Supplementary Information

Synthesis of well-defined poly(acrylates) in ionic liquids *via* copper (II) mediated photo-induced living radical polymerization

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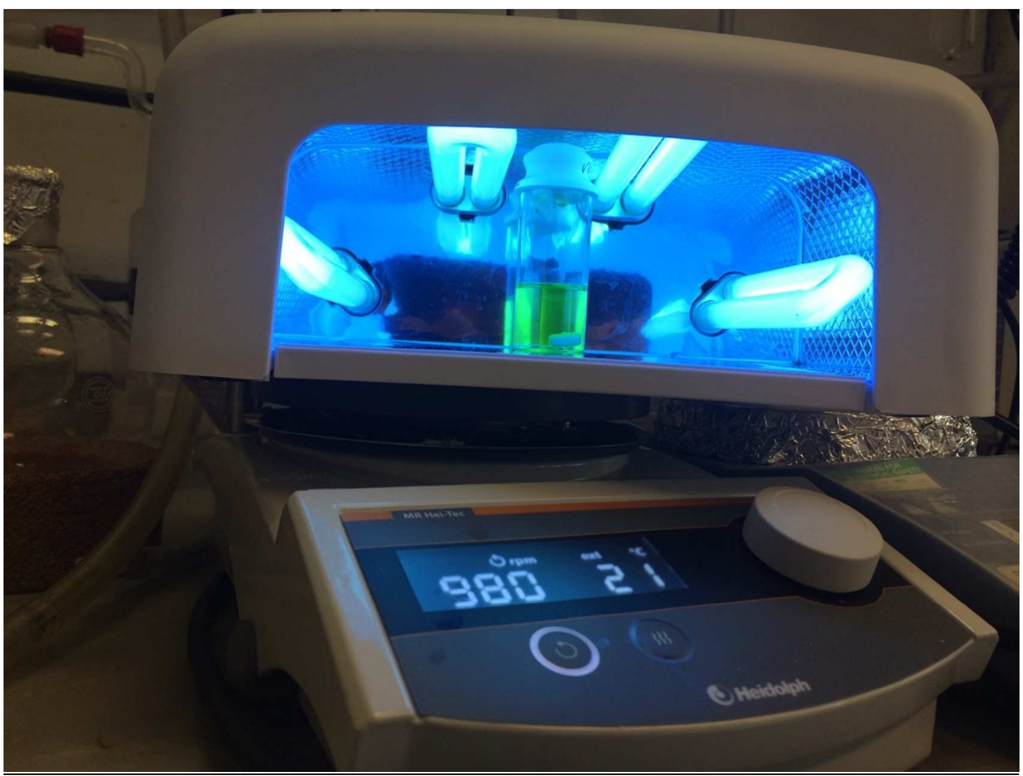
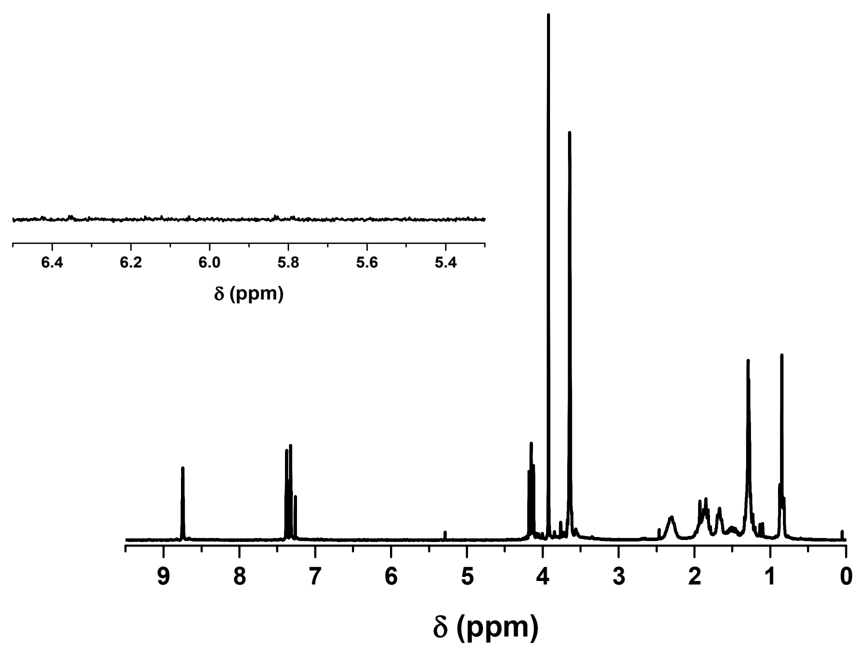


Figure S1: Typical set up for photoinduced polymerization.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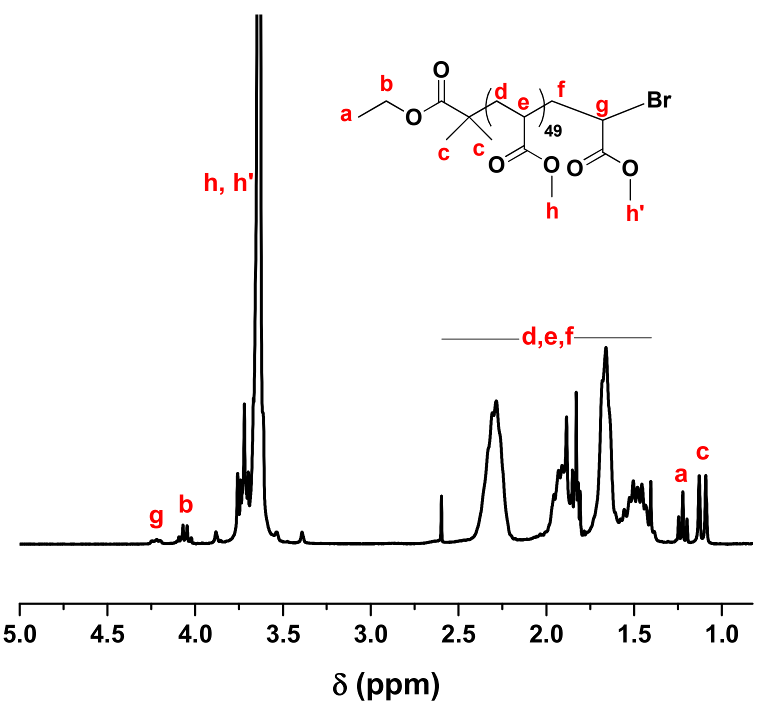
δ (ppm)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5.0
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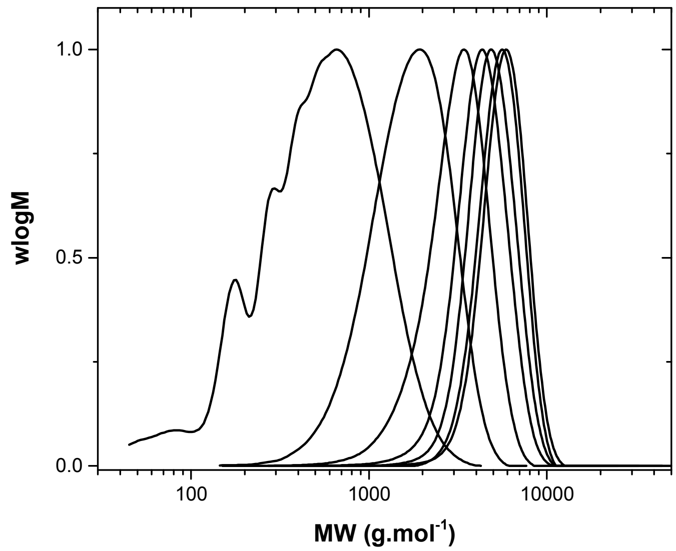
3.5
3.0
2.5
2.0
1.5
1.0
δ (ppm)

Figure S2: [1]H NMR spectrum of PMA in [C_6mim][BF_4] (50:50 *v/v* monomer/ionic liquid) [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] (up) and [1]H NMR of purified PMA, integrated ratio of g : c = 0.99 : 6.00



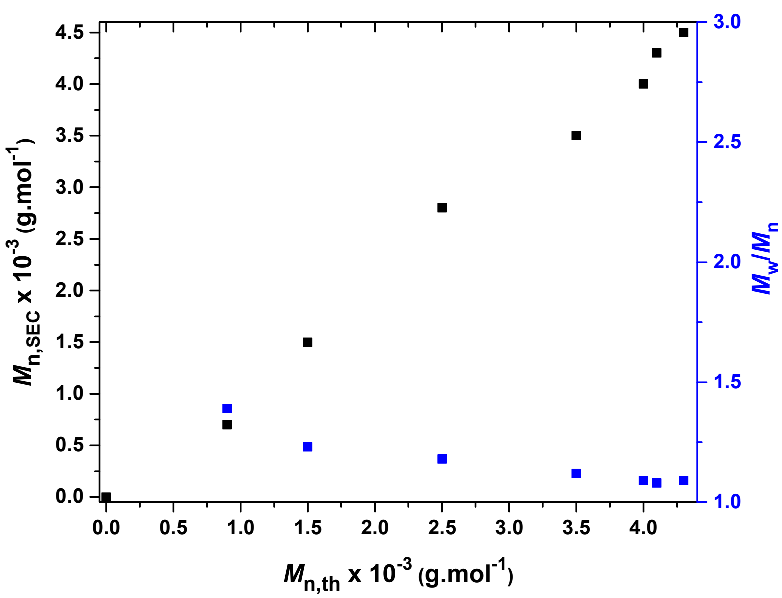


Figure S3: SEC analysis showing the molecular weight evolution during the kinetic experiment of photo-induced polymerization of MA in [C_6mim][BF_4] (up) and $M_{n,SEC}$ and M_w/M_n *vs.* theoretical molecular weight $M_{n,th}$ (down).

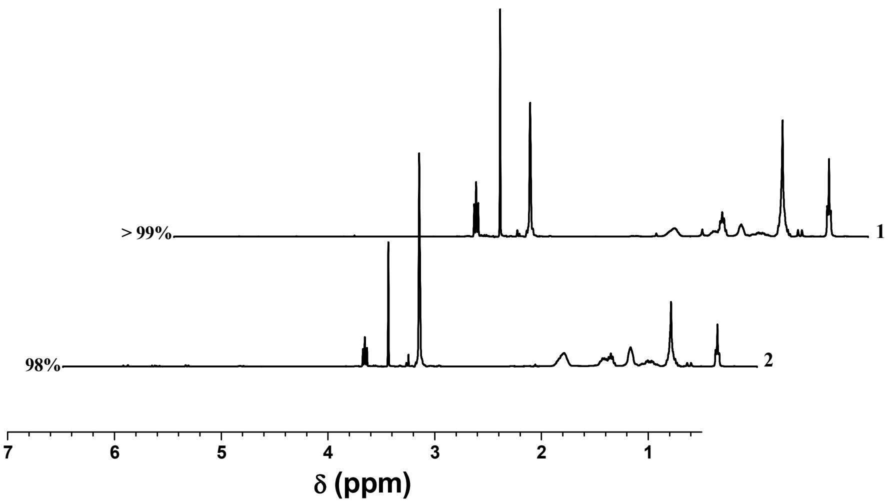


Figure S4: [1]H NMR for the *in situ* chain extension from a PMA macroinitiator in $[C_6mim][BF_4]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: $[MA]:[EBiB]:[CuBr_2]:[Me_6\text{-Tren}]$ = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of MA (50 equiv.) in $[C_6mim][BF_4]$ (33% *v/v*).

