Alkylborane Initiated RAFT Polymerization: Impact of Carboxylic Acid Deblockers

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1. Reagents

The monomer (M), N,N-dimethylacrylamide (DMA, 99.5% stabilized with 100 ppm 4-methoxyphenol, Alfa Aesar) was used immediately after removal of the inhibitor by passage through a basic alumina column. The alkylborane-amine complex (R3B-L), tri-n-butylborane methoxypropylamine, was donated by Callory LLC (Pittsburgh, PA) and stored in the glovebox until use. Propionic acid (PA, ≥ 99.1%, Sigma-Aldrich), formic acid (FA, 99%, Acros Organics), difluoroacetic acid (DFA, 98%, Thermo Scientific), and trifluoroacetic acid (TFA, > 99%, TCI Chemicals) were used as deblockers. The solvent used for all experiments was N,N-dimethylacetamide (DMac, > 99.5%, VWR). The internal standard for NMR was 1,3,5-trioxane (≥ 99%, Aldrich). 2,2,6,6-Tetramethylpiperidine 1-oxyl free radical (TEMPO, > 98%, TCI) was used as a radical quenching reagent. The chain transfer agents (CTA) were 2-dodecylthiocarbonothioylthio-2-methylpropionic acid (DDMAT, 98%, Sigma-Aldrich) and methyl 2-(dodecylthiocarbonothioylthio)-2-methylpropionate (MDMP, 97%, Sigma-Aldrich), which were used as received.

2. Equipment and Analytical Methods

2.1. Size Exclusion Chromatography (SEC): Relative number-average molecular weight (Mn), weight-average molecular weight, and polymer dispersity values were determined using SEC in N,N-dimethylacetamide. SEC analysis was conducted with a Shimadzu LC-20AD HPLC pump equipped with a Shimadzu RID-20A 120V refractive index detector using HPLC grade DMac containing 0.03 wt. % LiCl as the mobile phase. The polymer analytes were separated by two PLgel mixed-B Agilent columns connected in series at a flow rate of 1 mL/min and at 55°C. These columns were calibrated against 10 linear poly(methyl methacrylate) standards having Mn values between 800 and 2,570,000 g/mol.

2.2. Proton Nuclear Magnetic Resonance (1H NMR): 1H NMR was used to calculate monomer conversion. 1H NMR spectra were obtained using a Varian Unity Inova-300 MHz or 500 MHz spectrometer at room temperature with deuterated chloroform (CDCl3) as the NMR solvent. All spectra were recorded using 128 scans with a relaxation delay of 1 second. Trioxane was used as an internal standard for determining monomer conversion and all chemical shifts were referenced to chloroform.

3. Experimental Methods

3.1. AI-RAFT kinetic experiments: Kinetic experiments were performed at room temperature with PA as the deblocker and DDMAT as the CTA. A representative AI-RAFT kinetic procedure, formulated with 40 wt.% monomer and a molar ratio of [M]/[CTA]/[R3B-L]/[D] ≈ 400/1/1/60, was conducted as follows. To a 20 mL scintillation vial was added DMA monomer (2.174 g, 21.93 mmol), R3B-L (0.015 g, 0.0549 mmol), CTA (DDMAT, 0.02 g, 0.0549 mmol), trioxane (0.06 g), and 1.34 g DMac. The contents of the vial were then vortexed for 15 min, or longer, until complete dissolution occurred. Once a homogenous solution was obtained, a magnetic stir bar was added. The scintillation vial was then sealed using a rubber septum and electrical tape, and sparged with nitrogen for 1 h. After sparging, the scintillation vial was transferred into the glovebox, and a time zero sample was withdrawn for 1H NMR analysis. To commence polymerization, a solution of deblocker (0.243 g PA, 3.291 mmol) and dissolved oxygen in DMac, having no prior deoxygenation, was also transferred into the glovebox and injected into the scintillation vial via syringe. The injected solution volume was kept constant at 1.69 mL to maintain a consistent amount of O2 (8.78E-3 mmol) between experiments. After injecting the deblocker solution, the vial was briefly swirled and then placed on a stir plate for the course of polymerization. At each time point, an aliquot 0.02 mL, was withdrawn from the
polymerization and quenched by injection into a DMac solution containing a 10-fold excess of TEMPO to R3B-L to prevent any further polymerization. Polymerization samples were then immediately prepared for $^1$H NMR to determine monomer conversion and SEC to determine polymer molecular weight and dispersity. All kinetic experiments were conducted in at least duplicate.

