

Supplementary Material

Construction of Vinyl Polymer and Polyester or Polyamide Units in a Single Polymer Chain via Metal-Catalyzed Simultaneous Chain- and Step-Growth Radical Polymerization of Various Monomers

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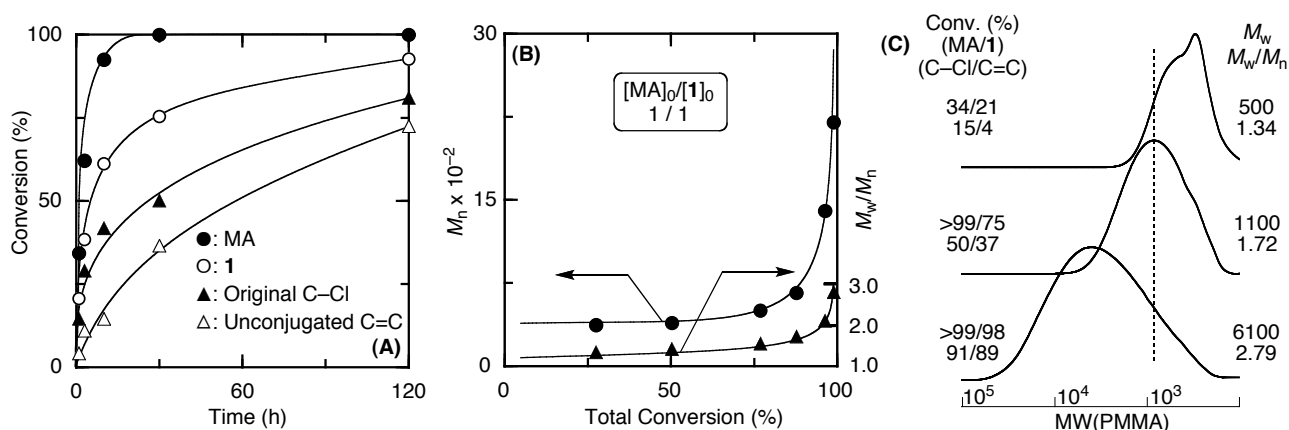


Fig. S1. Simultaneous chain- and step-growth radical polymerization of MA and **1** in toluene at 80 °C: $[MA]_0 = 2.0$ M; $[1]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of MA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of MA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of MA and **1**.

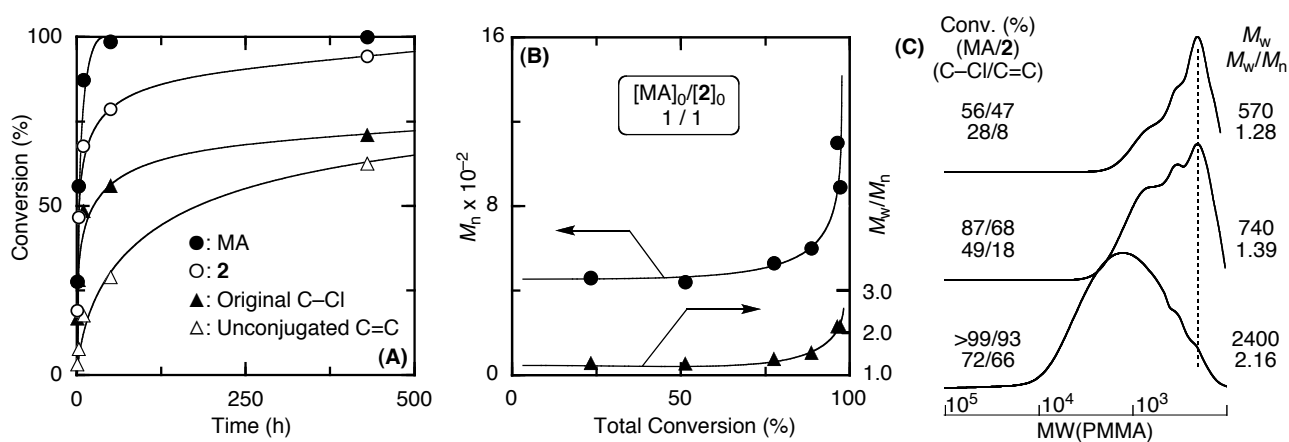


Fig. S2. Simultaneous chain- and step-growth radical polymerization of MA and **2** in toluene at 80 °C: $[MA]_0 = 2.0$ M; $[2]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of MA and **2** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of MA and **2**. (C) Size-exclusion chromatograms of the obtained copolymers of MA and **2**.