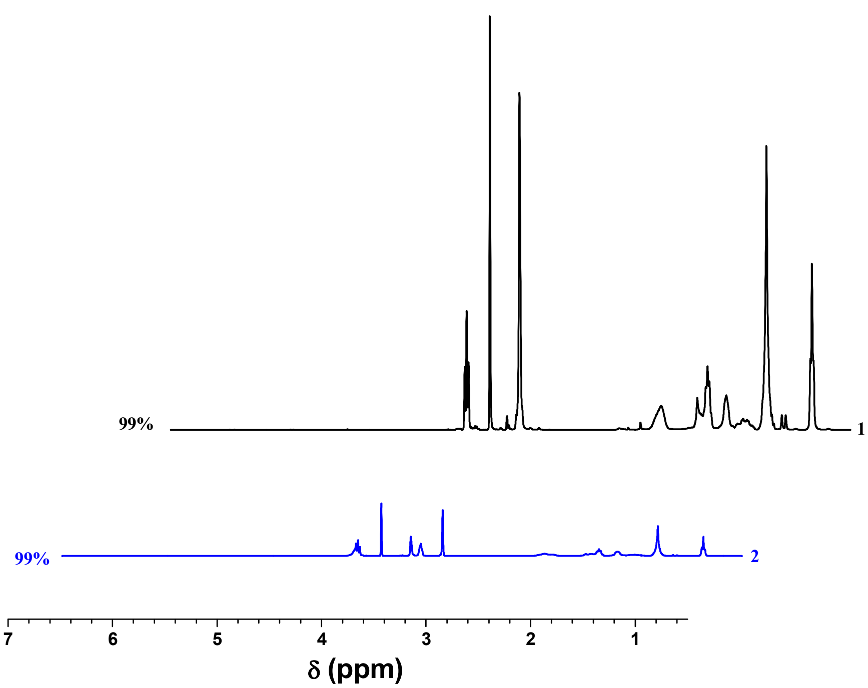
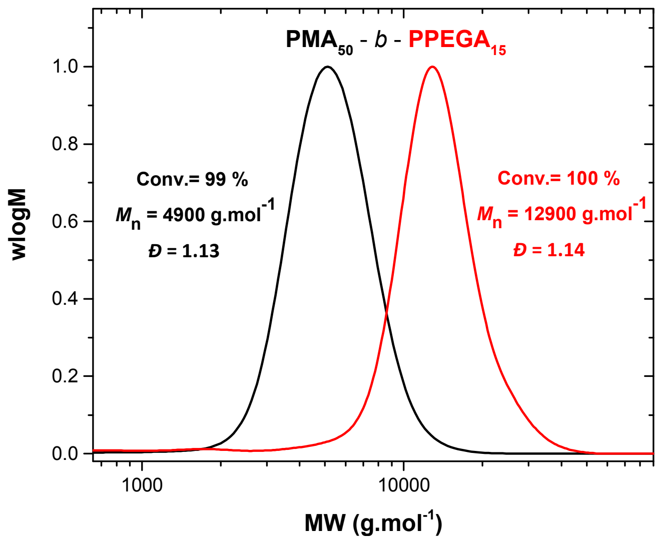


Figure S5: [1]H NMR for block copolymerization from a PMA macroinitiator in $[C_6mim][BF_4]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: $[MA]:[EBiB]:[CuBr_2]:[Me_6\text{-Tren}]$ = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of EGA (50 equiv.) in $[C_6mim][BF_4]$ (33% *v/v*).



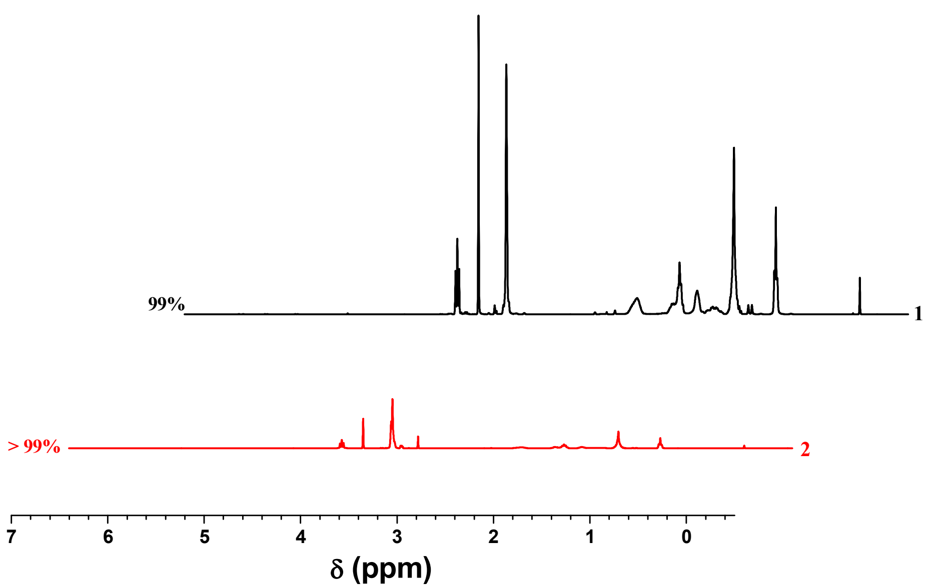


Figure S6: SEC and [1]H NMR analysis for block copolymerization from a PMA macroinitiator in [C_6mim][BF_4] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of PEGA (15 equiv.) in [C_6mim][BF_4] (33% *v/v*).

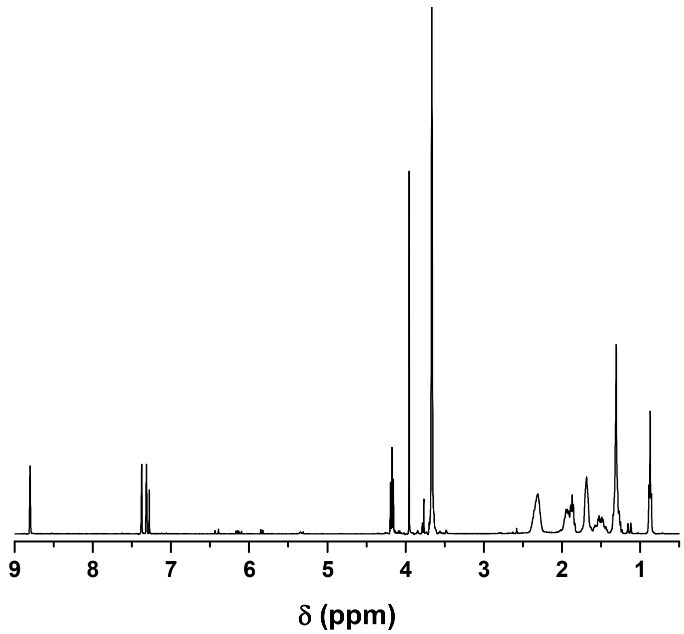


Figure S7: ^{1}H NMR spectrum for the synthesis of PMA_{200} in $[C_6mim][BF_4]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: $[MA]:[EBiB]:[CuBr_2]:[Me_6\text{-Tren}] = [200]:[1]:[0.02]:[0.12]$.

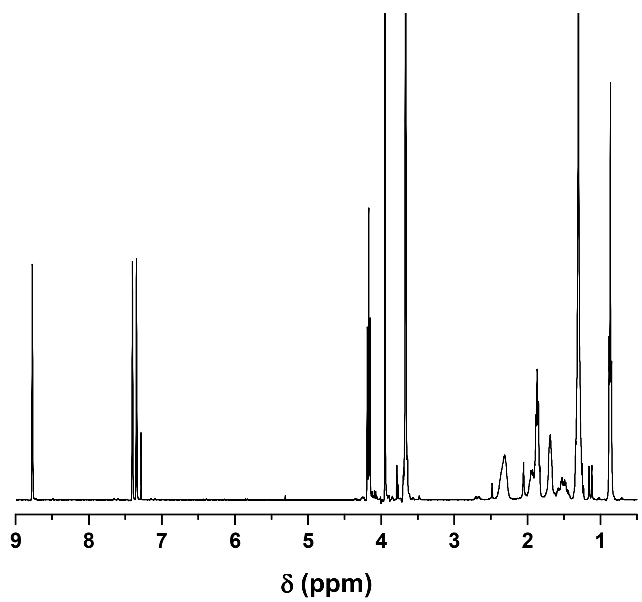


Figure S8: ^{1}H NMR spectrum for the synthesis of PMA_{400} in $[C_6mim][BF_4]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: $[MA]:[EBiB]:[CuBr_2]:[Me_6\text{-Tren}] = [400]:[1]:[0.02]:[0.12]$.

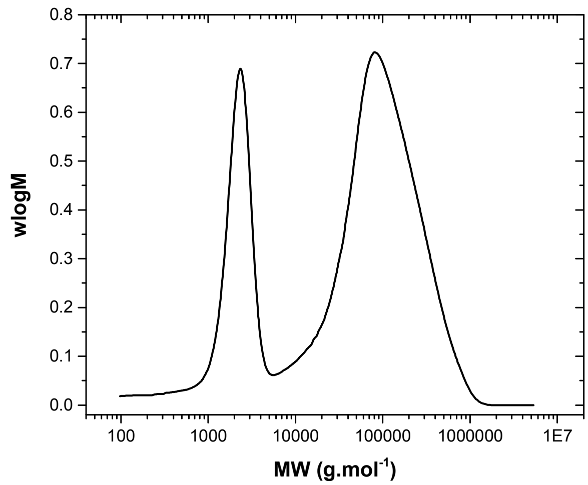
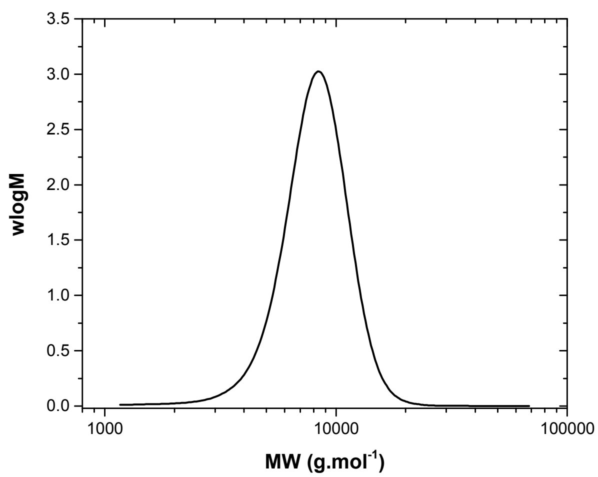


Figure S9: SEC analysis for the synthesis of PBA in [C_6mim][BF_4] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [*n*-BA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].



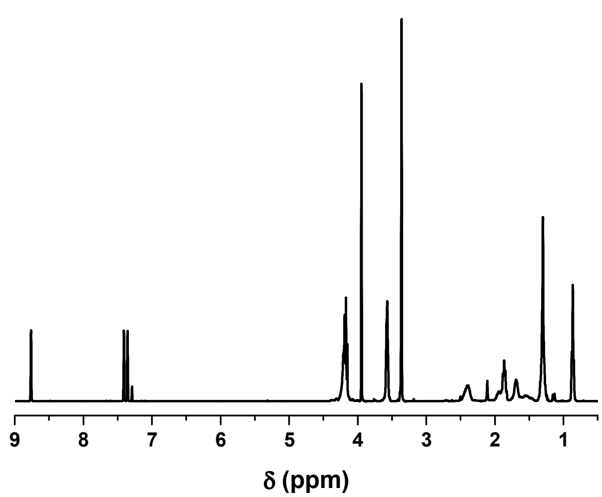
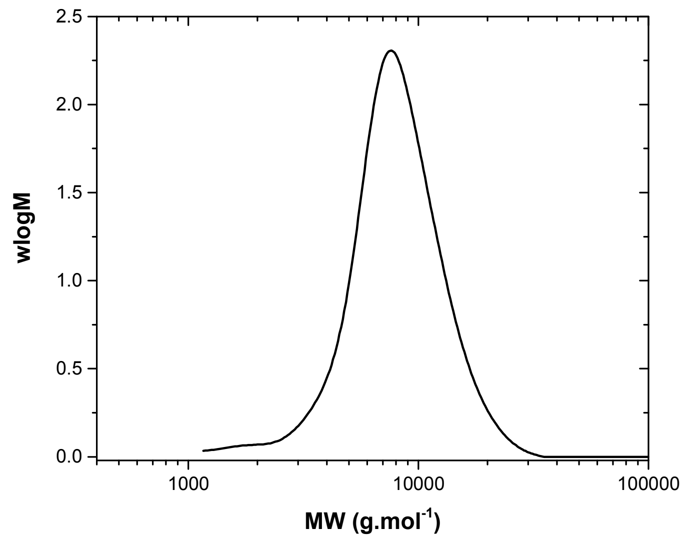


Figure S10: SEC and ^{1}H NMR analysis for the synthesis of PEGA in [C_6mim][BF_4] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [EGA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].



