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Applicability of Tetraphenylborate Salts as Free Radical Initiators

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ABSTRACT: The reactivity of a series of triphenylbutylborate and tetraphenylborate photoinitiators with various ammonium chromophores was studied. The relative initiator efficiency of the triphenylbutylborate salts as compared to the corresponding tetraphenylborate salts with a common chromophore was determined. When the reduction potential of the chromophore is near −1.3 V (vs SCE), tetraphenylborate salts become almost as efficient photoinitiators of free radical polymerization as the corresponding triphenylbutylborate salts. A method to measure relative initiator efficiency of salts with a common chromophore based on fluorescent probe technology is proposed.

Introduction

Arylalkylborate salts are well-known as free radical chain initiators for photocurable coating and ink formulations based on acrylates and methacrylates. Paired with appropriate cationic chromophores, the arylalkylborates are used as co-initiators in UV or visible light photoinitiator systems.[2,3] In particular, triphenylbutylborate salts have found practical applications due to their higher stability compared to substituted di-, tri-, and tetraalkyl borates.[4−8] The mechanism of radical chain initiation by the triphenylbutylborate salts involves photoinduced electron transfer from the borate anion to an excited state of the chromophore, likely forming a triphenylbutylborate radical, which in turn undergoes rapid cleavage to triphenylboron and butyl radical. Alkyl radicals have been shown to be the primary initiating species when triarylalkylborate salts are used.[9]

It is a common belief that useful organoborate salts must contain at least one alkyl group directly linked to the boron in order to be effective co-initiators for the photoinitiation of free radical polymerization. Tetraarylborate salts have been thought to be inefficient based on the general notion that aryl radicals are poorer initiating species, less stable and more difficult to generate from oxidized borates than alkyl radicals. In fact, in model studies with triphenylbutylborate co-initiators, there is no evidence whatsoever for a free phenyl radical.[9] However tetraarylborates, and in particular tetraphenylborates, are more stable and easier to make than the corresponding arylalkylborates, thus suggesting an important advantage. Preliminary studies indicated that tetraarylborates are able to initiate free radical polymerization in the manner of arylalkylborates and have better thermal stability. In principle, tetraarylborates may be used in place of arylalkylborates, because the photoinduced electron transfer (PTE) from the borate anion to the excited state of chromophore is thermodynamically favorable due to the relatively low oxidation potential of the borates.[10]

The recent development of a rapid scan fluorometer in our group afforded a tool for quantitative study of polymerization kinetics in the presence of various photoinitiators under steady-state irradiation conditions.[11−14] This prompted us to reevaluate, quantitatively, the applicability of tetrarylborates as free radical photoinitiators, by measurement of relative initiation efficiency of triphenylbutylborates compared to the corresponding tetraphenylborates.

In this paper, the polymerization kinetics of triethylene glycol diacrylate (TEGDA) in the presence of three pairs of borate initiators is compared. Each pair of borate salts contained the same light-absorbing chromophore as the cation and either tetraphenylborate or triphenylbutylborate as the counteranion. The borates studied are shown in Chart 1.

Experimental Part

TEGDA was purchased from Sartomer and used as received. Tetraphenylborates (**1a**−**3a**) and triphenylbutylborate (**1b**) were prepared as described previously.[15] Borates **2b** and **3b** were synthesized by the following general procedure.

Preparation of Borates 2b and 3b. The appropriate ammonium bromide[15] was dissolved in a minimum amount of

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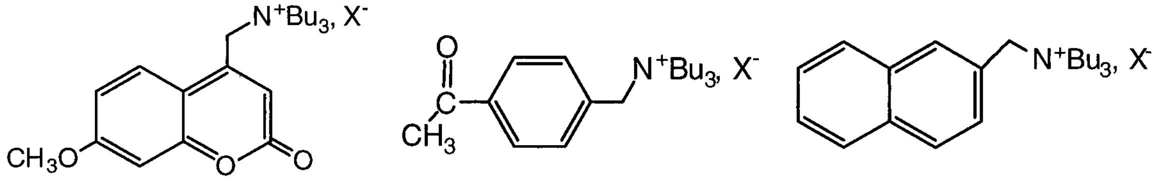
Chart 1. The Borate Initiators Studied



1a: X = Ph$_4$B
1b: X = Ph$_3$Bu

2a: X = Ph$_4$B
2b: X = Ph$_3$Bu

3a: X = Ph$_4$B
3b: X = Ph$_3$Bu

water and the solution was filtered to remove any undissolved residue. An equivalent amount of aqueous lithium triphenylbutylborate solution was added dropwise at room temperature with stirring. A thick white precipitate formed almost immediately. The mixture was diluted with water and the precipitate was filtered off. The crude product was recrystallized from appropriate solvents as needed. Yields: 85−87%.

