborate **1b** is ∼35% more efficient than tetraphenylborate **1a**. Bromide **1c** is the poorest initiator of the three due to the high oxidation potential of bromide ion and a resulting slower electron-transfer rate. A solution of bromide **1c** in acetonitrile, when irradiated in Rayonet reactor at 350 nm for 1 h, showed (∼10%) decomposition (NMR) which explains why **1c** has some activity as a free-radical initiator. Polymerization rates observed with compounds **2b** and **2c** follow the same trend with the bromide **2c** exhibiting a slower polymerization rate (see Table 1).

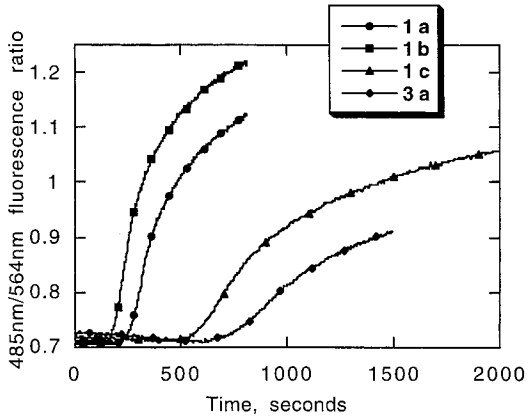

Figure 2. Real-time polymerization curves for TEGDA polymerization catalyzed by photoinitiators **1a**, **1b**, **1c**, and **3a** upon irradiation at 375 nm.

The initiating efficiency of **3a** is dramatically lower when compared to that of other compounds, and it is an even poorer initiator than bromide **1c** (Figure 2). The absence of the α-aminoalkyl functionality is assumed to be the reason for this. Since **3a** releases pyridine, the radical cation of which cannot easily lose a proton, therefore, the only radicals capable of initiation in the case of **3a** are the phenyl radical and *p*-benzoylbenzyl radical.[14] The formation of these radicals can be avoided if one photolyzes an equimolar mixture (7.1 × 10^{-3} M)

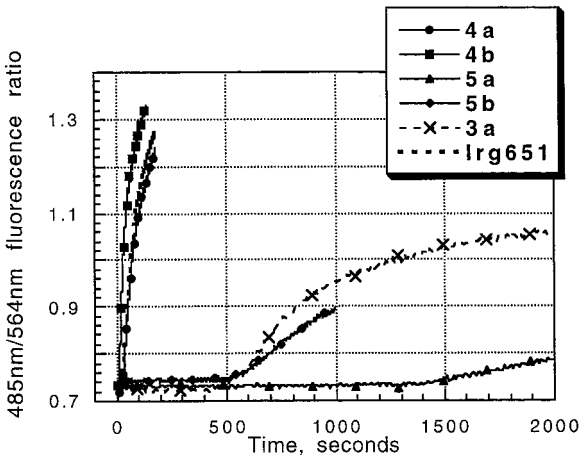

Figure 3. Real-time polymerization curves for TEGDA polymerization catalyzed by photoinitiators **4a**, **4b**, **5a**, **5b**, **3a**, and Irgacure 651 upon irradiation at 365 nm.

of pyridine and benzophenone in TEGDA, and this mixture was shown not to polymerize even after 2000 s irradiation at 350 nm. When pyridine was replaced in this system with either tributylamine or dimethyl-*p*-toluidine, a slow polymerization was detected (Table 1). Unfortunately, as noted in the Experimental Section, the synthesis of triphenylbutylborate compounds with either *p*-benzoylbenzylimidazolium or *p*-benzoylbenzylpyridinium failed.

Figure 3 shows real time kinetic profiles for TEGDA polymerization assisted by borates **4a**, **4b**, **5a**, and **5b**. Tetraphenylborate **5a** caused the slowest polymerization rate because it is incapable of producing either the butyl radical or the α-aminoalkyl radical. Similar to the case of borate **3a**,[14] polymerization in the case of **5a** is initiated only by the less effective phenyl and naphthacyl radicals. As seen from the data in Table 1, the rate of polymerization initiated by borate **4a** is 2 orders of magnitude faster than that of borate **5a**. This results mostly from the α-aminoalkyl radical that is produced in the former case. The change of the borate anion from tetraphenylborate (**5a**) to triphenylbutylborate (**5b**) also causes a polymerization rate increase though it is only 4-fold. This difference is still larger (the butyl radical is the only active radical produced in this case) than that for the borates which are capable of producing α-aminoalkyl radicals (**1a**, **1b**, **4a**, **4b**). Based on all observations, when the formation of an α-aminoalkyl radical is possible, its contribution is apparent in the rate of polymerization.

There are also other factors that may contribute to the 100-fold increase observable when the cation is changed from naphthacylimidazolium to naphthacyltributylammonium. The compounds might exhibit different degrees of dissociation in TEGDA, and this would influence the rate of initial electron transfer. Another possibility is that the release of tributylamine after the electron transfer proceeds faster than that of imidazole (or pyridine) because aromatic amines have higher ΔH and their complexes are less strained. Indeed, it was found that the quantum yield of formation of the aromatic amines from borate salts is only 3−7 times lower than that of the aliphatic amines.[14] Therefore, it is unlikely that the aforementioned factors contribute more to the observed significant change in the initiator efficiency than does the formation of the α-aminoalkyl radical.

Conclusions

Several borates and bromides were compared as free-radical initiators for TEGDA polymerization. Fluorescence probe techniques were used to obtain real-time polymerization profiles. DASB was used as a probe. It is clear that the borates must produce the α-aminoalkyl radical to be effective initiators. All tetraphenylborates that form such radicals are close in efficiency to the triphenylbutylborates of similar structure. Triphenylbutylborates that are not capable of producing α-aminoalkyl radical are inefficient radical initiators.

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