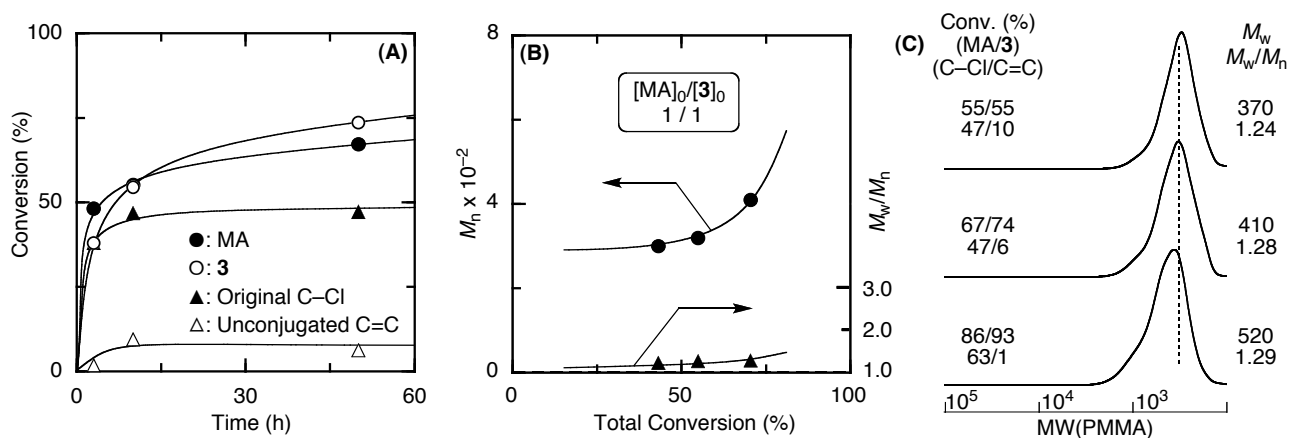


Fig. S3. Simultaneous chain- and step-growth radical polymerization of MA and **3** in toluene at 80 °C: $[MA]_0 = 2.0$ M; $[3]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of MA and **3** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of MA and **3**. (C) Size-exclusion chromatograms of the obtained copolymers of MA and **3**.

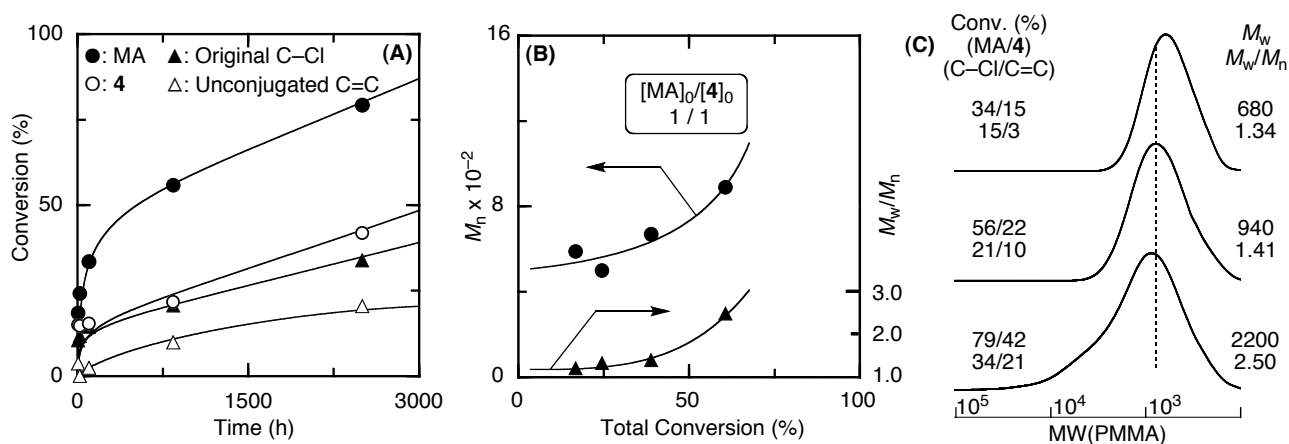


Fig. S4. Simultaneous chain- and step-growth radical polymerization of MA and **4** in toluene at 80 °C: $[MA]_0 = 2.0$ M; $[4]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of MA and **4** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of MA and **4**. (C) Size-exclusion chromatograms of the obtained copolymers of MA and **4**.

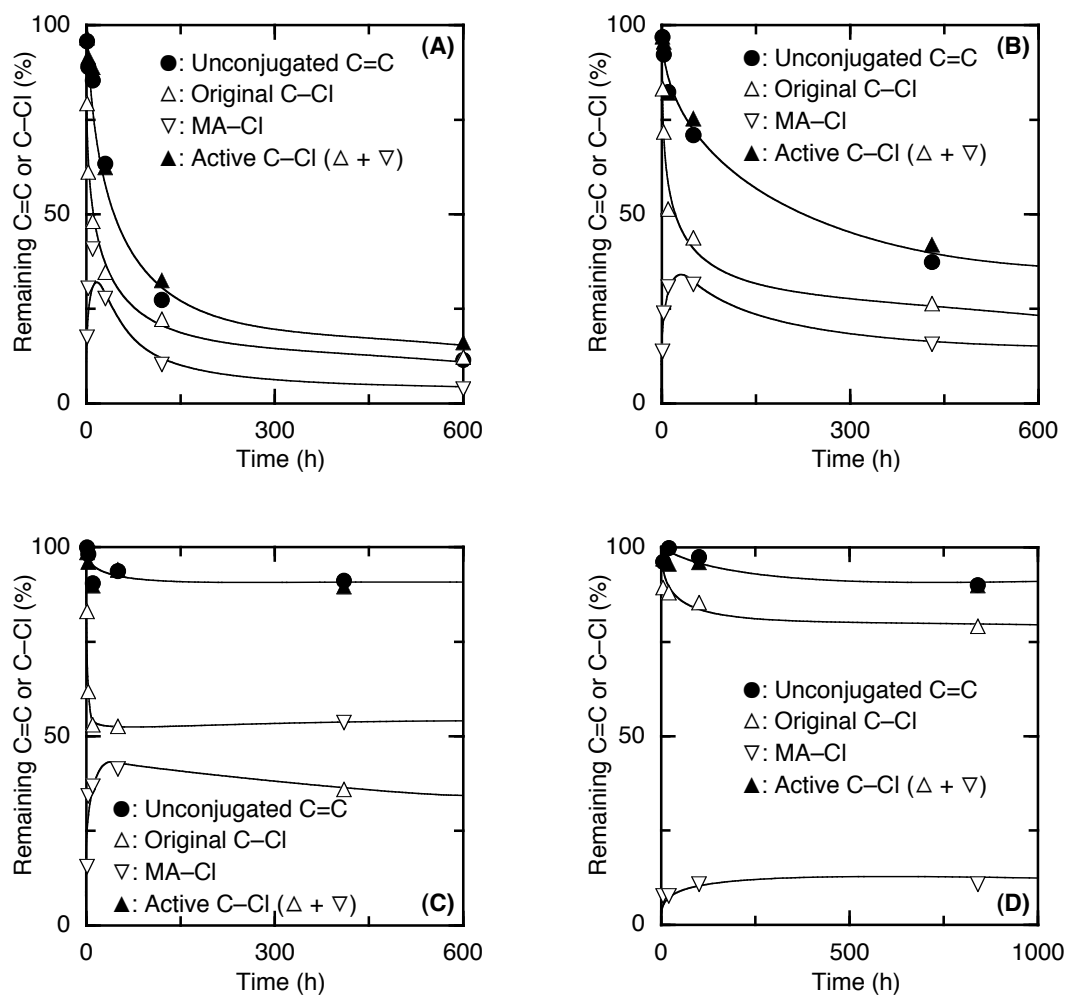


Fig. S5. Simultaneous chain- and step-growth radical polymerization of MA and (A) **1**, (B) **2**, (C) **3**, or (D) **4** in toluene at 80 °C: $[MA]_0 = 2.0$ M; $[1-4]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. Concentration of remaining unconjugated C=C, original C-Cl, MA-Cl, and sum of the active C-Cl (original C-Cl + MA-Cl) bonds in the reaction mixture measured by 1H NMR.

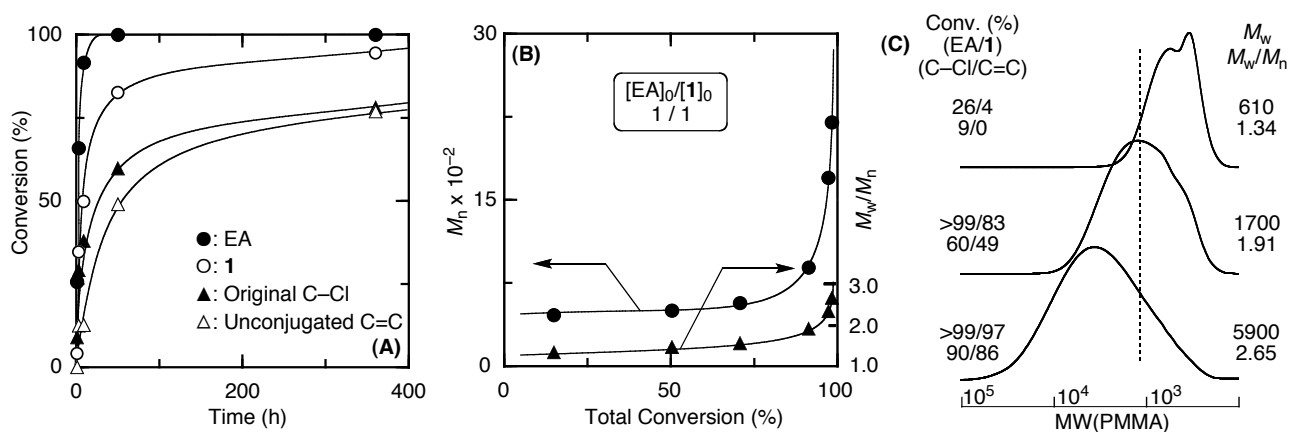


Fig. S6. Simultaneous chain- and step-growth radical polymerization of EA and **1** in toluene at 80 °C: $[EA]_0 = 2.0$ M; $[1]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of EA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of EA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of EA and **1**.

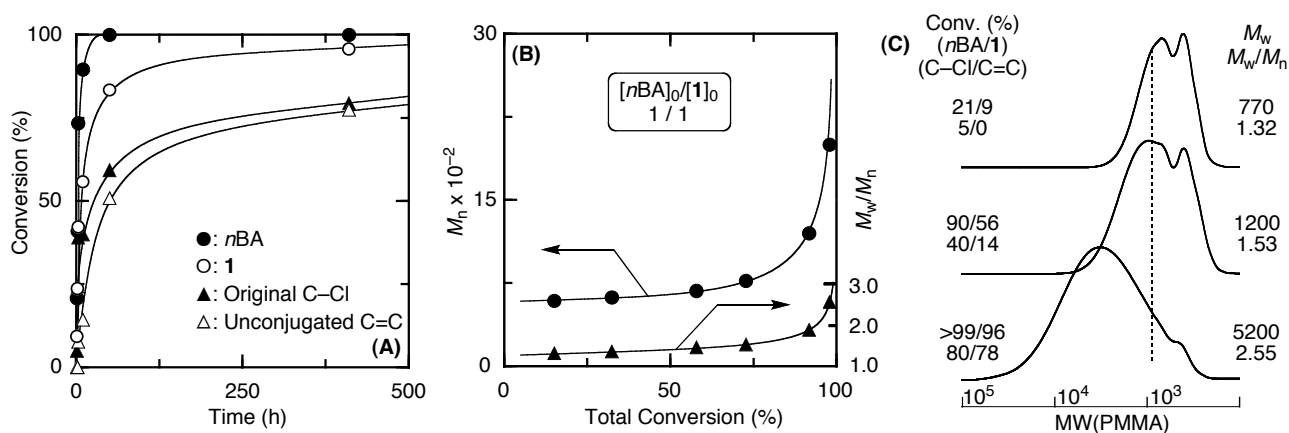


Fig. S7. Simultaneous chain- and step-growth radical polymerization of nBA and **1** in toluene at 80 °C: $[nBA]_0 = 2.0$ M; $[1]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of nBA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of nBA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of nBA and **1**.

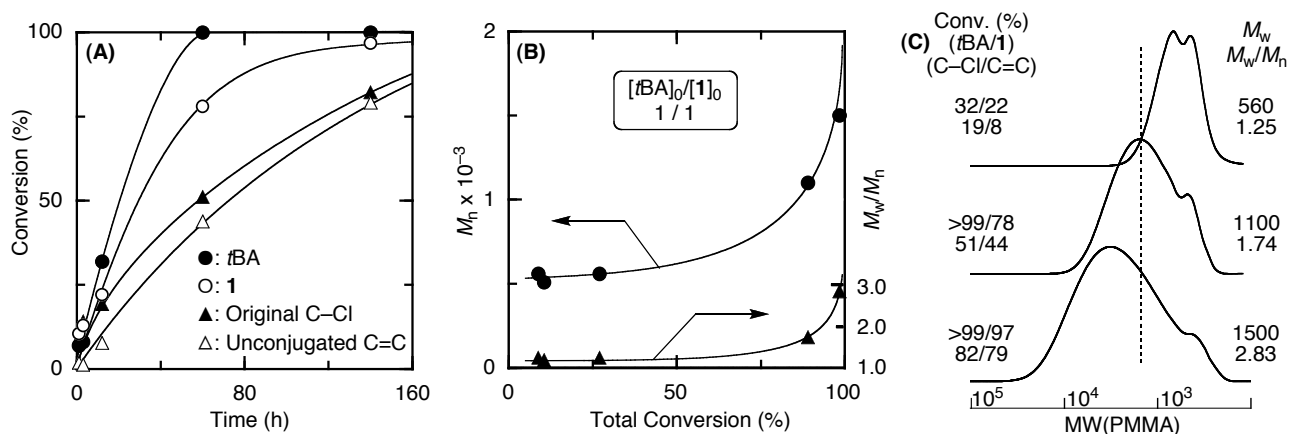


Fig. S8. Simultaneous chain- and step-growth radical polymerization of *t*BA and **1** in toluene at 80 °C: $[tBA]_0 = 2.0$ M; $[1]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of *t*BA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of *t*BA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of *t*BA and **1**.

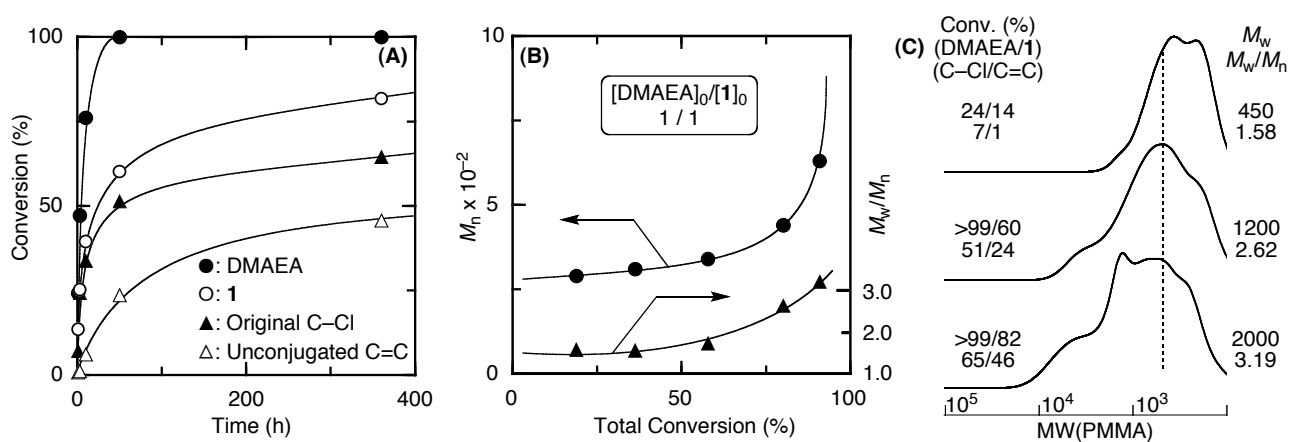


Fig. S9. Simultaneous chain- and step-growth radical polymerization of DMAEA and **1** in toluene at 80 °C: $[DMAEA]_0 = 2.0$ M; $[1]_0 = 2.0$ M; $[CuCl]_0 = 100$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of DMAEA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of DMAEA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of DMAEA and **1**.

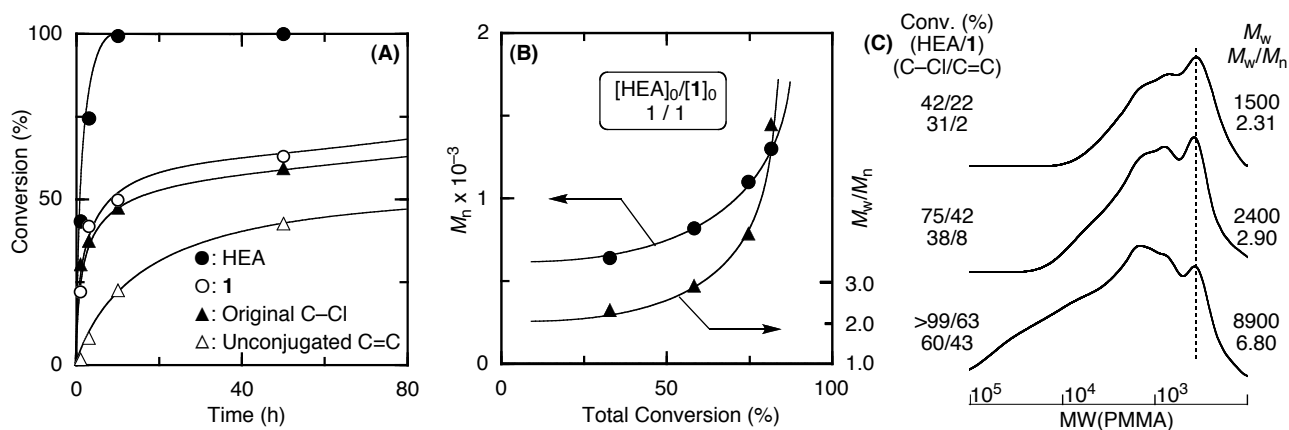


Fig. S10. Simultaneous chain- and step-growth radical polymerization of HEA and **1** in toluene at 80 °C: $[\text{HEA}]_0 = 2.0 \text{ M}$; $[\mathbf{1}]_0 = 2.0 \text{ M}$; $[\text{CuCl}]_0 = 100 \text{ mM}$; $[\text{HMTETA}]_0 = 100 \text{ mM}$. (A) Consumption of HEA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by ^1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of HEA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of HEA and **1**.

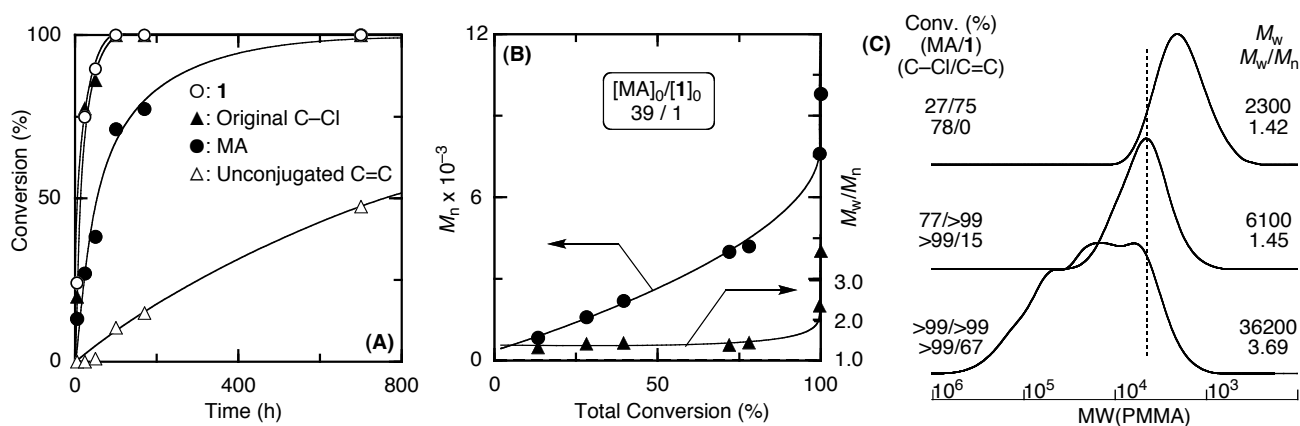


Fig. S11. Simultaneous chain- and step-growth radical polymerization of MA and **1** in bulk at 80 °C: $[\text{MA}]_0 = 9.75 \text{ M}$; $[\mathbf{1}]_0 = 0.25 \text{ M}$; $[\text{CuCl}]_0 = 10 \text{ mM}$; $[\text{CuCl}_2]_0 = 10 \text{ mM}$; $[\text{HMTETA}]_0 = 50 \text{ mM}$. (A) Consumption of MA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by ^1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of MA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of MA and **1**.

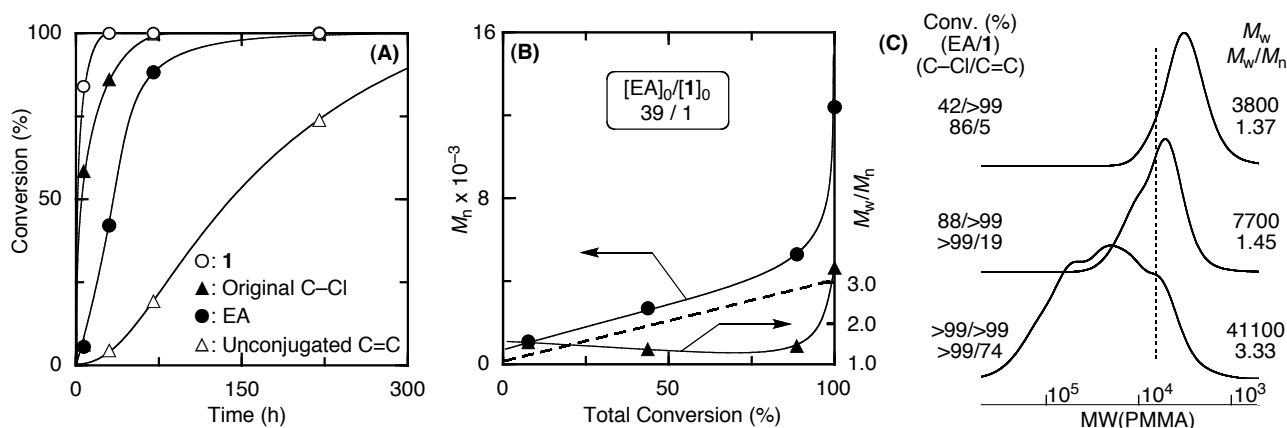


Fig. S12. Simultaneous chain- and step-growth radical polymerization of EA and **1** in bulk at 80 °C: $[EA]_0 = 7.8$ M; $[1]_0 = 0.20$ M; $[CuCl]_0 = 50$ mM; $[CuCl_2]_0 = 50$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of EA and **1** measured by gas chromatography and original C-Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of EA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of EA and **1**.

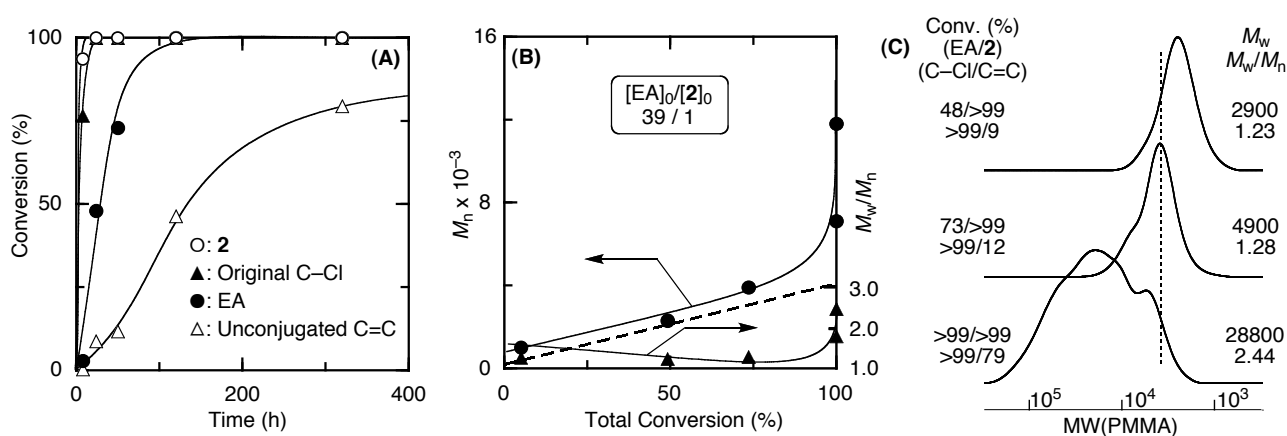


Fig. S13. Simultaneous chain- and step-growth radical polymerization of EA and **2** in bulk at 80 °C: $[EA]_0 = 7.8$ M; $[2]_0 = 0.20$ M; $[CuCl]_0 = 50$ mM; $[CuCl_2]_0 = 50$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of EA and **2** measured by gas chromatography and original C-Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of EA and **2**. (C) Size-exclusion chromatograms of the obtained copolymers of EA and **2**.

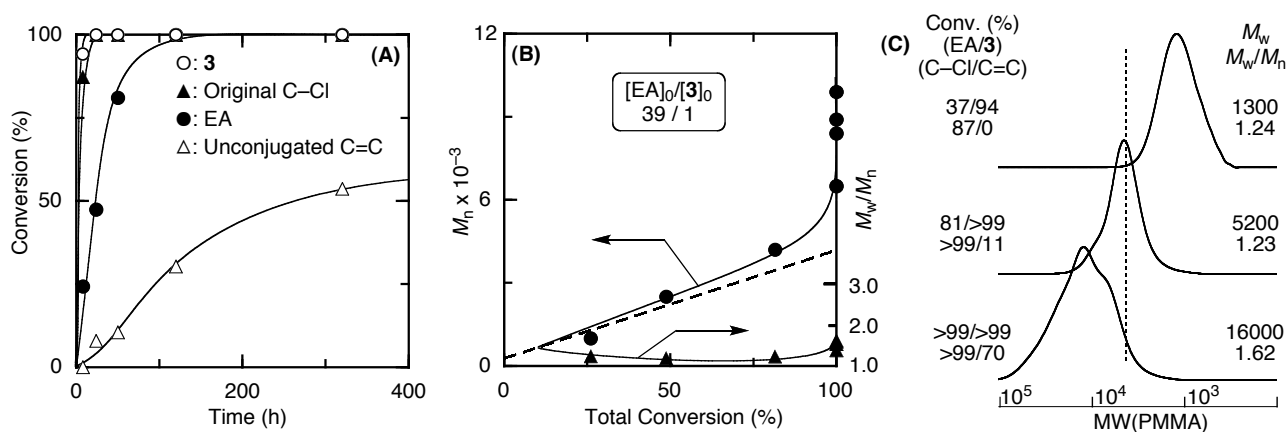


Fig. S14. Simultaneous chain- and step-growth radical polymerization of EA and **3** in bulk at 80 °C: $[EA]_0 = 7.8$ M; $[3]_0 = 0.20$ M; $[CuCl]_0 = 50$ mM; $[CuCl_2]_0 = 50$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of EA and **3** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of EA and **3**. (C) Size-exclusion chromatograms of the obtained copolymers of EA and **3**.

