List of Figures

Figure | Page
-------|------
2.1 | Laboratory-scale setup for polymerization under inert atmosphere | 44
2.2 | Flash distillation apparatus for solvent and monomer distillation | 45
2.3 | Bench-top reactor for group-transfer polymerization | 46
3.1 | $^1$H NMR spectrum of hydroxyl end-functional PMMA (Entry 9, table 3.2) in acetone-d$_6$ (500 MHz) | 58
3.2 | SEC trace of benzhydryl alcohol terminated PMMA, using RI and UV detector | 60
3.3 | HPLC (LACCC) analysis of PMMA, PMMA-OSiMe$_3$, and PMMA-OH using RI and UV detector | 61
3.4 | MALDI-TOF spectrum of hydroxyl end-functional PMMA prepared by GTP (using 0.1 mol% TBABB catalyst; entry 2, table 3.2). $M_n$=100.12(20)+H(1.0079)+107.1324(C$_7$H$_7$O)+K$^+$ (39.098). (Matrix: Dithranol and CF$_3$COOK for enhancement of ion formation) ($\Delta$= 6 Da) | 62
3.5 | MALDI-TOF spectrum of hydroxyl end-functional PMMA prepared by GTP (using 1 mol% TBABB catalyst entry 9, table 3.2). $M_n$=100.12(20)+H(1.0079)+107.1324(C$_7$H$_7$O)+Li$^+$ (6.941) (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) ($\Delta$= 14 Da) | 63
3.6 | MALDI-TOF spectrum of hydroxyl end-functional PMMA prepared by GTP (0.5 mol%, entry 8, table 3.2). $M_n$=100.12(20)+H(1.0079)+107.1324(C$_7$H$_7$O)+Li$^+$ (6.941) (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) ($\Delta$= 7 Da) | 65
4.1 | $^1$H NMR spectrum of cyclohexanone adduct in CDCl$_3$ (200 MHz) | 76
4.2 | $^{13}$C NMR spectrum of cyclohexanone adduct in CDCl$_3$ (50 MHz) | 76
4.3 | $^1$H NMR spectrum of isophorone adduct in CDCl$_3$ (200 MHz) | 76
4.4 | $^{13}$C NMR spectrum of isophorone adduct in CDCl$_3$ (50 MHz) | 77
4.5 | $^1$H NMR spectrum of cyclohexanone-end capped PMMA (entry 1, table 4.3) in CDCl$_3$ (500 MHz) | 79
4.6 | $^{13}$C NMR spectrum of cyclohexanone-end capped PMMA (entry 1, table 4.3) in CDCl$_3$ (500 MHz) | 79
4.3) in CDCl₃ (125 MHz)

4.7 MALDI-TOF spectrum of cyclohexanone-end functionalized PMMA prepared by GTP using TBABB catalyst for silyl ketene acetal ended PMMA and TBABB for functionalization reaction at room temperature (entry 1, table 4.3). \([M+Li]^- = 100.12 \text{(MMA)}^* n(\text{DP}) + H(1.0079) + EG^* (C_6H_7O) (97.1371) + 6.9(Li)\) (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) \((\Delta = 6 \text{ Da})\)

4.8 \(^1\text{H NMR spectrum of lactone adduct in CDCl₃ (500 MHz)}\)

4.9 \(^{13}\text{C NMR spectrum of lactone adduct in CDCl₃ (125 MHz)}\)

4.10 \(^1\text{H NMR spectrum of lactone adduct in CDCl₃ (200 MHz)}\)

4.11 \(^{13}\text{C NMR spectrum of lactone adduct in CDCl₃ (50 MHz)}\)

4.12 \(^1\text{H NMR spectrum of lactone adduct (entry 2, table 4.6) in CDCl₃ (200 MHz)}\)

4.13 \(^{13}\text{C NMR spectrum of lactone adduct (entry 2, table 4.6) in CDCl₃ (50 MHz)}\)

4.14 \(^1\text{H NMR spectrum of lactone-end capped PMMA (entry 1, table 4.7) in CDCl₃}\)

4.15 \(^{13}\text{C NMR spectrum of lactone-end capped PMMA (entry 1, table 4.7) in CDCl₃}\)