3.2. AI-RAFT extent of reaction experiments: A representative AI-RAFT kinetic procedure, formulated with 40 wt.% monomer and a molar ratio of [M]/[CTA]/[R3B-L]/[DMac] $\approx$ 400/1/1/60, was conducted as follows. Extent of reaction experiments were performed at room temperature with MDMP as the CTA. To a 20 mL scintillation vial was added DMA monomer (1.094 g, 11.04 mmol), R3B-L (0.007 g, 0.027 mmol), CTA (MDMP, 0.01 g, 0.027 mmol), trioxane (0.03 g), and 1.48 g DMac. The contents of the vial were then vortexed for 15 min, or longer, until complete dissolution occurred. Once a homogenous solution was obtained, a magnetic stir bar was added. The scintillation vial was then sealed using a rubber septum and electrical tape, and sparged with nitrogen for 1 h. After sparging, the scintillation vial was transferred into the glovebox, and a time zero sample was withdrawn for $^1$H NMR analysis. To commence polymerization, a solution of deblocker (0.117 g PA, 1.585 mmol) and dissolved oxygen in DMac, having no prior deoxygenation, was also transferred into the glovebox and injected into the scintillation vial via syringe. The injected solution volume was kept constant at 0.81 mL to maintain a consistent amount of O$_2$ between experiments. After injecting the deblocker solution, the vial was briefly swirled and then placed on a stir plate for the course of polymerization. The reaction was conducted for 20 h, and subsequently quenched by injection of a DMac solution containing a 10-fold excess of TEMPO to R3B-L to prevent any further polymerization. Polymerization samples were then immediately prepared for $^1$H NMR to determine monomer conversion and SEC to determine polymer molecular weight and dispersity.

3.4. pKa calculations for carboxylic acid deblockers: The pKa of each deblocker was predicted using MarvinSketch Software. Micspecies distribution plots were generated as a function of pH for each deblocker shown in Figure S6. The pKa is defined at the pH where 50% of the acid is deprotonated.

3.5. Calculation of moles of O$_2$ in oxygenated deblocker solutions containing deblocker and N,N-dimethylacetamide (DMac): The moles of O$_2$ added to the reaction mixture were estimated using the following equation given by Eq. S1.

$$\text{moles of } O_2 = \chi_G \times \text{moles of DMac}$$

Where $\chi_G$ is the solubility of O$_2$ in DMac at room temperature and atmospheric pressure, which has a value of 4.82E-4. [1] In a typical kinetic experiment, the deblocker solution contained 1.69 mL or 0.0182 mol of DMac. Therefore, the moles of O$_2$ in a typical AI-RAFT experiment is approximately 8.78E-6 mol. Thus, the molar ratio of O$_2$/R3B-L can be estimated at 0.16, which was kept constant across all reactions. It is important to emphasize that this calculation provides only a crude estimate of O$_2$ and doesn’t account for many factors including O$_2$ solubility changes from other reagents (monomer, deblocker, etc.) or the amount of oxygen residing in the reactors head space.
4. Mechanisms and Rate Equations

4.1 Association/dissociation equilibrium of the alkylborane-ligand complex

Lewis pairs involving organoboranes, including alkylborane-amines, are known to exist in equilibrium between their dissociated (uncoordinated) and associated (coordinated) states. [2-5] Thus, protonation of the amine ligand, and loss of its Lewis basicity, disassociates the alkylborane-amine complex and liberates free alkylborane according to the following equilibrium. The equilibrium is therefore defined by Eq. S2 and the concentration of $R_3B$ given by Eq. S3.