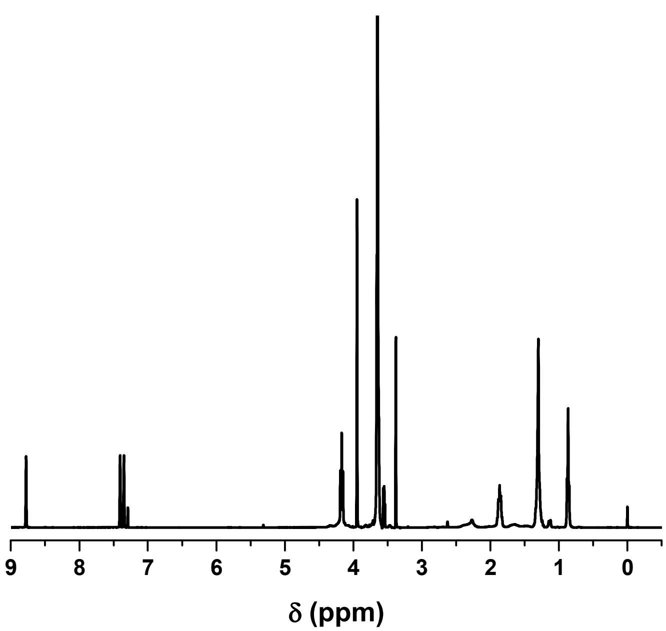
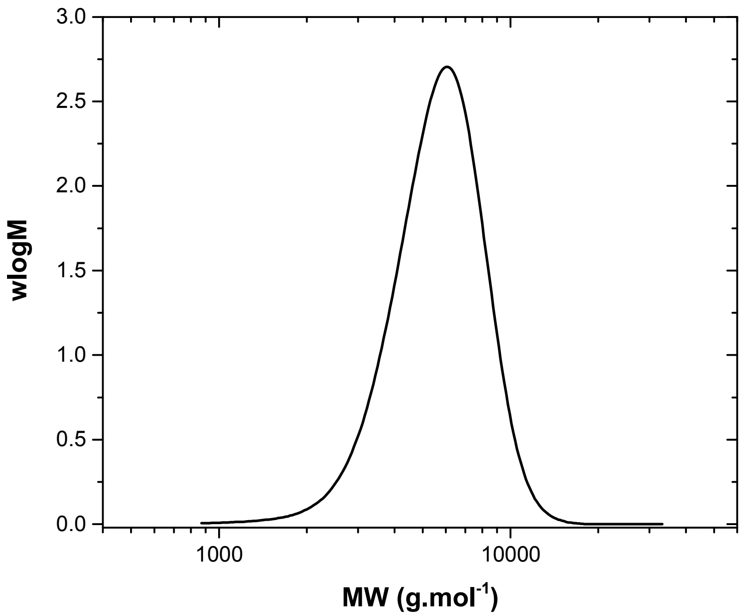


Figure S11: SEC and ^{1}H NMR analysis for the synthesis of PPEGA in [C_6mim][BF_4] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [PEGA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [15]:[1]:[0.02]:[0.12].



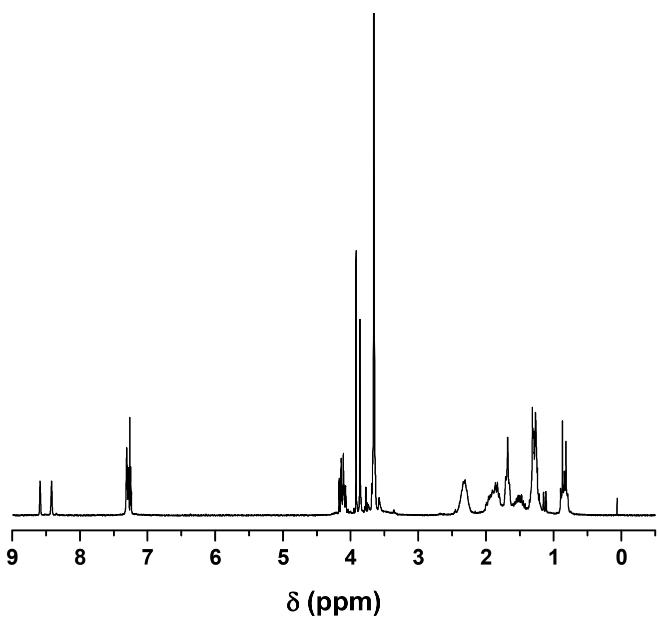
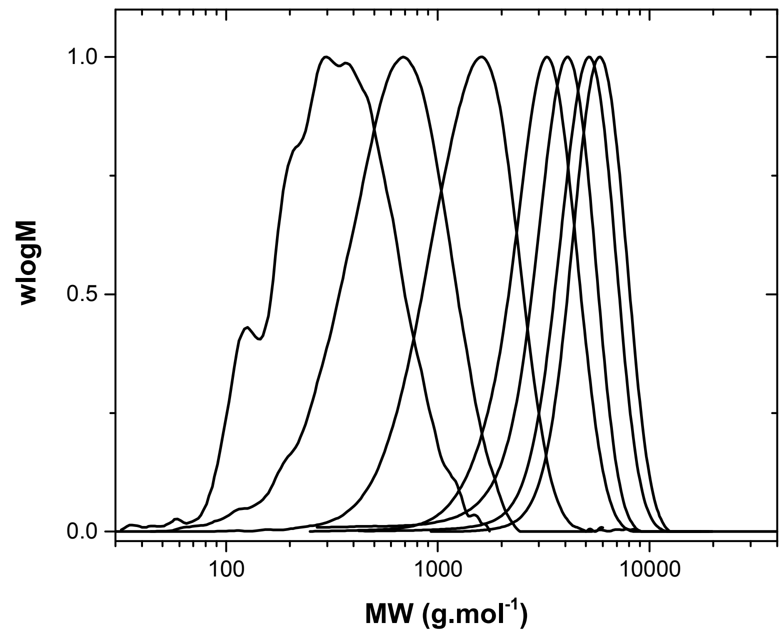


Figure S12: SEC and [1]H NMR analysis for the synthesis of PMA in [C_6mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].



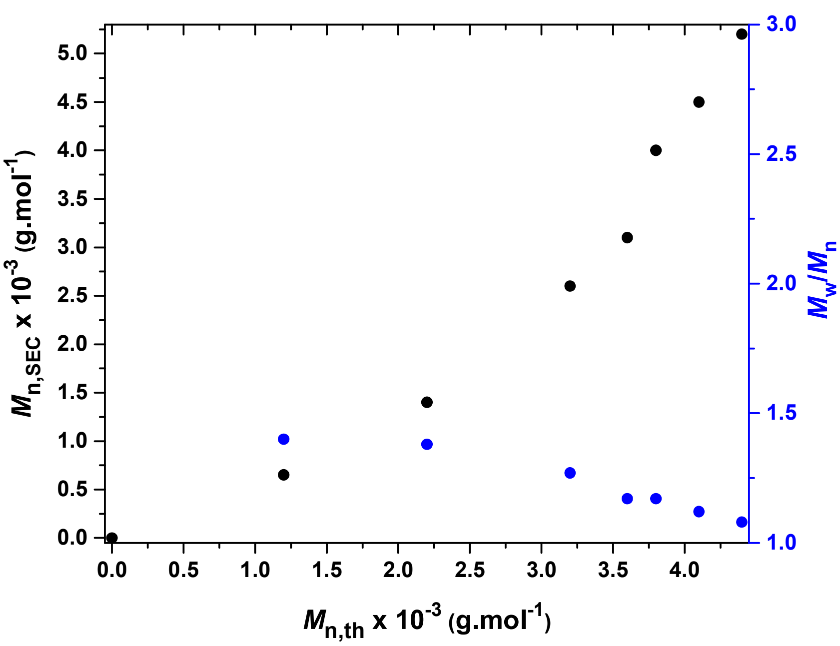


Figure S13: SEC analysis showing the molecular weight evolution during the kinetic experiment of photo-induced polymerization of MA in [C_6mim][PF_6] (up) and $M_{n,SEC}$ and M_w/M_n *vs.* theoretical molecular weight $M_{n,th}$ (down).

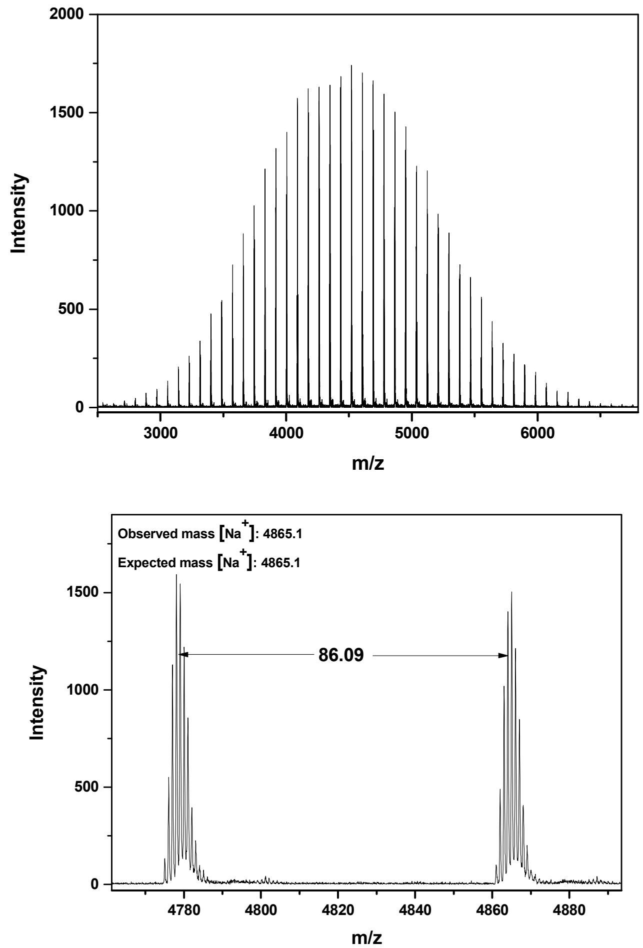
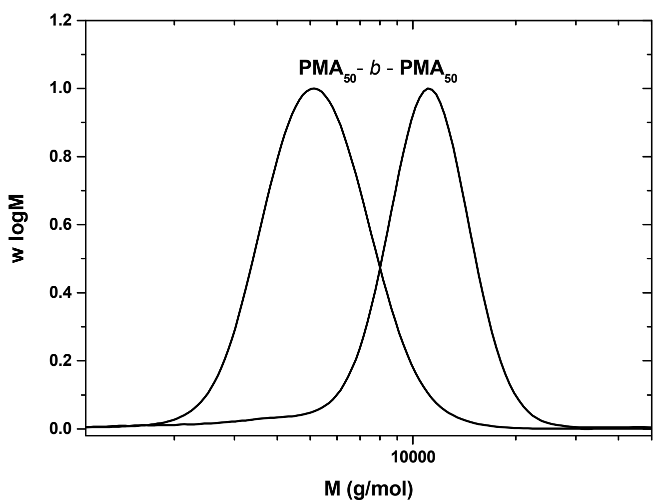


Figure S14: MALDI-ToF-MS spectrum of PMA obtained from the polymerization [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in [C_6mim][PF_6] (50:50 *v/v* monomer/ionic liquid).



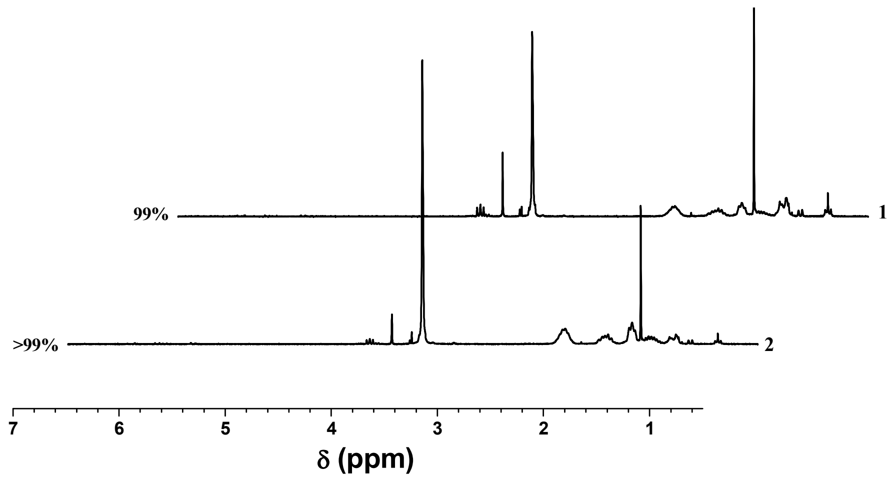
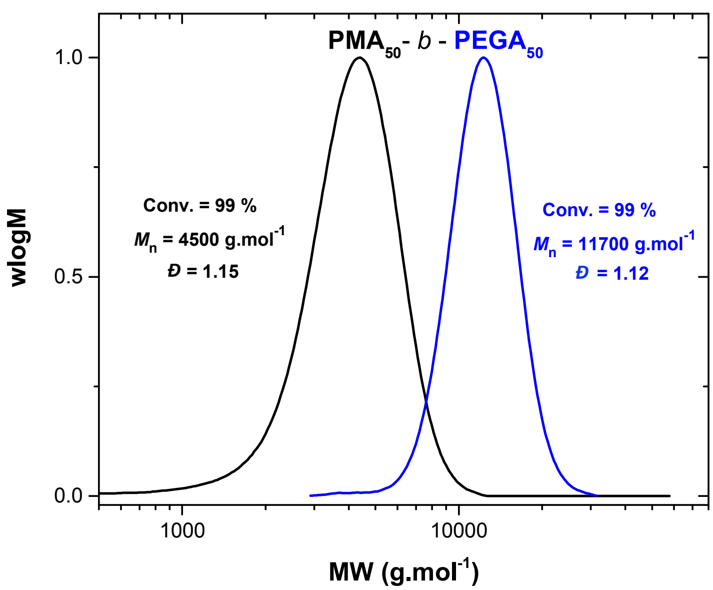


Figure S15: SEC and ^{1}H NMR analysis for the *in situ* chain extension from a PMA macroinitiator in [C_6mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of MA(50 equiv.) in [C_6mim][PF_6] (33% *v/v*).