4.16 MALDI-ToF spectrum of lactone-end capped PMMA prepared by GTP using 0.1-mol\% TBABB catalyst at 30°C (entry 1, table 4.7). \([M+Li]^+ = 100.12 \text{(MMA)}^* n(\text{DP}) + H(1.0079) + EG^* (C_5H_7O_2) (99.1096) + 6.9(Li)\) (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) \((\Delta = 6 \text{ Da})\)

4.17 MALDI-TOF spectrum of lactone-end capped PMMA prepared by GTP using TBABB catalyst for silyl ketene acetal ended PMMA and TBABB for functionalization reaction at room temperature (entry 2, table 4.7). \([M+Li]^- = 100.12 \text{(MMA)}^* n(\text{DP}) + H(1.0079) + EG^* (C_5H_7O_2) (99.1096) + 6.9(Li)\) (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) \((\Delta = 6 \text{ Da})\)

5.1 \(^1\text{H NMR spectrum of β-aminoester in CDCl₃ (200 MHz)}\)

5.2 \(^{13}\text{C NMR spectrum of β-amino ester in CDCl₃ (50 MHz)}\)
5.3 $^1$H NMR spectrum of amine-terminated PMMA (entry 1, table 5.2) in acetone-d$_6$

5.4 $^{13}$C NMR spectrum of amine-terminated PMMA (entry 1, table 5.2) in acetone-d$_6$ (50 MHz)

5.5 SEC trace of amine-terminated PMMA (entry 1, table 5.2)

5.6 MALDI-ToF spectrum of amine-terminated PMMA prepared by GTP using TBABB catalyst for silyl ketene acetal ended PMMA and Lewis acid Zn$_2$ for functionalization reaction at room temperature (entry 1, table 5.2).

\[ [M+Li]^+ = 100.12 \text{ (MMA) } * n \text{ (DP) } + H (1.0079) + \text{ Ar-CH-NH}_2 (106.1476) + \text{ Li }^+ (6.941). \text{ (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) } (\Delta = 7 \text{ Da}) \]

6.1 $^1$H NMR spectrum of crude product (entry 1, table 6.1) in CDCl$_3$ (200 MHz)

6.2 $^1$H NMR spectra of silyl ether adduct of itaconic anhydride adduct in acetone-d$_6$+CDCl$_3$ (200 MHz) (entry 8, table 6.1)

6.3 $^1$H NMR spectrum of diacid in CDCl$_3$ + acetone-d$_6$ (200 MHz) (entry 8, table 6.1)

6.4 $^1$H NMR spectrum of 1,2-adduct of citraconic anhydride in CDCl$_3$ (200 MHz) (entry 2, table 6.2)

6.5 $^1$H NMR spectrum of 1,2-adduct of citraconic anhydride in CDCl$_3$ (D$_2$O exchange) (200 MHz) (entry 2, table 6.2)

6.6 $^1$H NMR spectrum of crude product in CDCl$_3$ (200 MHz)

6.7 $^1$H NMR spectrum of 1,2-adduct of 2,3-dimethylmaleic anhydride in CDCl$_3$ (500 MHz) (entry 4, table 6.3)

6.8 $^{13}$C NMR spectrum of 1,2-adduct of 2,3-dimethylmaleic anhydride in CDCl$_3$ (125 MHz) (entry 4, table 6.3)

6.9 DEPT of 1,2-adduct of 2,3-dimethylmaleic anhydride in CDCl$_3$ (500 MHz) (entry 4, table 6.3)

6.10 $^1$H NMR spectrum of hydroxyl compound of 1,2-adduct of 2,3-dimethylmaleic Anhydride in CDCl$_3$ (500 MHz) (entry 4, table 6.3)

6.11 $^{13}$C NMR spectrum of hydroxyl compound of 1,2-adduct of 2,3-dimethylmaleic anhydride in CDCl$_3$ (125 MHz) (entry 4, table 6.3)
6.12 DEPT of hydroxyl compound of 1,2-adduct of 2,3-dimethylmaleic anhydride in CDCl₃ (500 MHz) (entry 4, table 6.3)