\[
K_{eq} = \frac{k_{\text{disassociation}}}{k_{\text{association}}} = \frac{[R_3B][L-D]}{[R_3B-L][D]}
\]

\[
[R_3B] = \frac{[R_3B-L][D]K_{eq}}{[L-D]}
\]

4.2 Autoxidation Mechanism 1 and Rate Equations

The first autoxidation mechanism of alkylboranes (AM1), adapted from literature, is provided below: [6-9]

**Autoxidation Mechanism 1 (AM1)**

1. \( R_3B + O_2 \rightarrow R_2BOO^\bullet + R^\bullet \)
2. \( R^\bullet + O_2 \rightarrow ROO^\bullet \)
3. \( ROO^\bullet + R_3B \rightarrow R_2BOO + R^\bullet \)

Overall: \( 2R_3B + 2O_2 \rightarrow R_2BOO^\bullet + R_2BOOR + R^\bullet \)

According to the above scheme, the rate of initiation \( (R_i) \) is:

\[
R_i = \frac{d[P^\bullet]}{dt} = k_{AM1}[R_3B]^2[O_2]^2
\]

The rate of bimolecular termination \( (R_t) \) in radical polymerization is given by:

\[
R_t = -\frac{d[P^\bullet]}{dt} = k_t[P^\bullet]^2
\]
Thus, under steady state conditions, $R_i = R_t$, and the concentration of propagating radicals ($[P\cdot]$) is:

$$[P\cdot] = \frac{\sqrt{k_{AM1}[R_3B][O_2]^2}}{k_t} = \left(\frac{k_{AM1}}{k_t}\right)^{1/2} [R_3B][O_2]$$

To relate the above expression to an alkylborane complex and a known quantity in the formulation of AI-RAFT, $[R_3B]$ can be substituted for $[R_3B-L]$ using Eq. S3 to give the following expression:

$$[P\cdot] = \left(\frac{k_{AM1}}{k_t}\right)^{1/2} \left(\frac{[R_3B-L][D]K_{eq}}{[L-D]}\right) [O_2]$$

Thus, the overall rate of polymerization according to mechanism AM1 is:

$$R_p = -\frac{d[M]}{dt} = k_p[P\cdot][M] = k_p \left(\frac{k_{AM1}}{k_t}\right)^{1/2} \left(\frac{[R_3B-L][D]K_{eq}}{[L-D]}\right) [O_2][M]$$

### 4.3 Autoxidation Mechanism 2 and Rate Equations

The second autoxidation mechanism, adapted from literature, is provided below: [10-13]

**Autoxidation Mechanism 2 (AM2)**

```markdown
1
R3B + O2 \rightarrow R2BOOR
```

```markdown
2
R2BOOR \rightarrow R2BO\cdot + RO\cdot
```

**overall**

```markdown
R3B + O2 \rightarrow R2BO\cdot + RO\cdot
```

According to the above scheme, the rate of initiation ($R_i$) is:

$$R_i = \frac{d[P\cdot]}{dt} = k_{AM2} [R_3B][O_2]$$

The rate of bimolecular termination ($R_t$) in radical polymerization is given by:

$$R_t = -\frac{d[P\cdot]}{dt} = k_t [P\cdot]^2$$

Thus, under steady state conditions, $R_i = R_t$, and the concentration of propagating radicals ($[P\cdot]$) is:

$$[P\cdot] = \sqrt{\frac{k_{AM2}[R_3B][O_2]^2}{k_t}} = \left(\frac{k_{AM2}}{k_t}\right)^{1/2} [R_3B]^{1/2} [O_2]^{1/2}$$