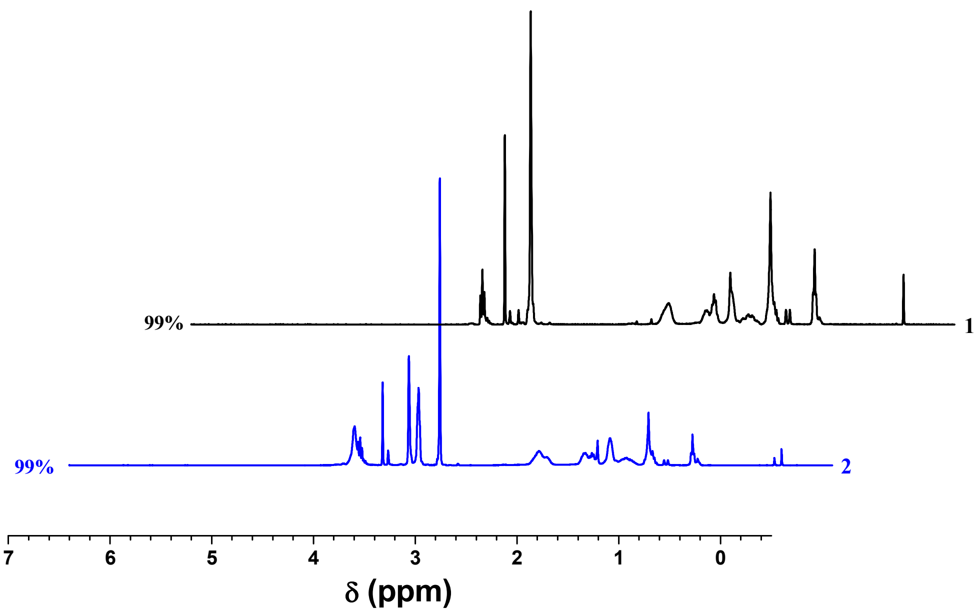
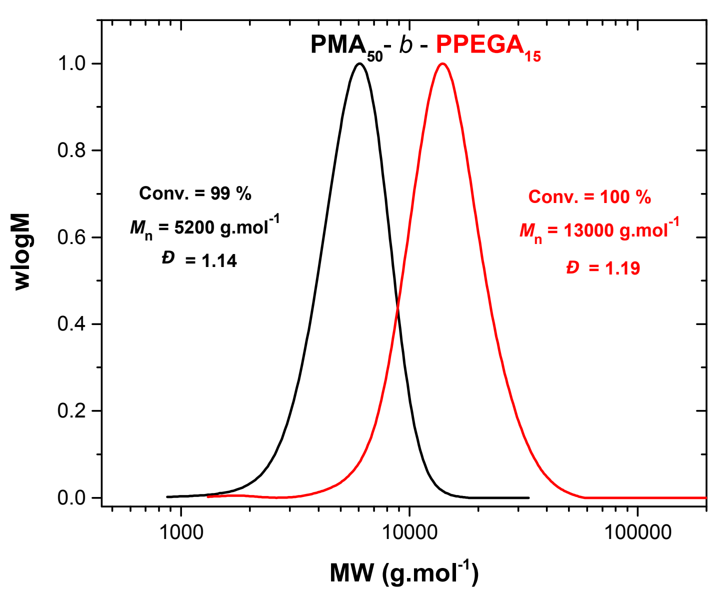


Figure S16: SEC and [1]H NMR analysis for block copolymerization from a PMA macroinitiator in $[C_6mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:$[CuBr_2]$:$[Me_6$-Tren] = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of EGA (50 equiv.) in $[C_6mim][PF_6]$ (33% *v/v*).



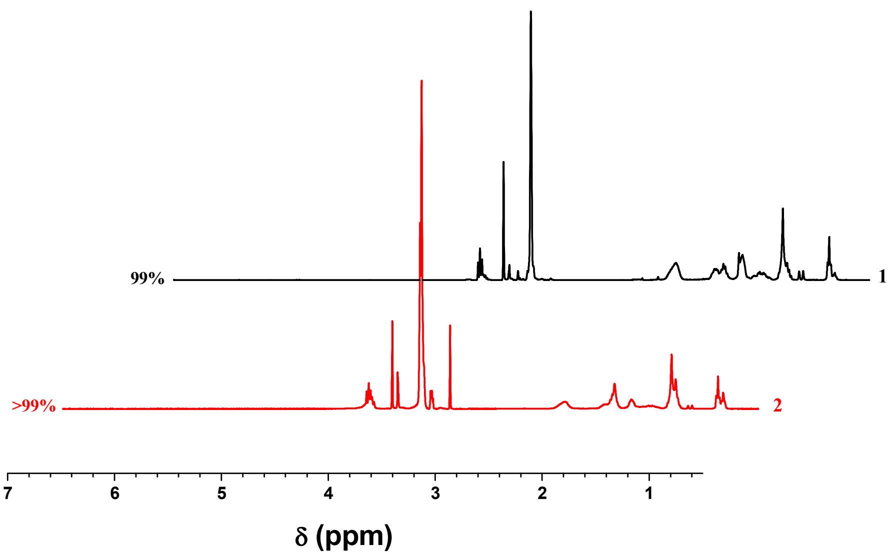
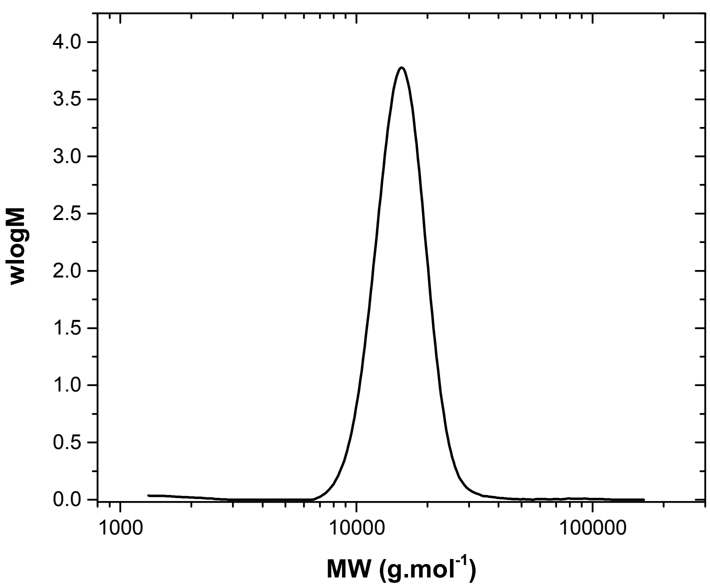


Figure S17: SEC and [1]H NMR analysis for block copolymerization from a PMA macroinitiator in $[C_6mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:$[CuBr_2]$:$[Me_6\text{-Tren}]$ = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of PEGA (15 equiv.) in $[C_6mim][PF_6]$ (33% *v/v*).



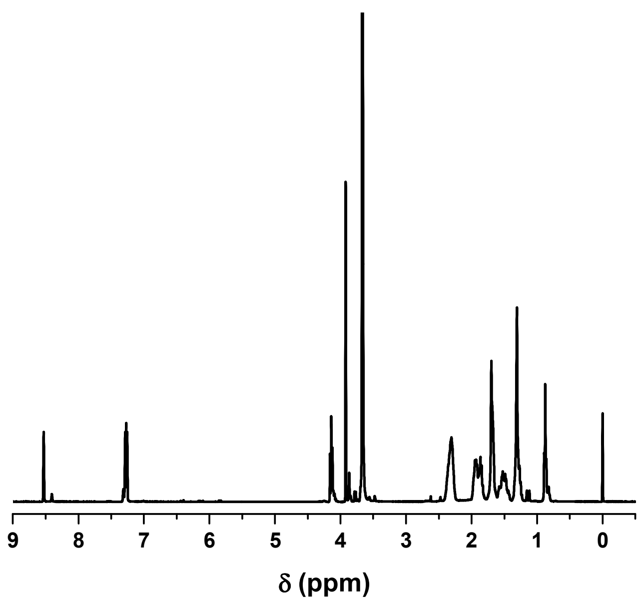
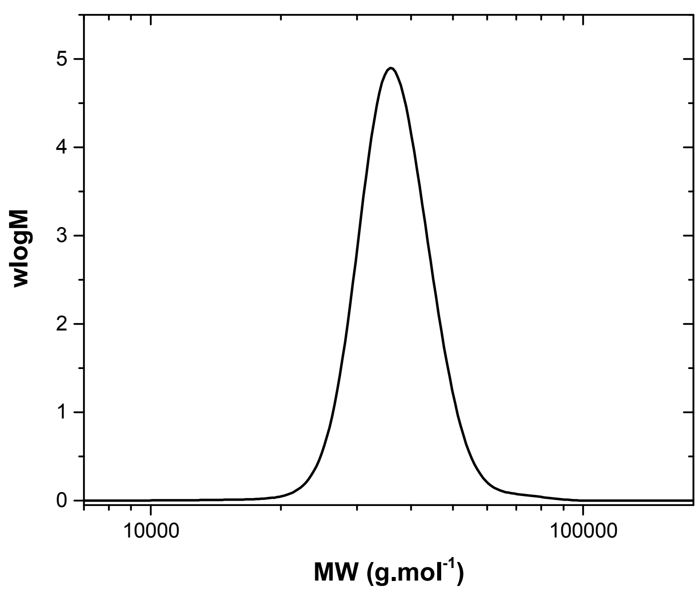


Figure S18: SEC and ^{1}H NMR analysis for the synthesis of PMA_{200} in $[C_6mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:$[CuBr_2]$:$[Me_6$-Tren] = [200]:[1]:[0.02]:[0.12].



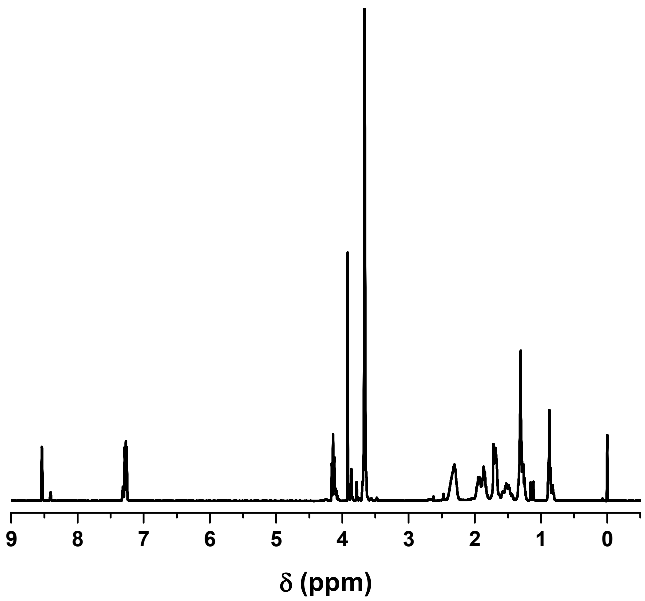
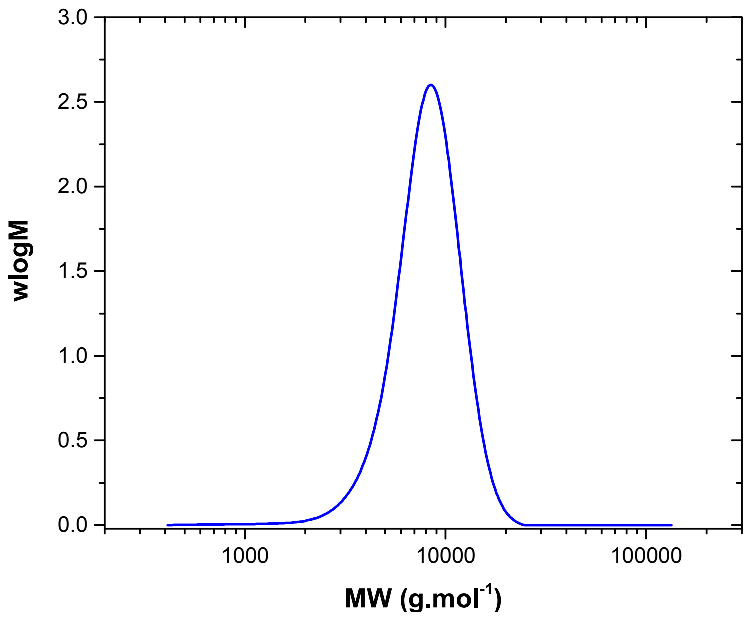


Figure S19: SEC and [1]H NMR analysis for the synthesis of PMA_{400} in $[C_6mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:$[CuBr_2]$:$[Me_6$-Tren] = [400]:[1]:[0.02]:[0.12].



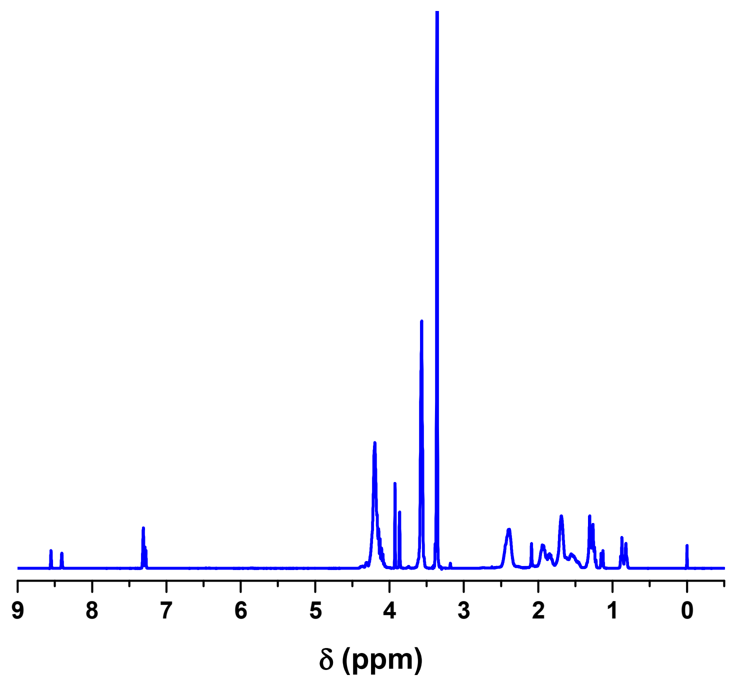
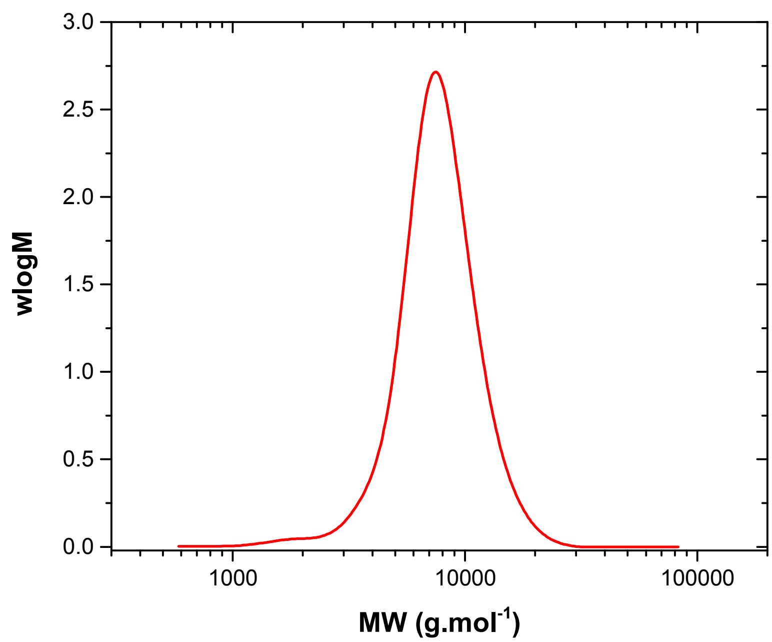


Figure S20: SEC and ^{1}H NMR analysis for the synthesis of PEGA in [C_6mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [EGA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].



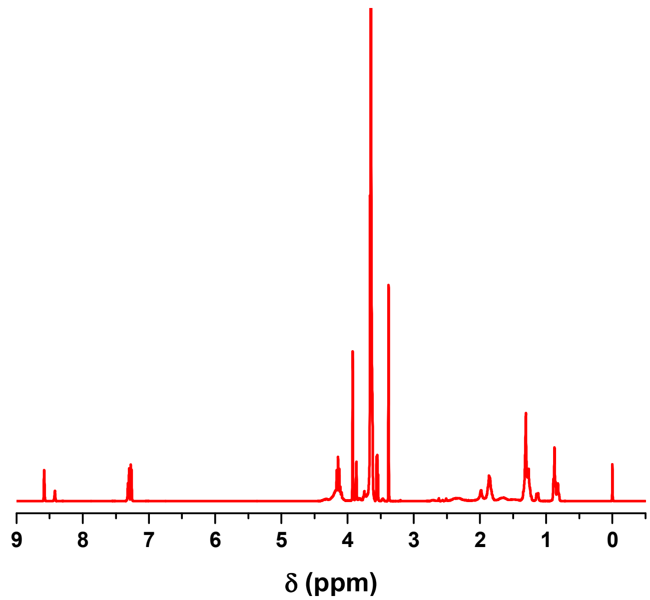


Figure S21: SEC and [1]H NMR analysis for the synthesis of PPEGA in [C$_6$mim][PF$_6$] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [PEGA]:[EBiB]:[CuBr$_2$]:[Me$_6$-Tren] = [15]:[1]:[0.02]:[0.12].

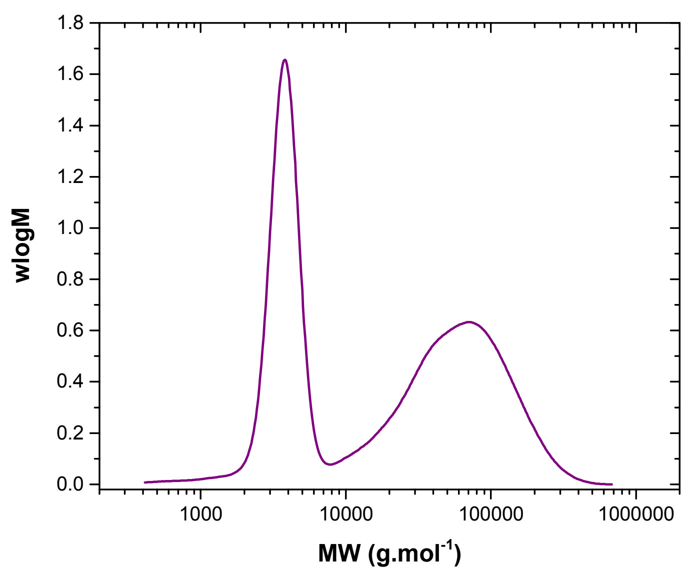
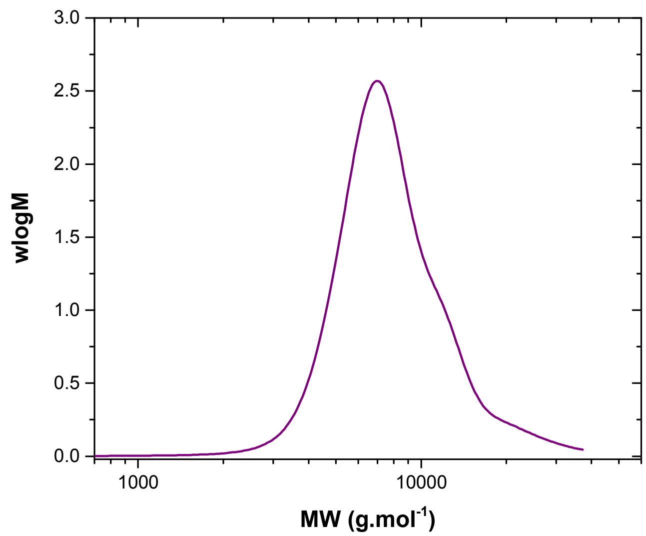


Figure S22: SEC analysis for the synthesis of PBA in [C$_6$mim][PF$_6$] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [*n*-BA]:[EBiB]:[CuBr$_2$]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12].



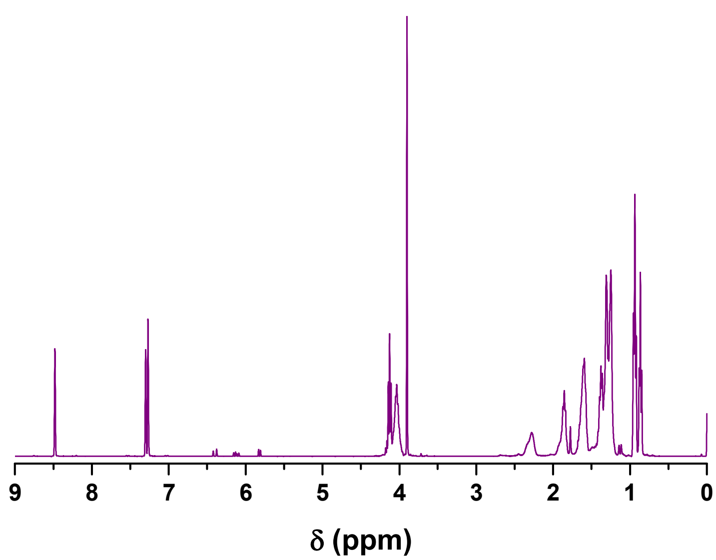


Figure S23: SEC and [1]H NMR analysis for the synthesis of PBA in [C_8mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [*n*-BA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].

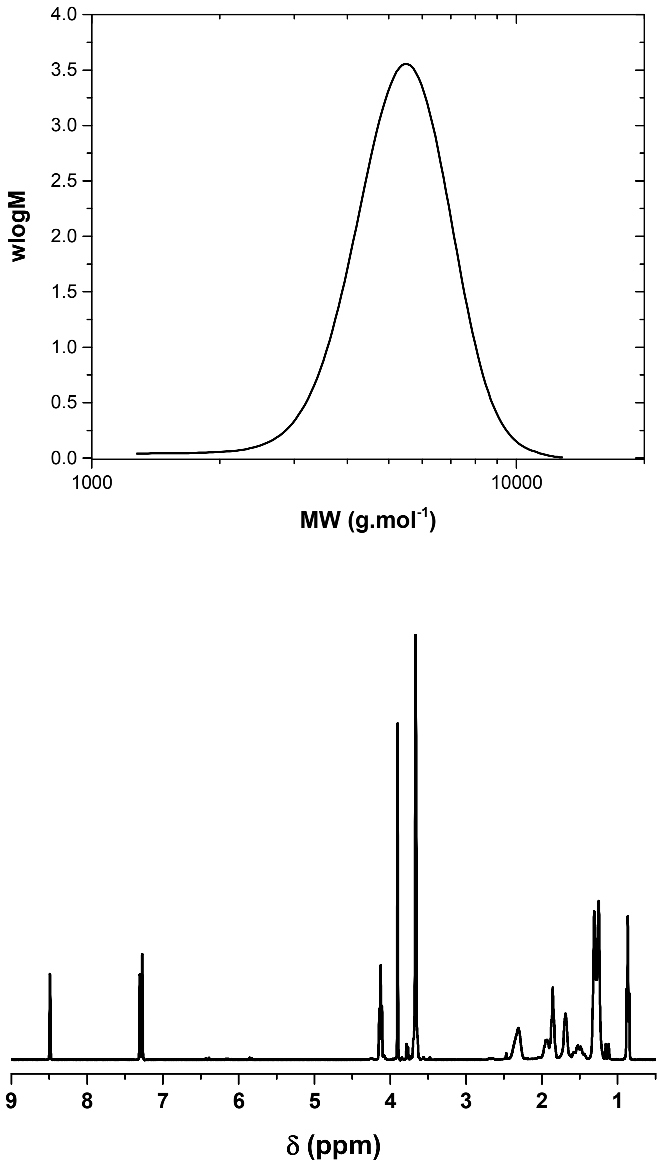
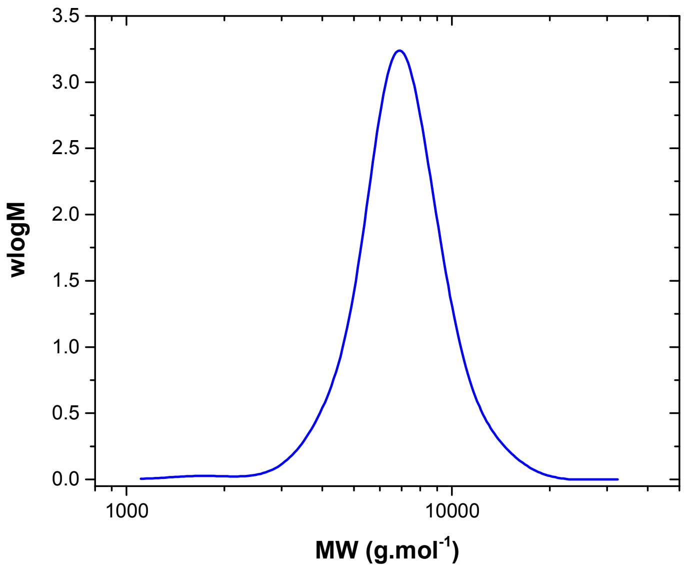


Figure S24: SEC and ^{1}H NMR analysis for the synthesis of PMA in [C_8mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].



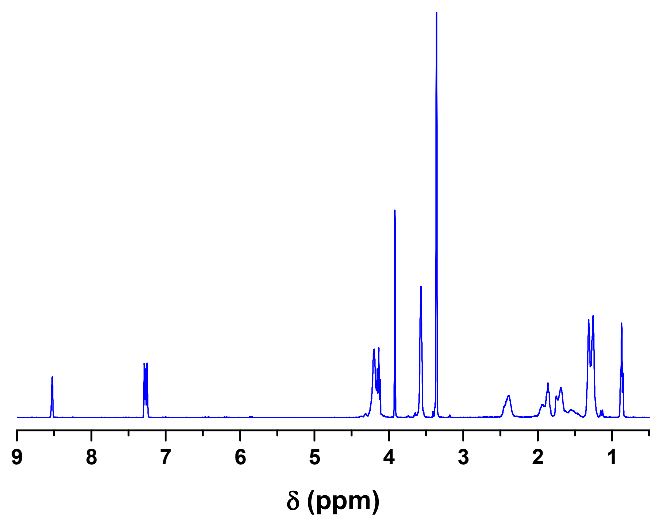
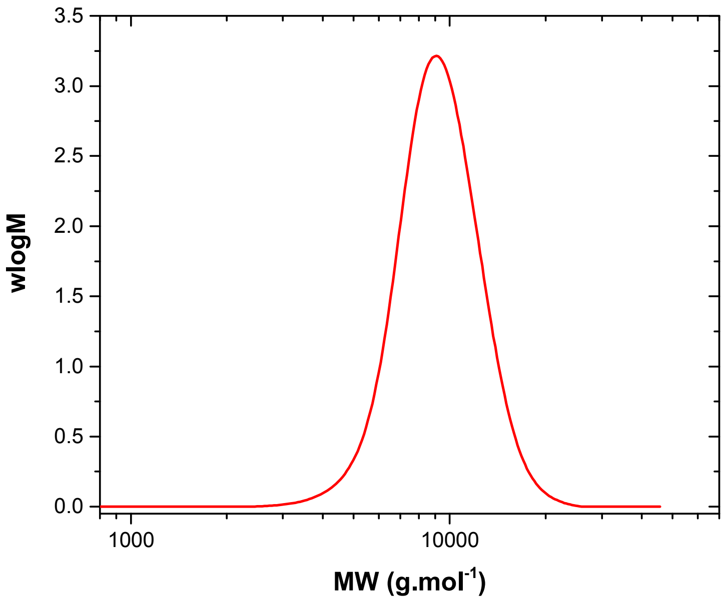


Figure S25: SEC and ^{1}H NMR analysis for the synthesis of PEGA in [C_8mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [EGA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].



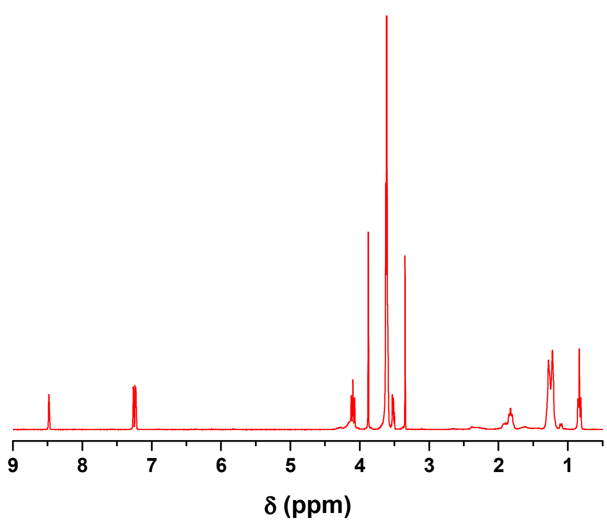


Figure S26: SEC and [1]H NMR analysis for the synthesis of PPEGA in [C_8mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [PEGA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [15]:[1]:[0.02]:[0.12].

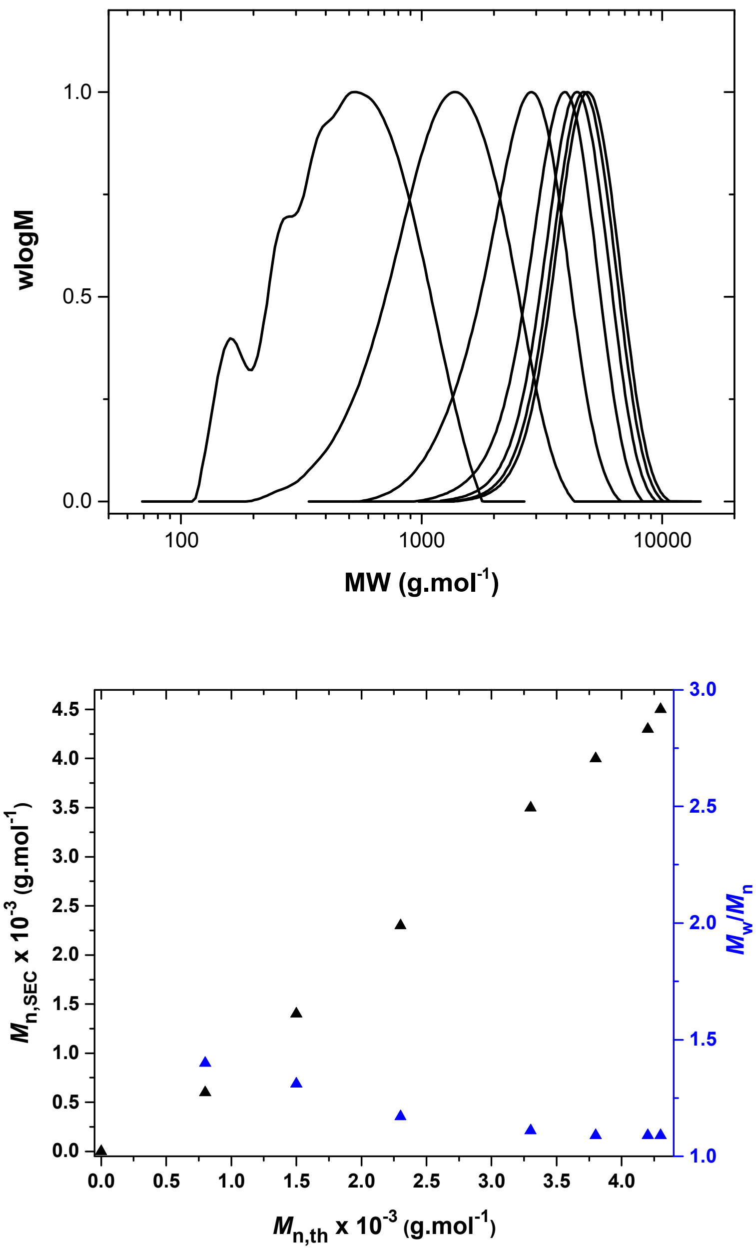


Figure S27: SEC analysis depicting the molecular weight evolution during the kinetic experiment of photo-induced polymerization of MA in [C_8mim][PF_6] (up) and $M_{n,SEC}$ and M_w/M_n *vs.* theoretical molecular weight $M_{n,th}$ (down).

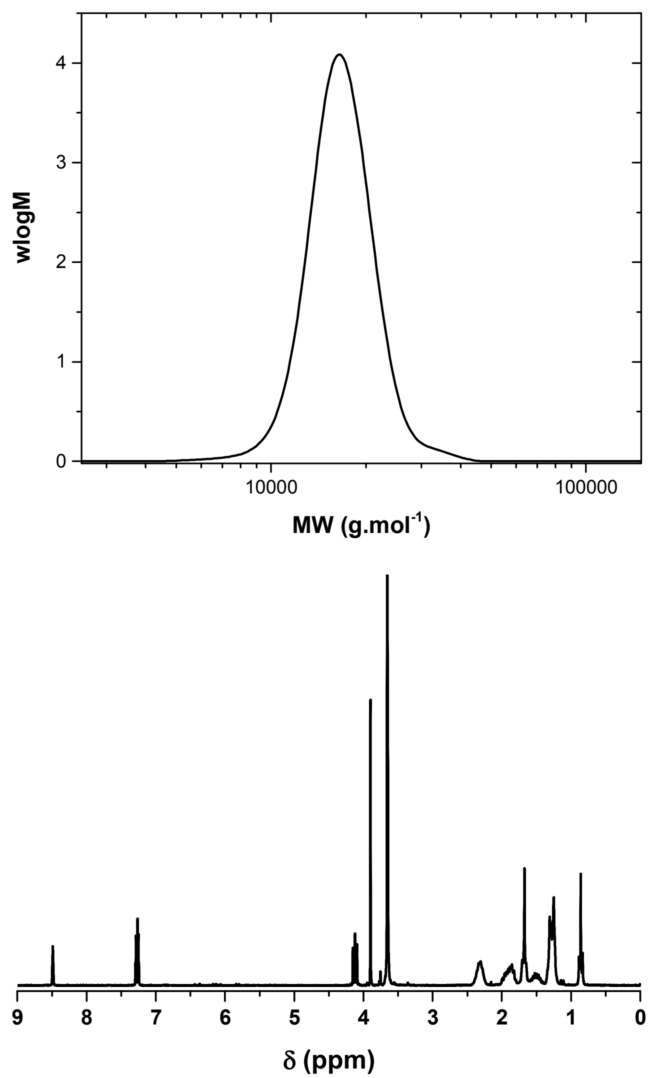


Figure S28: SEC and [1]H NMR analysis for the synthesis of PMA_{200} in $[C_8mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:$[CuBr_2]$:$[Me_6$-Tren] = [200]:[1]:[0.02]:[0.12].

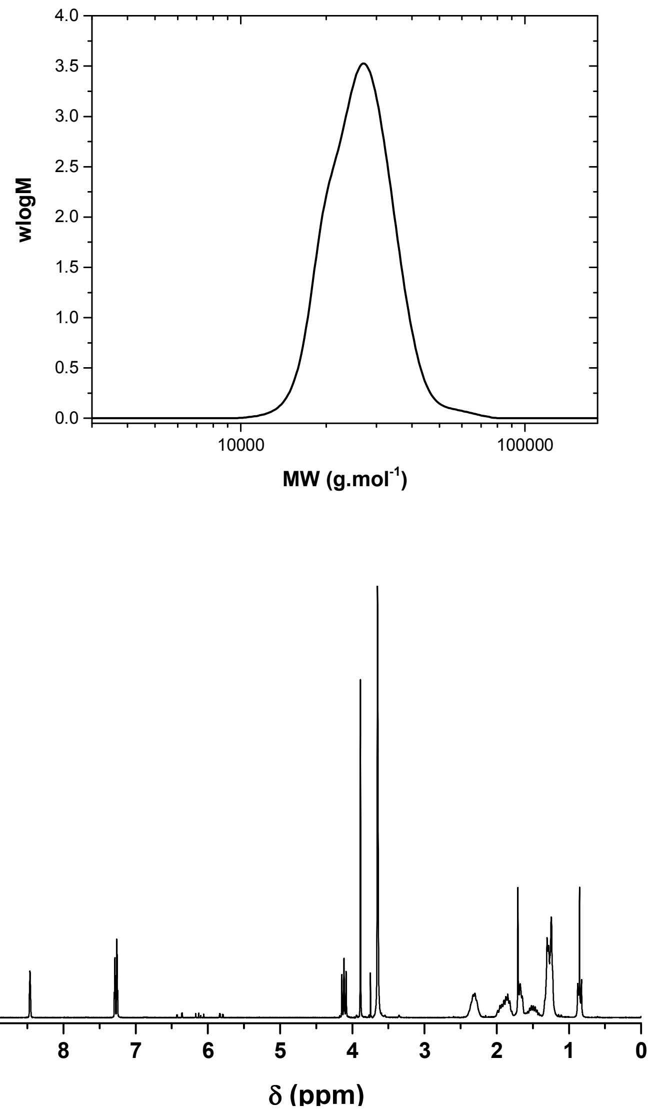
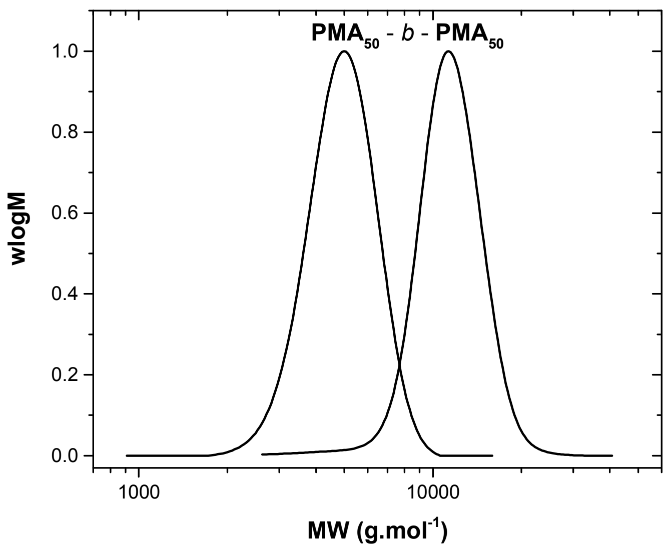


Figure S29: SEC and ^{1}H NMR analysis for the synthesis of PMA_{400} in $[C_8mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:$[CuBr_2]$:$[Me_6$-Tren] = [400]:[1]:[0.02]:[0.12].



