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 ^{o}C. The reaction mixture was reacted at –5 ^{o}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 ^{o}C. IR (KBr wafer, cm^{-1}): 1770, 1050, 3100, 750. Anal.

Calcd for $C_{37}H_{40}BNO_2$: C, 82.1; H, 7.45; N, 2.6; B, 2.06. Found: C, 82.41; H, 7.65; N, 2.63; B, 2.06.

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 ^{o}C. The reaction mixture was reacted at –20 ^{o}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 recrystalized from acetone/water (1:1) mixture. Melting point: 138 ^{o}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 ^{o}C. The reaction mixture was reacted at –20 ^{o}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 recrystalized from acetone/water (1:1) mixture. Melting point: 166 ^{o}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 ^{o}C. The reaction mixture was reacted at –20 ^{o}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 recrystalized from acetone/water (1:1) mixture. Melting point: 135 ^{o}C. IR (KBr wafer, cm^{-1}): 1750, 1050, 3100, 740. Anal. Calcd for $C_{31}H_{36}BNO_2$: 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 ^{o}C. The reaction mixture was reacted at –20 ^{o}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 recrystalized from acetone/water (1:1) mixture. Melting point: 134 ^{o}C. IR (KBr wafer, cm^{-1}): 1755, 1050, 3100, 740. Anal. Calcd for $C_{30}H_{34}BNO_2$: 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 ^{o}C. The reaction mixture was reacted at –20 ^{o}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 recrystalized from acetone/water (1:1) mixture. Melting point: 121 ^{o}C. IR (KBr wafer, cm^{-1}): 1750, 1050, 3105, 740. Anal. Calcd for $C_{32}H_{38}BNO_2$: 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 (0.886g, 8.76 mmol), lauroyl peroxide (3.49 g, 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 into ice to which had been added sodium chloride to bring the temperature to –5 ^{o}C. The reaction mixture was reacted at –5 ^{o}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 recrystalized from acetone/water (1:1) mixture. Melting point: 205 ^{o}C. IR (KBr wafer, cm^{-1}): 1760, 1050, 3105, 740. Anal. Calcd for $C_{42}H_{58}BNO_2$: 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 (1g, 13.3 mmol), acetic anhydride (1.386 g, 13.3 mmol), sodium tetraphenyl borate (4.55g , 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 ^{o}C. The reaction mixture was reacted at –20 ^{o}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 recrystalized from acetone/water (1:1) mixture. Melting point: 170 ^{o}C. IR (KBr wafer, cm^{-1}): 1765, 1050, 3105, 740. Anal. Calcd for $C_{29}H_{32}BNO_2$: 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 (1.61g, 13.3 mmol), benzoic anhydride (3.34 g, 13.3 mmol), sodium tetraphenyl borate (4.55g, 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 ^{o}C. The reaction mixture was reacted at –20 ^{o}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 ^{o}C. IR (KBr wafer, cm^{-1}): 1770, 1050, 3100, 740. Anal. Calcd for $C_{36}H_{36}BNO_3$: 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.