Supplementary data

Preparation, isolation and evaluation of novel N-acyloxytrialkylammonium salts as initiators for free radical polymerization of methacrylates under mildly thermal and accelerant promoted conditions.

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Experimental

N-acyloxytrialkylammonium salts

¹: N-benzoyloxytriethylammonium tetraphenylborate. Route 1 (Method 1).
Triethylamine (0.886g, 8.76 mmol), benzoylperoxide (2.12g, 8.76 mmol), sodium tetraphenyl borate (3g, 8.76 mmol), ethanol (50 mL) and toluene (50 mL) were added into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic stirrer. The flask was immersed in ice to which had been added sodium chloride to bring the temperature to −5 °C. The reaction mixture was reacted at −5 °C for 30 hours. The white precipitate was filtered out and dried under vacuum at room temperature to give 1.52 g of product (33% yield). The product was recrystalized from acetone/water (1:1) mixture. Melting point: 128 °C. IR (KBr wafer, cm⁻¹): 1770, 1050, 3100, 750. Anal.
2: N-benzoyloxytrimethylammonium tetraphenylborate. Route 2 (Method 2).
Trimethylamine N-oxide (0.3g, 4 mmol), benzoic anhydride (0.9g, 4 mmol), sodium tetraphenyl borate (1.37g, 0.004 mmol), ethanol (50 mL) and toluene (50 mL) were added into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic stirrer. The flask was immersed into dry ice to which had been added carbon tetrachloride to bring the temperature to –20 °C. The reaction mixture was reacted at –20 °C for 4 hours. The white precipitate was filtered out and dried under vacuum at room temperature to give 1.35 g of product (70% yield). The product was recrystallized from acetone/water (1:1) mixture. Melting point: 138 °C. IR (KBr wafer, cm\(^{-1}\)): 1770, 1050, 3100, 750. Anal. Calcd for C\(_{34}\)H\(_{34}\)BNO\(_2\): C, 81.9; H, 6.9; N, 2.87; B, 2.21. Found: C, 82.09; H, 6.97; N, 2.85; B, 2.22.

3: N-benzoyloxytrimethylammonium perchlorate.
Trimethylamine N-oxide (3g, 39.6 mmol), benzoic anhydride (9.96g, 39.6 mmol), sodium perchlorate (4.86g, 39.6 mmol), ethanol (50 mL) and toluene (50 mL) were added into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic stirrer. The flask was immersed into dry ice to which had been added carbon tetrachloride to bring the temperature to –20 °C. The reaction mixture was reacted at –20 °C for 4 hours. The white precipitate was filtered out and dried under vacuum at room temperature to give 9.39 g of product (85% yield). The product was recrystallized from acetone/water (1:1) mixture. Melting point: 166 °C. IR (KBr wafer, cm\(^{-1}\)): 1760, 1050, 3066, 700. Anal. Calcd for C\(_{10}\)H\(_{14}\)NClO\(_6\): C, 43; H, 5; N, 5; Cl, 12.5. Found: C, 43.05; H, 5.08; N, 5.02; Cl, 12.52.

4: N-butyloyloxytriethylammonium tetraphenylborate.
Trimethylamine N-oxide (1g, 13.3 mmol), butyric anhydride (2.10g, 13.3 mmol), sodium tetraphenyl borate (4.55 g, 13.3 mmol), ethanol (50 mL) and toluene (50 mL) were added into a 500 mL one-necked round bottom flask. To the mixture was added a
magnetic stirrer. The flask was immersed into dry ice to which had been added carbon tetrachloride to bring the temperature to –20 °C. The reaction mixture was reacted at –20 °C for 4 hours. The white precipitate was filtered out and dried under vacuum at room temperature to give 4.5 g of product (73% yield). The product was recrystallized from acetone/water (1:1) mixture. Melting point: 135 °C. IR (KBr wafer, cm⁻¹): 1750, 1050, 3100, 740. Anal. Calcd for C₃₁H₃₆BNO₂: C, 80; H, 7.35; N, 3.01; B, 2.33. Found: C, 80.24; H, 7.38; N, 3.19; B, 2.25.

5: N-propyloyloxytriethylammonium tetraphenylborate.
Trimethylamine N-oxide (1g, 13.3 mmol), propanoic anhydride (1.731g, 13.3 mmol), sodium tetraphenyl borate (4.55 g , 13.3 mmol), ethanol (50 mL) and toluene (50 mL) were added into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic stirrer. The flask was immersed into dry ice to which had been added carbon tetrachloride chloride to bring the temperature to –20 °C. The reaction mixture was reacted at –20 °C for 4 hours. The white precipitate was filtered out and dried under vacuum at room temperature to give 4.26g of product (71% yield). The product was recrystallized from acetone/water (1:1) mixture. Melting point: 134 °C. IR (KBr wafer, cm⁻¹): 1755, 1050, 3100, 740. Anal. Calcd for C₃₀H₃₄BNO₂: C, 79.86; H, 7.54; N, 3.1; B, 2.4. Found: C, 79.64; H, 7.49; N, 3.10; B, 2.30.

6: N-pentyloyloxytriethylammonium tetraphenylborate.
Trimethylamine N-oxide (1g, 13.3 mmol), pentanoic anhydride (2.48 g, 13.3 mmol), sodium tetraphenyl borate (4.55 g , 13.3 mmol), ethanol (50 mL) and toluene (50 mL) were added into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic stirrer. The flask was immersed into dry ice to which had been added carbon tetrachloride to bring the temperature to –20 °C. The reaction mixture was reacted at –20 °C for 4 hours. The white precipitate was filtered out and dried under vacuum at room temperature to give 4.14 g of product (65% yield). The product was recrystallized from acetone/water (1:1) mixture. Melting point: 121 °C. IR (KBr wafer, cm⁻¹): 1750, 1050, 3105, 740. Anal. Calcd for C₃₂H₃₈BNO₂: C, 80.2; H, 7.94; N, 2.92; B, 2.26. Found: C, 80.38; H, 7.74; N, 2.96; B, 2.24.
7: N-lauryloyloxytriethylammonium tetraphenylborate. (Method 1)

Triethylamine (0.886 g, 8.76 mmol), lauroyl peroxide (3.49 g, 8.76 mmol), sodium
tetraphenyl borate (3 g, 8.76 mmol), ethanol (50 mL) and toluene (50 mL) were added
into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic
stirrer. The flask was immersed into ice to which had been added sodium chloride to
bring the temperature to –5 °C. The reaction mixture was reacted at –5 °C for 4 hours.
The white precipitate was filtered out and dried under vacuum at room temperature to
give 3.19 g of product (60% yield). The product was recrystallized from acetone/water
(1:1) mixture. Melting point: 205 °C. IR (KBr wafer, cm⁻¹): 1760, 1050, 3105, 740. Anal.
Calcd for C₄₂H₅₈BNO₂: C, 81.45; H, 9.37; N, 2.26; B, 1.75. Found: C, 81.38; H, 9.34; N,
2.28; B, 1.74.

8: N-acetoxytrimethylammonium tetraphenylborate.

Trimethylamine N-oxide (1 g, 13.3 mmol), acetic anhydride (1.386 g, 13.3 mmol), sodium
tetraphenyl borate (4.55 g, 13.3 mmol), ethanol (50 mL) and toluene (50 mL) were added
into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic
stirrer. The flask was immersed into dry ice to which had been added carbon tetrachloride
to bring the temperature to –20 °C. The reaction mixture was reacted at –20 °C for 4 hours.
The white precipitate was filtered out and dried under vacuum at room temperature to
give 4.6 g of product (79% yield). The product was recrystallized from acetone/water
(1:1) mixture. Melting point: 170 °C. IR (KBr wafer, cm⁻¹): 1765, 1050, 3105, 740. Anal.
Calcd for C₂₉H₃₂BNO₂: C, 79.67; H, 7.33; N, 3.21; B, 2.47. Found: C, 79.69; H, 7.33; N,
3.28; B, 2.51.

9: N-benzoyloxy, N-(4-methylmorpholinyl)ammonium tetraphenylborate.

4-methylmorpholine N-oxide (1.61 g, 13.3 mmol), benzoic anhydride (3.34 g, 13.3
mmol), sodium tetraphenyl borate (4.55 g, 13.3 mmol), ethanol (50 mL) and toluene (50
mL) were added into a 500 mL one-necked round bottom flask. To the mixture was
added a magnetic stirrer. The flask was immersed into dry ice to which had been added
carbon tetrachloride to bring the temperature to –20 °C. The reaction mixture was reacted
at –20 °C for 4 hours. The white precipitate was filtered out and dried under vacuum at
room temperature to give 5.1 g of product (71% yield). The product was recrystalized from acetone/water (1:1) mixture. Melting point: 124 °C. IR (KBr wafer, cm⁻¹): 1770, 1050, 3100, 740. Anal. Calcd for C₃₆H₃₆BNO₃: C, 79.88; H, 6.66; N, 2.59; B, 2.00. Found: C, 79.81; H, 6.65; N, 2.6; B, 2.05.