To relate the above expression to a known quantity and an alkylborane complex used in the formulation of AI-RAFT, $[R_3B]$ can be substituted for $[R_3B-L]$ using Eq. 3 to give the following expression:

$$[P\cdot] = \left(\frac{k_{AM2}}{k_t}\right)^{1/2} \left(\frac{[R_3B-L][D]K_{eq}}{[L-D]}\right)^{1/2} [O_2]^{1/2}$$

Thus, the overall rate of polymerization according to mechanism AM2 is:

$$R_p = -\frac{d[M]}{dt} = k_p[P\cdot][M] = k_p \left(\frac{k_{AM2}}{k_t}\right)^{1/2} \left(\frac{[R_3B-L][D]K_{eq}}{[L-DB]}\right)^{1/2} [O_2]^{1/2} [M]$$
5. Supplemental Figures and Tables

Figure S1: (A) Monomer conversion versus time without external added deblocker (no PA) using either DDMAT or MDMP as the CTA. Reaction conditions: [M]/[CTA]/[R3B-L]/[D] ≈ 400/1/1/0, [M] ≈ 3.84 M or 40 wt.%. (B) Chemical structures of the CTAs. (C) Monomer conversion versus time for a control experiment without R3B-L using DDMAT as the CTA and PA as the deblocker. Reaction conditions: [M]/[CTA]/[R3B-L]/[D] ≈ 400/1/0/20, [M] ≈ 3.84 M or 40 wt.%.

Figure S2: (A) First order kinetic plot and (B) molecular weight and dispersity versus conversion plot for [D] = [COOH] = 0.192 M. Reaction conditions: [M]/[CTA]/[R3B-L]/[D] ≈ 400/1/1/20, [M] ≈ 3.84 M or 40 wt.%.
Figure S3: (A) First order kinetic plot and (B) molecular weight and dispersity versus conversion plot for [D] = [COOH] = 0.384 M. Reaction conditions: \([M]/[CTA]/[R_3B-L]/[D] \approx 400/1/1/40\), \([M] \approx 3.84\) M or 40 wt.%.

Figure S4: (A) First order kinetic plot and (B) molecular weight and dispersity versus conversion plot for [D] = [COOH] = 0.575 M. Reaction conditions: \([M]/[CTA]/[R_3B-L]/[D] \approx 400/1/1/60\), \([M] \approx 3.84\) M or 40 wt.%.
Figure S5: (A) First order kinetic plot and (B) molecular weight and dispersity versus conversion plot for $[D] = [\text{COOH}] = 0.764$ M. Reaction conditions: $[M]/[\text{CTA}]/[\text{R}_3\text{B-L}]/[D] \approx 400/1/1/80$, $[M] \approx 3.84$ M or 40 wt.%. 

Figure S6: Microspecies distribution curves used to calculate the pKa for all deblockers. The pKa is the point when 50% of each acid species has been deprotonated: (A) propionic acid has pKa $\sim 4.75$, (B) formic acid has pKa $\sim 4.27$, (C) difluoroacetic acid has pKa $\sim 1.30$, and (D) trifluoroacetic acid has pKa $\sim 0.05$. 

\[ k_{\text{app}} = 0.971 \text{ h}^{-1} \] 
\[ k_{\text{app}} = 1.017 \text{ h}^{-1} \] 
\[ k_{\text{app}} = 1.022 \text{ h}^{-1} \]
Table S1: Summary of AI-RAFT formulations and results with four different carboxylic acid deblockers.

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a: Each entry represents an individual polymerization. All polymerizations were conducted at room temperature for 20 h using 40 wt. % monomer in DMac. Polymerizations were initiated using 0.81 mL of DMac solutions of deblocker without deoxygenation.

b: Monomer conversion was calculated using $^1$H NMR with a trioxane internal standard.

c: Theoretical molecular weight was determined as, $M_n$ theo. = $M_W$ monomer · ([DMA]/[CTA]) · conversion + $M_W$ CTA.
Supporting Information References:


