

## Supporting Information

# Evaluation of a Potential Ionic Contribution to the Polymerization of Highly Reactive (Meth)Acrylate Monomers

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## Synthesis and Purification

Synthesis and purification techniques of the monomers used in these studies are presented. Synthesis yields are not indicated, as monomer purity was higher priority. Included are the 400Mhz  $^1\text{H}$ , and  $^{13}\text{C}$  NMR frequencies in ppm, the IR spectra in  $\text{cm}^{-1}$ , and the elemental analysis results. Elemental analysis was performed by Galbraith Laboratories, Inc. (Knoxville, TN). Boiling point ( $^{\circ}\text{C}$ ) and corresponding pressure (mm Hg) or melting point ( $^{\circ}\text{C}$ ) are also included, where applicable. The abbreviations are means of identification in the main manuscript.

### 1. Cyclic Carbonate Methacrylate

IUPAC Name: 2-Methyl acrylic acid 2-oxo-[1,3]-dioxolan-4-ylmethyl ester

Common Name: Cyclic Carbonate Methacrylate

Abbreviation: CCMA

**Synthesis.** Eighteen grams of 4-hydroxymethyl-1,3-dioxolan-one (0.15 mol, Huntsman Inc., Salt Lake City, UT, 93.5%), 16 g of triethylamine (0.16 mol, Aldrich Chemical, Milwaukee, WI, 99.5%), and 100 ml of methylene chloride were introduced into a three-neck flask equipped with a magnetic stir bar, nitrogen purge, and addition funnel. The flask was immersed in an ice water bath to maintain the reaction temperature below  $5^{\circ}\text{C}$ . The addition funnel was charged with 15 g of methacryloyl chloride (0.14 mol, Aldrich Chemical, Milwaukee, WI, 97%) and diluted with 30 ml of methylene chloride. The methacryloyl chloride solution was added dropwise to the alcohol solution over one hour and allowed to react overnight. After the reaction had reached completion, the triethylamine salt was removed via vacuum assisted filtration. The liquid phase was

washed three times with saturated sodium bicarbonate solution and three times with saturated sodium chloride solution, followed by drying overnight over sodium sulfate (Aldrich Chemical, Milwaukee, WI,  $\geq 99.0\%$ ). After filtering and removing the solvent via rotary evaporation, the crude product was purified via column chromatography using silica gel (Aldrich Chemical, Milwaukee, WI pore size 60 Å, particle size 70-270 mesh) and 3:1 hexanes:ethyl acetate as eluant. A slightly yellow liquid was recovered as the final product. MW 186.16 g/mol;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ 6.12 (s, 1H),  $\delta$ 5.61 (s, 1H),  $\delta$ 4.95 (m, 1H),  $\delta$ 4.58 (t, 1H),  $\delta$ 4.4 (m, 1H),  $\delta$ 4.3 (m, 1H),  $\delta$ 1.9 (s, 3H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ 166.9,  $\delta$ 154.8,  $\delta$ 135.4,  $\delta$ 127.5,  $\delta$ 74.1,  $\delta$ 66.4,  $\delta$ 63.7,  $\delta$ 18.4; IR (thin film) 2986, 2963, 2929, 1798, 1723, 1639, 1481, 1453, 1394, 1320, 1294, 1164, 1105, 1092, 1054, 1013, 949, 814, 770, 714  $\text{cm}^{-1}$ ; Anal. Calc. for  $\text{C}_8\text{H}_{10}\text{O}_5$ : C, 51.61; H, 5.43. Found: C, 51.22; H, 5.50; N,  $<0.50$ .

B.P.: 155°C/0.5mmHg

## 2. Cyclic Carbonate Carbamate (OCN) Methacrylate

IUPAC Name: 2-Methyl-acrylic acid 2-(2-oxo-[1,3]dioxolan-4-ylmethoxycarbonyl-amino)-ethyl ester

Common Name: Cyclic carbonate carbamate methacrylate

Abbreviation: CCCMA

**Synthesis.** Three grams of 4-hydroxymethyl-1,3-dioxolan-one (25 mmol), two drops of triethyl amine ( $< 1$  mmol), and 50 ml of methylene chloride were introduced into a three-neck flask equipped with a magnetic stir bar, reflux condenser, and nitrogen purge. The flask was immersed in an ice water bath to maintain the reaction temperature

below 5°C. To this alcohol mixture, 3.9 g of 2-isocyanatoethyl methacrylate (25 mmol, Aldrich Chemical, Milwaukee, WI, 98%) was added dropwise over one hour and allowed to react overnight. After the reaction was completed, the organic phase was washed with 1 wt% aqueous sodium hydroxide solution, 1 wt% aqueous hydrochloric acid solution, and three times with saturated sodium chloride solution, followed by drying over sodium sulfate overnight. After filtering and removing the solvent via rotary evaporation, the crude product was purified via recrystallization from a 1:4 chloroform:hexanes solution. A white solid was recovered as the final product. MW 259.21 g/mol; <sup>1</sup>H NMR (400 Mhz, CDCl<sub>3</sub>) δ6.12 (s, 1H), δ5.8 (s, 1H), δ5.15 (s, 1H), δ4.95 (m, 1H), δ4.58 (t, 1H), δ4.3 (m, 5H), δ3.5(m, 2H), δ1.95 (s, 3H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ167.6, δ155.9, δ155.0, δ136.2, δ126.6, δ74.6, δ66.2, δ63.9, δ63.6, δ40.7, δ18.7; IR (thin film) 3372, 2960, 2930, 2894, 1798, 1721, 1634, 1532, 1453, 1399, 1320, 1299, 1253, 1169, 1090, 1054, 952, 816, 773, 714 cm<sup>-1</sup>; Anal. Calcd for C<sub>11</sub>H<sub>15</sub>NO<sub>5</sub>: C, 48.37; H, 5.55; N, 5.13. Found: C, 48.27; H, 5.41; N, 4.95.

M.P.: 66-68°C

### 3. Phenyl Carbamate Methacrylate

IUPAC Name: 2-Methyl-acrylic acid 2-phenylcarbamoyloxy-ethyl ester

Common Name: Phenyl Carbamate Methacrylate

Abbreviation: PhNCO MA

**Synthesis.** In the reaction, 6.4 g of the purified 2-hydroxyethyl methacrylate (49 mmol, Polysciences, Inc, Warrington, PA, ≥99%), two drops of dibutyltin dilaurate (<1

mmol, Aldrich Chemical, Milwaukee, WI, 95%), and 75 ml of ethyl acetate were added to a three-neck flask equipped with a magnetic stir bar and nitrogen purge. The flask was immersed in an ice water bath to maintain the reaction temperature below 5°C. To this monomer mixture, 5 ml of phenyl isocyanate (46 mmol, Aldrich Chemical, Milwaukee, WI, ≥98%) was added dropwise over one hour and the reaction was allowed to react overnight. After the reaction had reached completion, the crude product was condensed via rotary evaporation. The crude product was then purified via recrystallization using a 5:1 hexanes:ethyl acetate solution. Approximately eight grams (32 mmol) of a white solid was recovered as the final product. MW 249.26 g/mol; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ7.4 (t, 2H), δ7.3 (t, 2H), δ7.05 (t, 1H), δ6.7 (s, 1H), δ6.2 (s, 1H), δ5.6 (s, 1H), δ4.4 (m, 4H), δ1.9 (s, 3H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ167.5, δ153.4, δ137.9, δ136.2, δ129.4, δ126.5, δ123.8, δ119.0, δ63.2, δ63.0, δ18.6; IR (thin film) 3341, 3064, 2958, 2929, 1720, 1637, 1601, 1537, 1501, 1445, 1409, 1312, 1299, 1218, 1167, 1087, 946, 813, 755, 693 cm<sup>-1</sup>; Anal. Calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub>: C, 62.64; H, 6.08; N, 5.62. Found: C, 62.74; H, 6.19; N, 5.43.

