

Supplementary Information

**From-syndiotactic-to-isotactic stereogradient methacrylic polymers by RAFT
copolymerization of methacrylic acid and its bulky esters**

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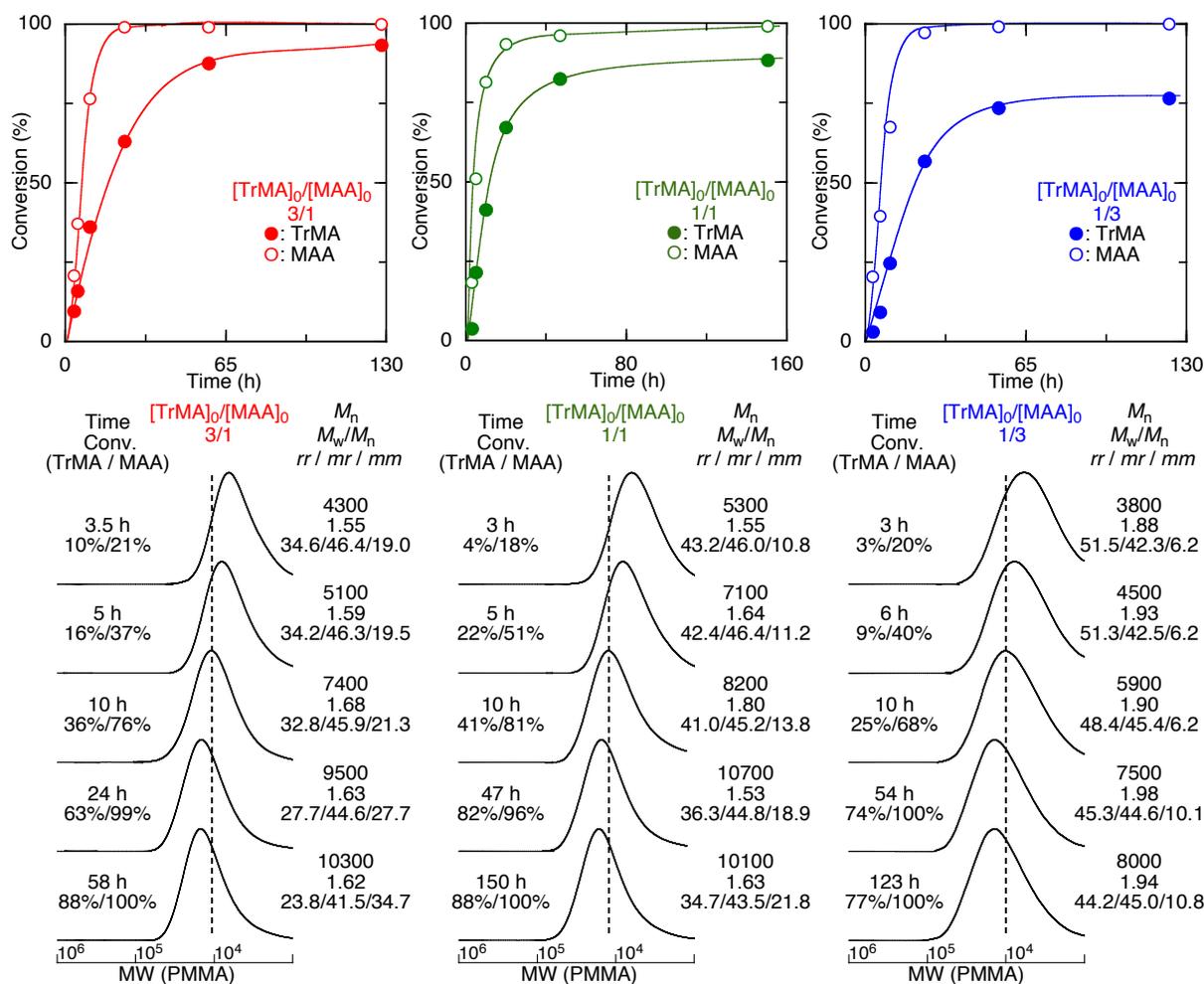


Figure S1. Effects of initial charge ratio of TrMA and MAA on the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene at 60 °C: $[TrMA]_0 + [MAA]_0 = 1.0$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM; $[TrMA]_0/[MAA]_0 = 3/1$ (red), $1/1$ (green), or $1/3$ (blue). SEC curves: poly(MMA) converted from the obtained copolymers.

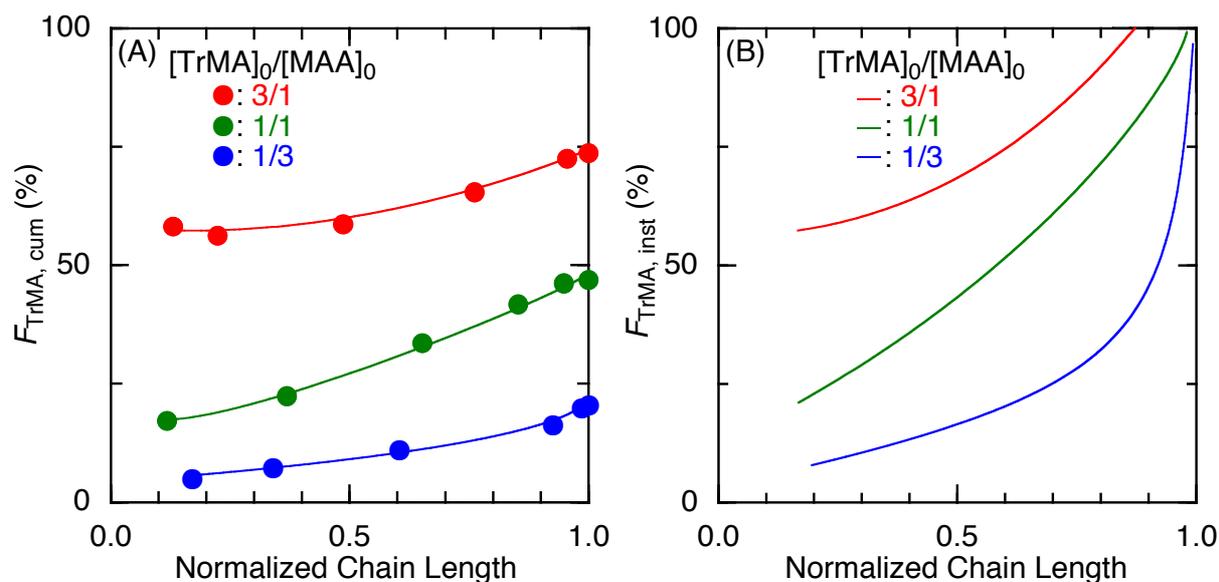


Figure S2. Effects of initial charge ratio of TrMA and MAA on the dependences of cumulative (A) and instantaneous (B) TrMA contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene at 60 °C: $[\text{TrMA}]_0 + [\text{MAA}]_0 = 1.0 \text{ M}$; $[\text{CDB}]_0 = 10 \text{ mM}$; $[\text{AIBN}]_0 = 5.0 \text{ mM}$; $[\text{TrMA}]_0/[\text{MAA}]_0 = 3/1$ (red), 1/1 (green), or 1/3 (blue).