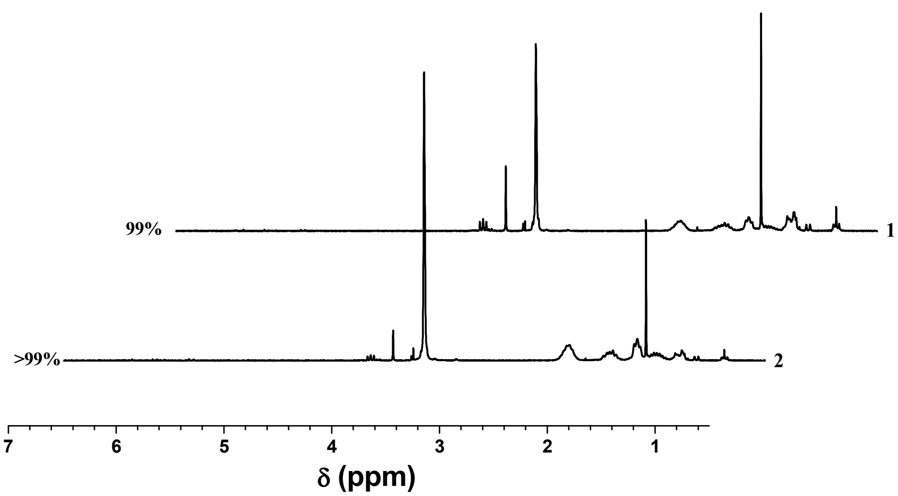


Figure S30: SEC and [1]H NMR analysis for the *in situ* chain extension from a PMA macroinitiator in [C_8mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of MA(50 equiv.) in [C_8mim][PF_6] (33% *v/v*).

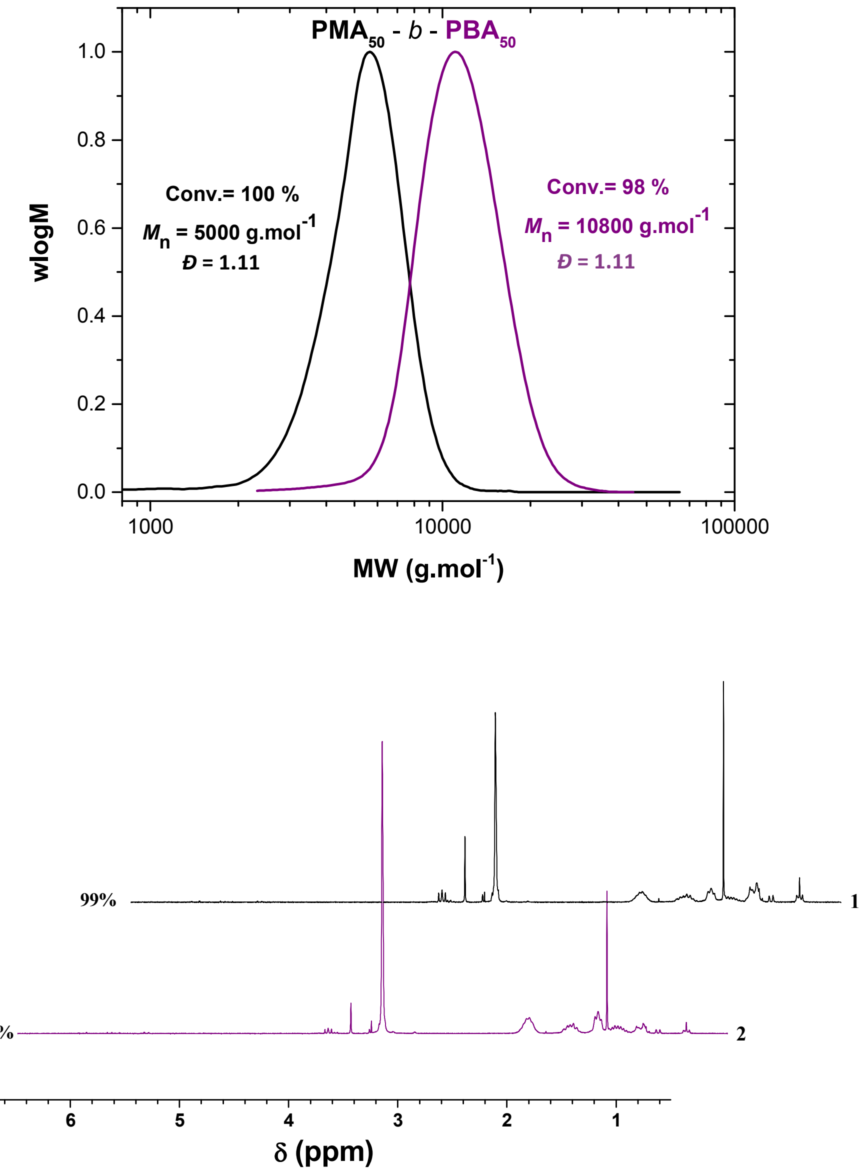
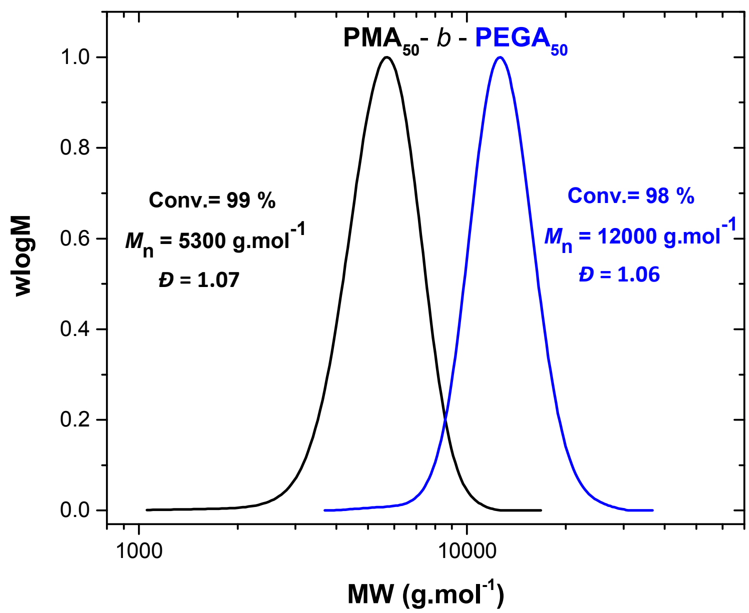


Figure S31: SEC and [1]H NMR analysis for block copolymerization from a PMA macroinitiator in $[C_8mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:$[CuBr_2]$:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of *n*-BA(50 equiv.) in $[C_8mim][PF_6]$ (33% *v/v*).



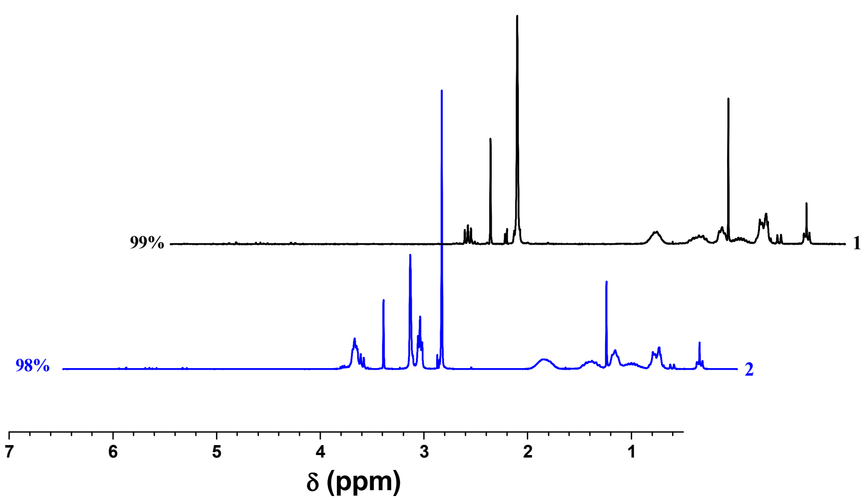


Figure S32: SEC and ^{1}H NMR analysis for block copolymerization from a PMA macroinitiator in [C_8mim][PF_6] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12]. Chain extension achieved upon addition of an aliquot of EGA (50 equiv.) in [C_8mim][PF_6] (33% *v/v*).

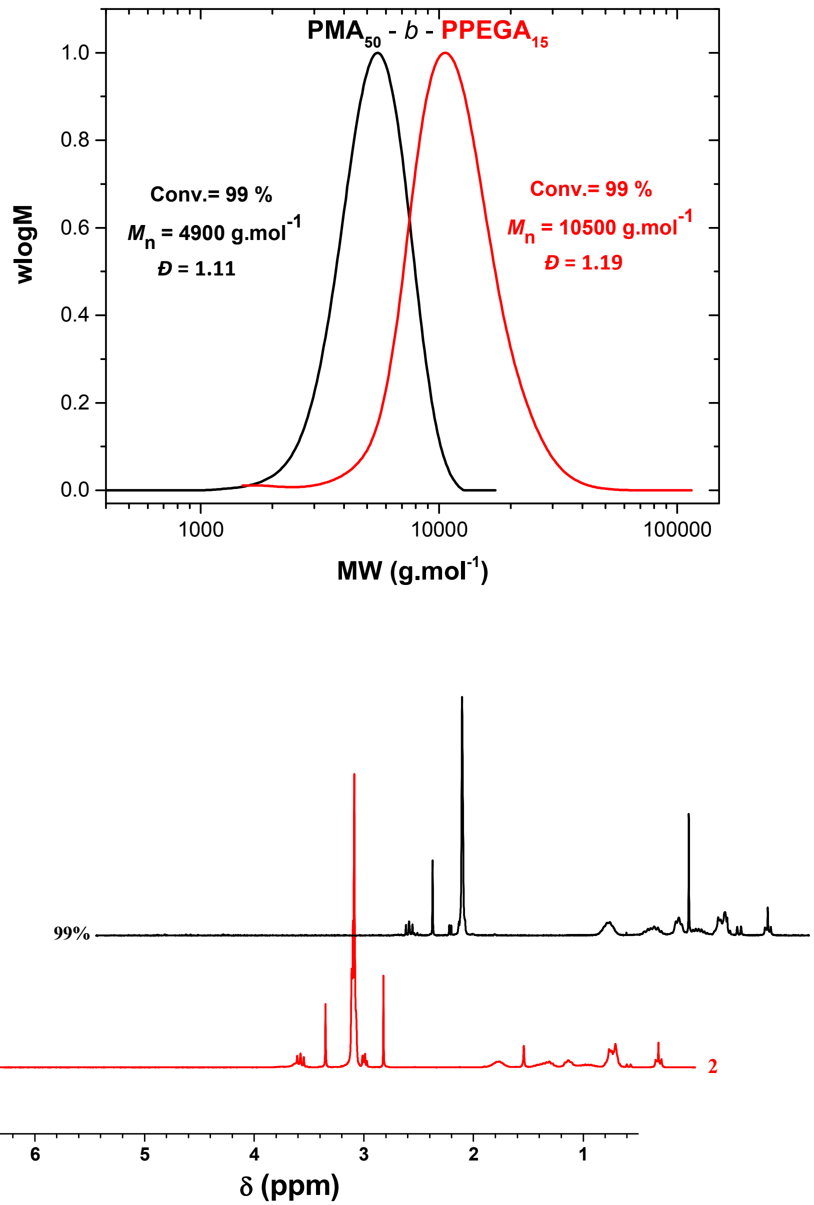
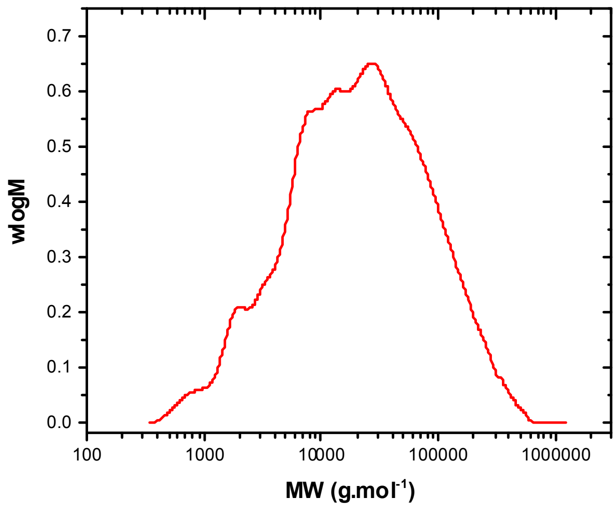


Figure S33: SEC and [1]H NMR analysis for block copolymerization from a PMA macroinitiator in $[C_8mim][PF_6]$ (50:50 *v/v* monomer/ionic liquid). Initial conditions: $[MA]:[EBiB]:[CuBr_2]:[Me_6\text{-}Tren] = [50]:[1]:[0.02]:[0.12]$. Chain extension achieved upon addition of an aliquot of PEGA (15 equiv.) in $[C_8mim][PF_6]$ (33% *v/v*).



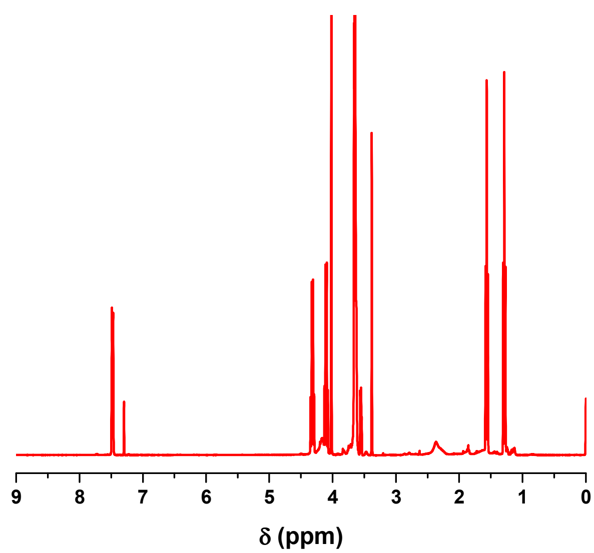


Figure S34: SEC and [1]H NMR analysis for the synthesis of PPEGA in [emim][$EtSO_4$] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [PEGA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [15]:[1]:[0.02]:[0.12].

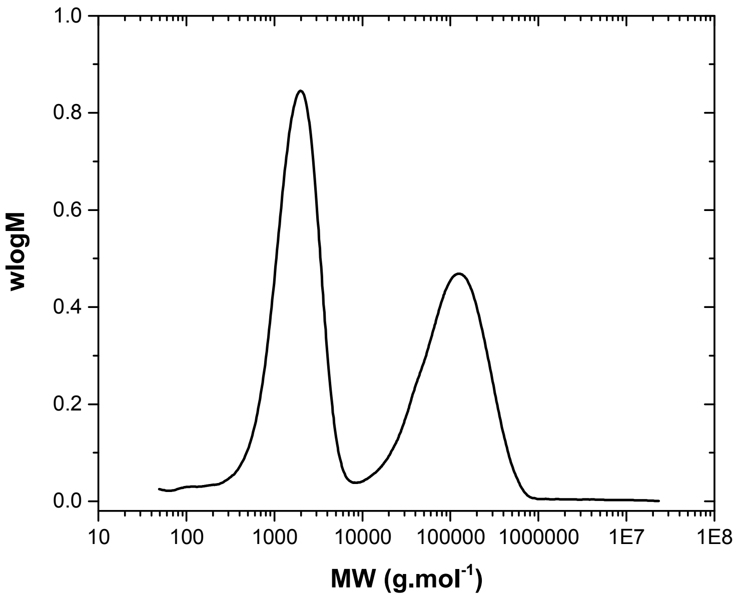


Figure S35: SEC analysis for the synthesis of PMA in [C_7mim][Br] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [MA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].

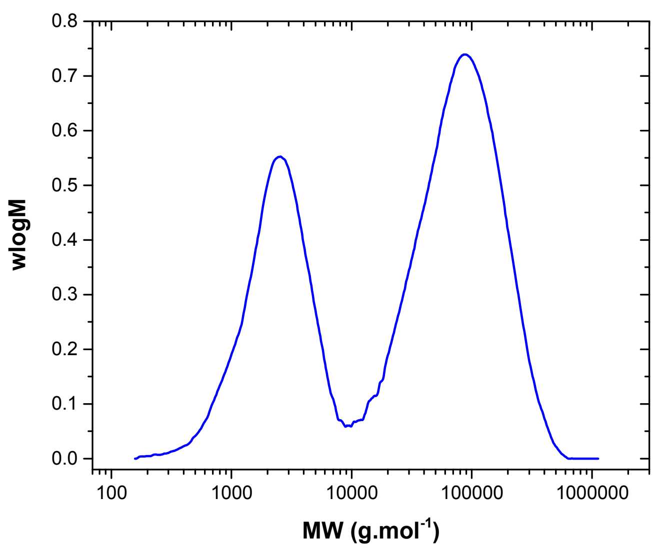


Figure S36: SEC analysis for the synthesis of PEGA in [C_7mim][Br] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [EGA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].

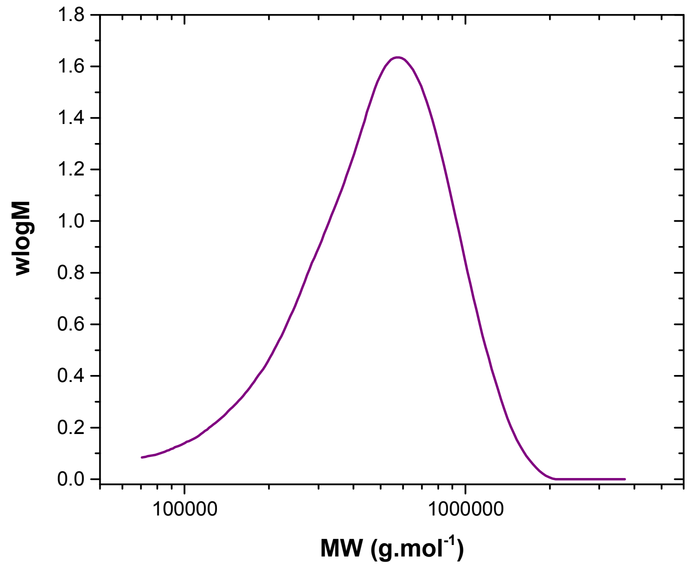


Figure S37: SEC analysis for the synthesis of PBA in [C_7mim][Br] (50:50 *v/v* monomer/ionic liquid). Initial conditions: [*n*-BA]:[EBiB]:[$CuBr_2$]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12].

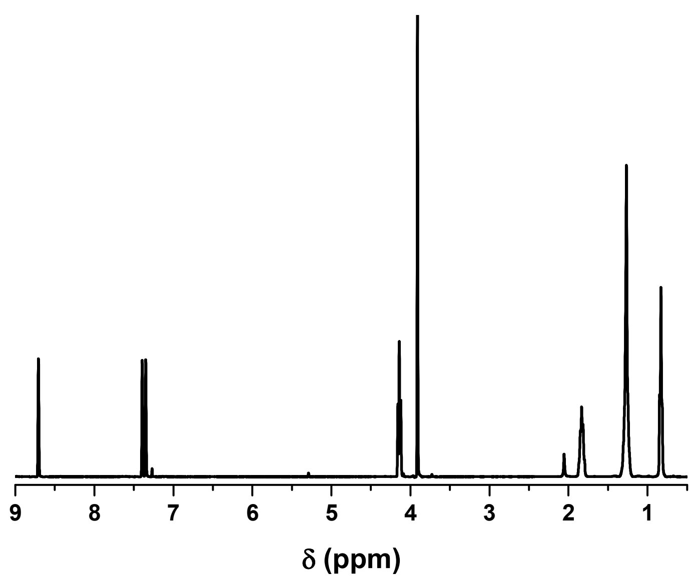


Figure S38: ^{1}H NMR spectrum of the extracted ionic liquid (polymer-free phase).

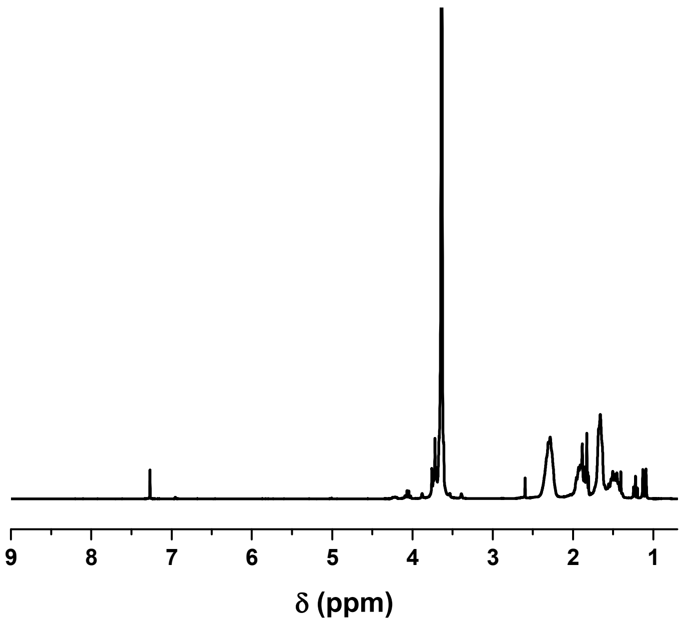
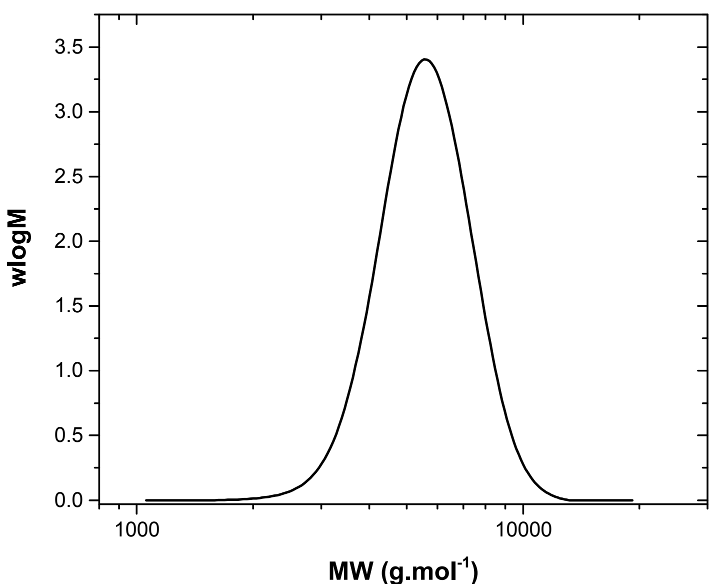


Figure S39: ^{1}H NMR spectrum of the extracted PMA.



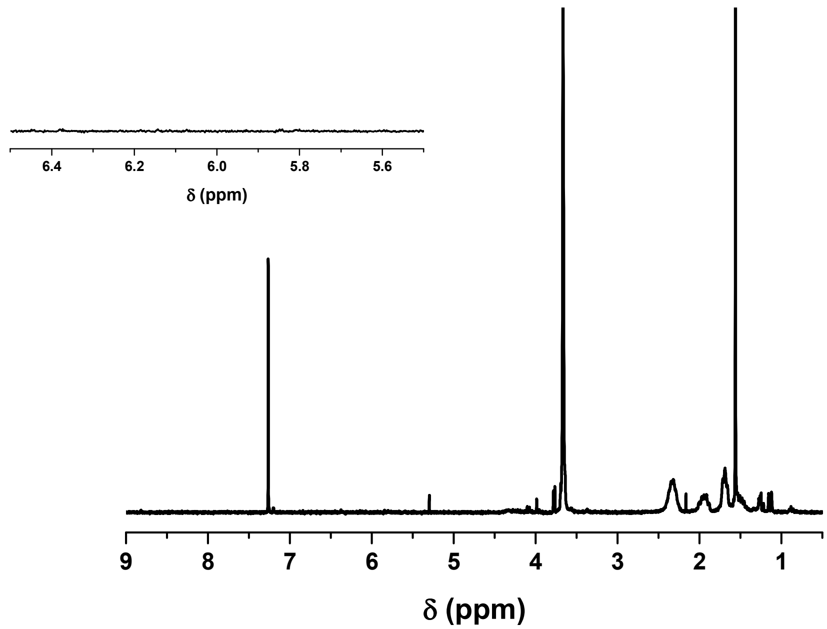


Figure S40: SEC and [1]H NMR analysis for the synthesis of PMA in recycled [C_8mim][PF_6] (50:50 *v/v* monomer/ionic liquid).