2b: mp 153−154 °C (ethanol/acetone). Anal. Calcd for $C_{34}H_{42}BNO$: C, 83.14; H, 8.55; N, 2.85. Found: C, 83.21; H, 8.58; N, 2.84. ^{1}H NMR (acetone): δ 8.10 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.35 (m, 6H, ortho to B), 6.90 (m, 6H, meta to B), 6.73 (m, 3H, para to B), 4.66 (s, 2H), 3.19 (s, 9H) 2.62 (s, 3H), 1.23 (m, 2H), 1.02 (m, 4H), 0.78 (t, J = 7.4 Hz, 3H).

3b: mp 122−123 °C (ethyl acetate/ethanol). Anal. Calcd for $C_{45}H_{60}BN$: C, 86.44; H, 9.60; N, 2.24. Found: C, 86.53; H, 9.65; N, 2.22. ^{1}H NMR (acetone): δ 8.20 (s, 1H), 8.05 (m, 3H), 7.69 (m, 3H), 7.37 (m, 6H, ortho to B), 6.89 (m, 6H, meta to B), 5.73 (m, 3H, para to B), 4.88 (s, 2H) 3.42 (m, 6H), 2.08 (m, 6H), 1.48 (m, 6H), 1.23 (m, 2H, B−CH_2) 1.03 (m, 13H, 3CH_3 and 2CH_2), 0.78 (t, J = 7.4 Hz, 3H).

Kinetic Measurements. Triethylene glycol diacrylate (TEGDA) was selected as the monomer for testing the initiators because it is one of the most common components of photocurable monomer systems. Solutions of each of the borates in TEGDA containing 0.14 wt % of a microenvironment-sensitive fluorescent probe (i.e., the DASD probe[13]) were prepared. The concentration of the borate was 8.3×10^{-3} M in each solution. The polymerization kinetics of the solutions were measured by fluorescent probe technology using the CM 1000 Cure Monitor.[11−14,16] A 0.1 mm layer of each solution was prepared by squeezing a drop of the solution between glass slides (75 × 25 × 1 mm) separated by appropriate spacers, and a small spot on the layer was cured with an excitation beam of CM 1000, while changes of the probe fluorescence caused by the polymerization process were monitored. The ratio of the intensity of the fluorescence at two wavelengths was used as the indicator of polymerization progress. The ratio monitoring wavelengths were 485 and 564 nm and corresponded to optimized wavelengths for the DASD-probe/TEGDA system. The wavelengths used for probe excitation, as well as for initiation of the polymerization were 375 nm for **1a** and **1b** and 310 nm in the case of the other initiators. Real time kinetic profiles for TEGDA polymerization were obtained under steady-state irradiation conditions. Relative kinetic parameters were determined from the profiles as described below. All measurements were carried out at ambient temperature (23 °C).

Determination of the Relative Initiation Efficiency. Since the borate concentration, monomer structure, irradiation and measurement conditions, and the probe concentration were identical for each borate pair studied, the kinetic profiles allow one to compare the rate of initiation of TEGDA polymerization with each borate. The slope measured immediately after the start of polymerization is proportional to initial rate of polymerization, which in turn is related to the rate of initiation by the following classical equation (eq 1).

$$R_{p_0} = k_p \sqrt{\frac{R_i}{k_t}}[M]_0 \qquad (1)$$

where R_{p_0} is the starting rate of polymerization, R_i is the rate of initiation, k_p and k_t are the propagation and termination rate constants, respectively, and $[M]_0$ is the starting concentration of monomer.

For the same monomer k_p, k_t, and $[M]_0$ are constant. Hence the ratio of the polymerization rates for two initiators is equal to the square root from the rates of initiation under particular conditions (eq 2).

$$\frac{R_{po_b}}{R_{po_a}} = \sqrt{\frac{R_{i_b}}{R_{i_a}}} \qquad (2)$$

In the case of photoinduced polymerization with monochromatic light, the initiation rate is proportional to the initiation quantum yield and to the amount of light absorbed by the sample per unit of time. If concentration and absorption characteristics of two initiators are the same as in the case of the pairs of borates studied, the light absorbed is identical. Thus the ratio of initiation rates at the same initiator concentration becomes equal to the ratio of initiation quantum yields and represents the relative initiation efficiency of the initiators as defined by eq 3

$$\Phi_{rel} = \frac{\Phi_b}{\Phi_a} = \frac{R_{i_b}}{R_{i_a}} \qquad (3)$$

where Φ_{rel} is the relative initiation efficiency, Φ_a and Φ_b are the initiation quantum yields of initiators a and b, and R_{i_a} and R_{i_b} are the rates of initiation.