M.P.: 58-60°C

#### **4. Cyclic Carbonate Acrylate**

IUPAC name: 4-acryloyloxymethyl-1,3-dioxolan-2-one

Common name: cyclic carbonate acrylate

Abbreviation: CCA

**Synthesis.** Eighteen grams of 4-hydroxymethyl-1,3-dioxolan-one (0.15 mol), 16 g of triethylamine (0.16 mol), and 100 ml of chloroform were introduced into a three-necked flask in an ice water bath equipped with a magnetic stirrer, reflux condenser and N<sub>2</sub> gas purge. 15 g of acryloyl chloride (0.18 mol, Aldrich Chemical, Milwaukee, WI, 98%) were added dropwise to the solution while maintaining the temperature below 5 °C, and the reaction was continued at room temperature for 6 more hours. The mixture was filtered, and the liquid phase was washed with 1 wt % aqueous NaOH solution, 1 wt % aqueous HCl solution, and saturated NaCl solution three times, followed by drying over sodium sulfate overnight. After filtering and removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel with hexane:ethyl acetate (3:1 by volume) mixture as the eluent. MW 172.04 g/mol; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ6.42 (d, 1H), δ6.15 (dd, 1H), δ5.9 (d, 1H), δ4.95 (m, 1H), δ4.58 (t, 1H), δ4.4 (q, 1H), δ4.3 (m, 2H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ165.6, δ154.8, δ132.8, δ127.4, δ74.1, δ66.3, δ63.4; IR (thin film) 3586, 3443, 2993, 2960, 2930, 1798, 1731, 1637, 1621, 1481, 1412, 1366, 1294, 1274, 1172, 1095, 1057, 980, 809, 773, 714 cm<sup>-1</sup>; Anal. Calcd for C<sub>7</sub>H<sub>8</sub>O<sub>5</sub>: C, 48.84; H, 4.69. Found: C, 48.67; H, 4.85; N, <0.5.

B.P.: 130 °C/0.5 mmHg

## 5. Phenyl Carbamate (NCO) Acrylate

IUPAC name: Acrylic acid 2-phenylcarbamoyloxy-ethyl ester

Common name: phenyl carbamate (NCO) acrylate

Abbreviation: phenyl NCO Acr

**Synthesis.** In the reaction, 5.5 grams of 2-hydroxyethyl acrylate (47 mmol, Aldrich Chemical, Milwaukee, WI, 96%), two drops of dibutyltin dilaurate (< 1 mmol), and 50 ml of ethyl acetate were added to a three-necked flask under nitrogen purge with magnetic stirring at 0 °C. 5 ml of phenyl isocyanate (46 mmol) was added to the solution dropwise over a one-hour period and the reaction was allowed to react overnight. After the reaction was completed, the organic phase was washed with 1 wt % aqueous NaOH solution, 1 wt % aqueous HCl solution, and three times with a saturated NaCl solution. It was then dried over sodium sulfate overnight and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel using hexane:ethyl acetate (3:1 by volume) eluent. Finally, the product was recrystallized from a chloroform:hexane (1:5 by volume) solution. MW 235.08 g/mol; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ7.4 (m, 5H), δ7.05 (m, 1H), δ6.7 (s, 1H), δ6.42 (d, 1H), δ6.05 (dd, 1H), δ5.82 (d, 1H), δ4.4 (s, 4H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ166.3, δ153.4, δ137.9, δ131.9, δ129.4, δ128.3, δ124.0, δ119.0, δ63.2, δ62.9; IR (thin film) 3343, 3060, 3039, 2960, 1940, 1729, 1636, 1598, 1537, 1501, 1445, 1409, 1315, 1297, 1220, 1190, 1087, 985, 809, 755, 691 cm<sup>-1</sup>; Anal. Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub>: C, 61.27; H, 5.58; N, 5.95. Found: C, 61.23; H, 5.72; N, 5.90.

M.P: 65-67 °C

### **Polymerization Example**

Unaltered phenyl carbamate acrylate sample was prepared by massing 0.00026 g (1.0 μmol) of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone into a 1-dram vial. Into this vial 0.2589 g (1.1 mmol) of phenyl carbamate acrylate monomer was added to make a 0.1 wt% initiator mixture. This mixture was heated to 70°C in a water bath and

stirred via a magnetic stir bar for approximately 5 minutes to ensure a homogeneous mixture. Approximately 5  $\mu\text{L}$  of the monomer was laminated between NaCl crystals and placed into a custom temperature cell, which maintained sample temperature at 67°C. The sample was irradiated with 5  $\text{mW}/\text{cm}^2$  ultraviolet (UV) light (filtered and centered at a wavelength of 365 nm) from an EXFO Ultracure 100ss light source for five minutes. The monomer attained approximately 100% conversion during the exposure, as monitored by RT-FTIR.