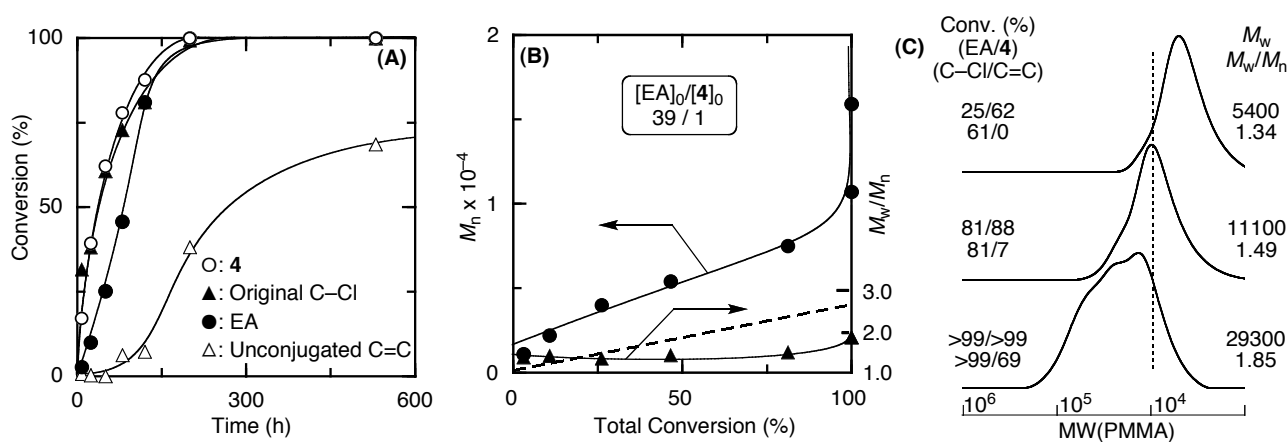


Fig. S15. Simultaneous chain- and step-growth radical polymerization of EA and **4** in bulk at 80 °C: $[EA]_0 = 7.8$ M; $[4]_0 = 0.20$ M; $[CuCl]_0 = 50$ mM; $[CuCl_2]_0 = 50$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of EA and **4** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of EA and **4**. (C) Size-exclusion chromatograms of the obtained copolymers of EA and **4**.

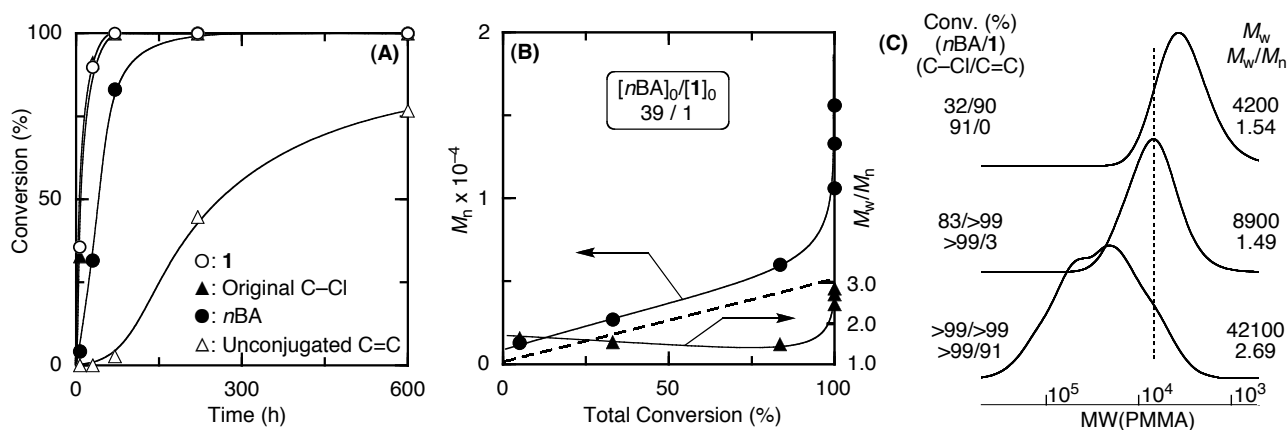


Fig. S16. Simultaneous chain- and step-growth radical polymerization of *n*BA and **1** in bulk at 80 °C: $[nBA]_0 = 6.24$ M; $[1]_0 = 0.16$ M; $[CuCl]_0 = 50$ mM; $[CuCl_2]_0 = 50$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of *n*BA and **1** measured by gas chromatography and original C-Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of *n*BA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of *n*BA and **1**.

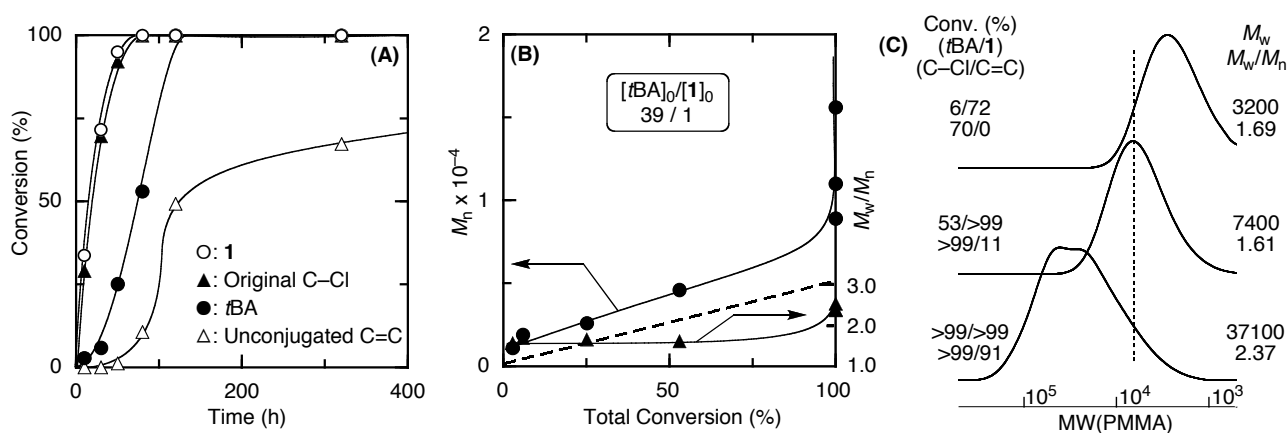


Fig. S17. Simultaneous chain- and step-growth radical polymerization of *t*BA and **1** in bulk at 80 °C: $[tBA]_0 = 6.24$ M; $[1]_0 = 0.16$ M; $[CuCl]_0 = 50$ mM; $[CuCl_2]_0 = 50$ mM; $[HMTETA]_0 = 100$ mM. (A) Consumption of *t*BA and **1** measured by gas chromatography and original C-Cl and unconjugated C=C bonds measured by 1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of *t*BA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of *t*BA and **1**.

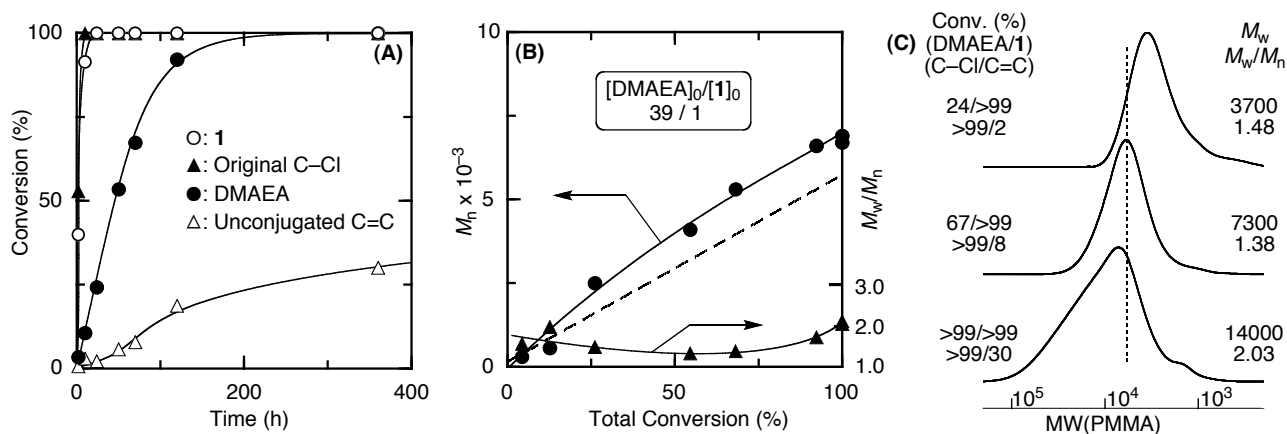


Fig. S18. Simultaneous chain- and step-growth radical polymerization of DMAEA and **1** in bulk at 80 °C: $[\text{DMAEA}]_0 = 5.85 \text{ M}$; $[\mathbf{1}]_0 = 0.15 \text{ M}$; $[\text{CuCl}]_0 = 50 \text{ mM}$; $[\text{CuCl}_2]_0 = 50 \text{ mM}$; $[\text{HMTETA}]_0 = 100 \text{ mM}$. (A) Consumption of DMAEA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by ^1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of DMAEA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of DMAEA and **1**.

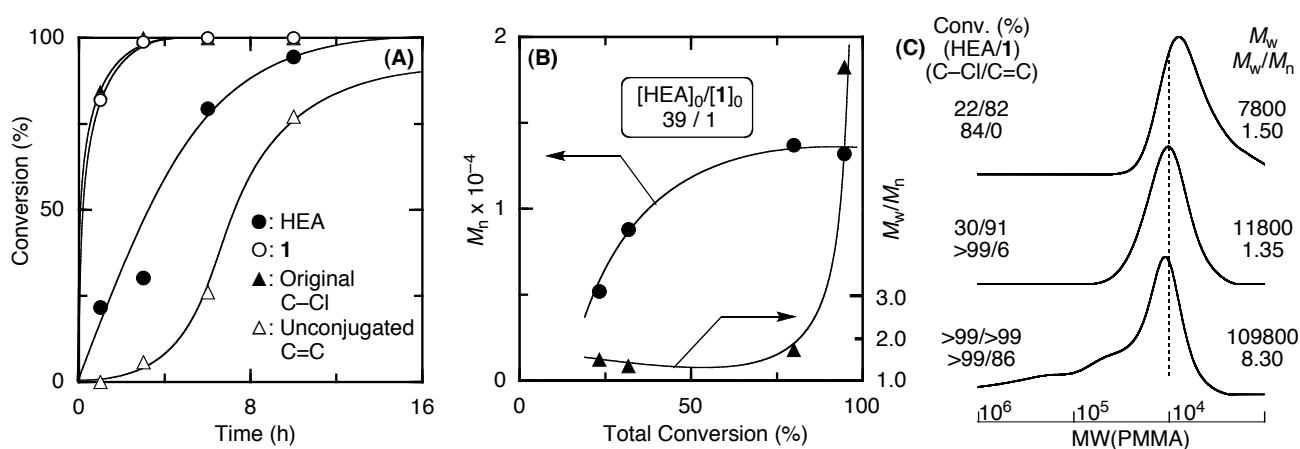


Fig. S19. Simultaneous chain- and step-growth radical polymerization of HEA and **1** in bulk at 80 °C: $[\text{HEA}]_0 = 5.85 \text{ M}$; $[\mathbf{1}]_0 = 0.15 \text{ M}$; $[\text{CuCl}]_0 = 50 \text{ mM}$; $[\text{CuCl}_2]_0 = 50 \text{ mM}$; $[\text{HMTETA}]_0 = 100 \text{ mM}$. (A) Consumption of HEA and **1** measured by gas chromatography and original C–Cl and unconjugated C=C bonds measured by ^1H NMR. (B) M_n and M_w/M_n values of the obtained copolymers vs total monomer conversion of HEA and **1**. (C) Size-exclusion chromatograms of the obtained copolymers of HEA and **1**.