The curves obtained by the fluorescence probe technique represent kinetic profiles expressed in terms of a fluorescence intensity ratio change. They can be converted to "true" kinetic curves representing double bond conversion as a function of time by calibrating the ratios to actual conversations. Usually the calibration is done by relating the ratios to the conversion by a polynomial (eq 4).[13]

$$r = r_0 + A\alpha + B\alpha^2 + C\alpha^3 + ... + N\alpha^n \qquad (4)$$

where: r is the fluorescence intensity ratio measured at any polymerization time, r_0 is the ratio before polymerization, α is the double bond conversion ($\alpha = ([M]_0 - [M])/[M]_0$), and A to N are the polynomial coefficients found experimentally. However, for determination of the relative initiation efficiency, this calibration is not necessary. For the same probe/monomer system, the calibration equation is independent of the initiator, provided that the initiator does not fluoresce in a range that could overlap with the probe response. Hence, if the rate of polymerization is measured at the starting point after the induction period (i.e., where $\alpha = 0$), then the higher order terms in the calibration equation equal zero, and the rate of polymerization becomes directly proportional to the slope of the ratio vs time profile (eq 5).

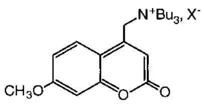
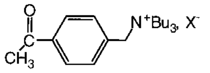
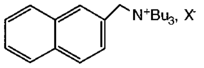
$$R_{p_0} = [M]_0\left(\frac{d\alpha}{dt}\right)_{\alpha=0} = \frac{[M]_0}{A}\left(\frac{dr}{dt}\right)_{r=r_0} \qquad (5)$$

Substitution of eqs 5 and 2 into eq 3 and rearrangement give

Table 1. Kinetic Data for Polymerization of TEGDA in the Presence of Various Borate Initiators under the Conditions Studied

initiator	$10^3(\mathrm{d}r/\mathrm{d}t)_{r=r_0}$ (s^{-1})	induction time (s)
1a	19.12	20
1b	23.22	16
2a	1.493	358
2b	2.409	203
3a	0.987	393
3b	3.988	124

Table 2. Influence of the Type of Chromophore on Relative Initiation Efficiency of Triphenylbutylborates Compared to Tetraphenylborates

chromophore	rel initiation efficiency Φ_{rel}	chromophore reduction potential[a] (V vs SCE)
	1.47	−1.30
	2.60	−1.62
	16.3	−2.10

[a] Measured by cyclic voltammetry in acetonitrile, using tetrabutylammonium perchlorate as the supporting electrolyte (ref 15).

an expression on relative efficiency of the initiators with common chromophore (eq 6).

$$\Phi_{\mathrm{rel}} = \frac{\left(\frac{\mathrm{d}r}{\mathrm{d}t}\right)_{\mathrm{b}}^{2}}{\left(\frac{\mathrm{d}r}{\mathrm{d}t}\right)_{\mathrm{a}}^{2}} \tag{6}$$

where $(\mathrm{d}r/\mathrm{d}t)_{\mathrm{a}}$ and $(\mathrm{d}r/\mathrm{d}t)_{\mathrm{b}}$ are initial slopes of the kinetics profiles in the presence of initiators a and b respectively.

Equation 6 was used to determine the relative initiation efficiency of the initiator pairs studied. The $(\mathrm{d}r/\mathrm{d}t)$ values were determined from the slopes of the kinetic profiles obtained in the presence of triphenylbutylborates (b) and tetraphenylborates (a) with the same chromophore as the cation. The results are shown in Table 1, while the relative initiation efficiencies of the triphenylbutylborates compared to the corresponding tetraphenylborates are listed in Table 2.

Results and Discussion

Each of the borates absorbed UV light with a significant absorption shoulder above 300 nm. This allowed us to apply the excitation beam of the CM 1000 for both the excitation of the probe and the initiation of the free radical polymerization. Were this not the case, separate monochromatic beams would have to be used for the initiation and probe excitation. Application of the CM-1000 provided up to three-digit precision for the fluorescence intensity ratios at a scanning rate of 1 scan/s or faster, which in turn afforded sufficient data points for precise measure of the polymerization kinetics. Figure 1 shows example polymerization profiles for polymerization of TEGDA in the presence of photonitiators **1a** and **1b**. Similar kinetic curves were obtained for the other initiator pairs.

The kinetic profiles expressed in terms of the fluorescence intensity ratios (Figure 1) have all of the features of regular kinetic curves, such as those representing monomer conversion as a function of time, obtained by other techniques such as RT FTIR, or PDSC. After an induction period during which polymerization inhibitors are consumed, the polymerization starts causing an increase of medium microviscosity and decrease of its micropolarity, which in turn results in a shift in probe fluorescence spectrum and an increase of the fluorescence intensity ratio. With progress of polymerization, reactive functional groups are consumed and polymerization eventually stops as indicated by the plateau of the kinetic profile (Figure 1). Even though uncalibrated profiles do not represent the polymerization kinetics explicitly, they can be used for relative comparison of the polymerization kinetics, because in the same probe/monomer system the calibration equation relating the ratios to the conversion is the same. In our study, we needed just the initial slope of the profiles and eq 6 to calculate the relative initiation efficiency of the pairs of initiators studied.

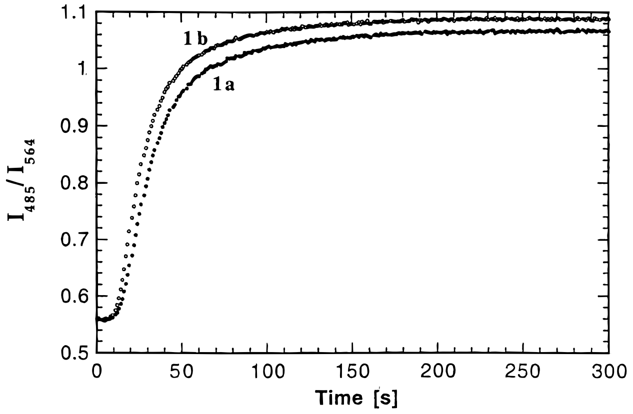


Figure 1. Comparison of the polymerization kinetics of TEGDA in the presence of initiators **1a** and **1b**.

In general, the triphenylbutylborates studied reacted faster than the corresponding tetraphenylborates at the same initiator concentration and irradiation conditions as indicated by the slopes (Table 1). However, the difference in the initiation efficiencies between the tetraaryl- and the triphenylbutylborates strongly depends on the structure of the chromophore (Table 2). In some cases, as in the case of coumarin derivatives **1a** and **1b**, the tetraphenylborate is almost as efficient as the triphenylbutylborate; borate **1b** is only about 50% more efficient than the borate **1a**. When it is taken into account that the rate of polymerization is proportional to the square root of the initiator efficiency, the difference between rates of polymerization induced by borates **1a** and **1b** becomes even less; the rate of polymerization in the presence of **1b** would be only 20% faster than in the case of **1a**.

The relative initiation efficiency seems to strongly depend on the reduction potential of the cation in borate initiators. Table 2 includes the potentials of the chromophore cations used with the borates. The easier it is to reduce the chromophore of the initiator (i.e., the less negative is its reduction potential), the smaller the difference in initiation efficiency observed between the tetraphenyl- and triphenylbutylborate derivatives. This indicates that the electron-transfer processes (i.e., the forward and the competitive back electron transfer between the excited chromophore and the borate anion within the ion pairs) are dominant factors effecting the kinetics of the free radical generation from the borate anion, because the $E^{0,0}$ energy of the chromophores studied and oxidation potential of the triphenylbutyl- and tetraphenylborates are similar. Moreover, the data in Table 2 indicate that by appropriate selection of the cation in the borate salts, initiators can be designed that may contain a tetraarylborate anion combined with a chromophore with reduction potential more positive than that of coumarin. Such initiators can be expected to have better thermal stability than the corresponding triarylalkylborates, while having comparable initiation efficiency to that of the triarylalkylborates.

Conclusions

The data indicate that by appropriate selection of the cation, borate initiators can be designed that are equally efficient no matter whether triphenylbutylborate or tetraphenylborate anion is used. Because the stability of tetraarylborates is greater compared to the corresponding triarylalkyborates, replacement of triarylalkylborates with appropriately designed tetraarylborates is likely to improve the thermal stability of photocurable monomer systems based on the borate photoinitiators. The coumarin initiator **1a** is the first example of an initiator that has very close initiation efficiency to its triphenylbutyl analogue, while the efficiency of acetophenone initiators **2a** and **2b** differs only by a factor of 2.6.

The application of fluorescent probe technology and CM 1000 Cure Monitor affords a useful tool for quantitative comparison of photoinitiator performance.

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