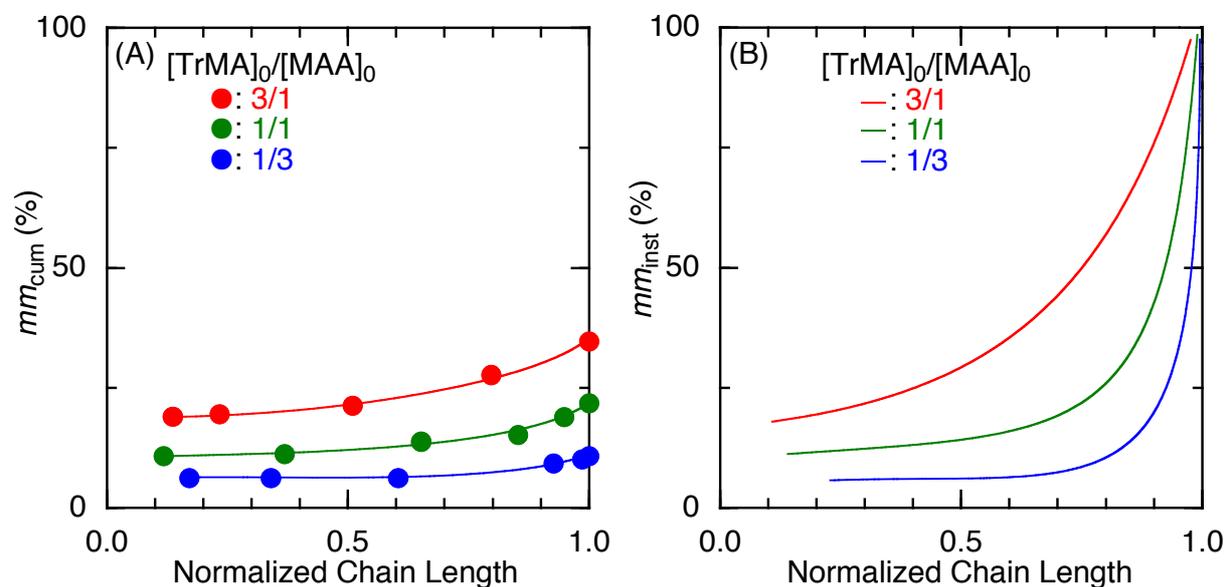


Figure S3. Effects of initial charge ratio of TrMA and MAA on the dependences of cumulative (A) and instantaneous (B) mm contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene at 60 °C: $[\text{TrMA}]_0 + [\text{MAA}]_0 = 1.0 \text{ M}$; $[\text{CDB}]_0 = 10 \text{ mM}$; $[\text{AIBN}]_0 = 5.0 \text{ mM}$; $[\text{TrMA}]_0/[\text{MAA}]_0 = 3/1$ (red), 1/1 (green), or 1/3 (blue).

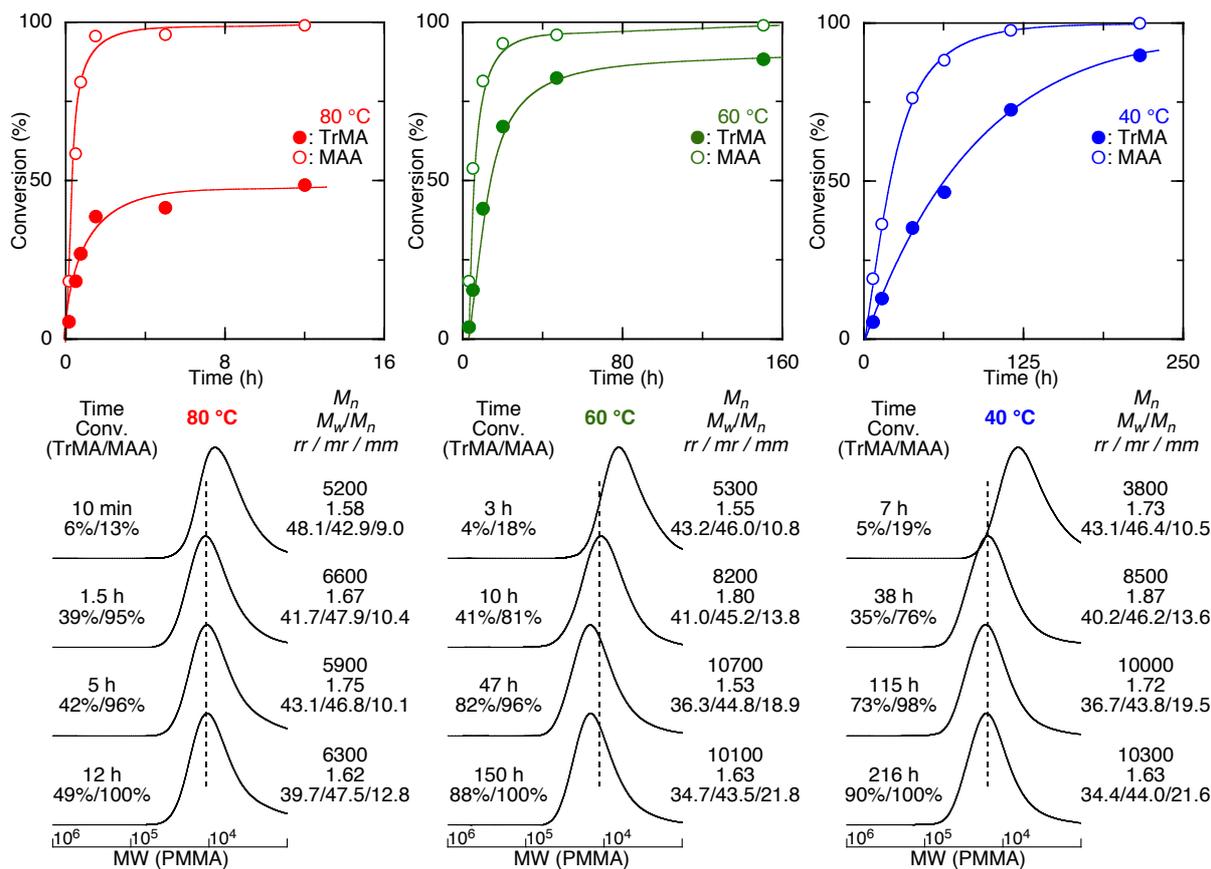


Figure S4. RAFT copolymerization of TrMA and MAA with CDB/AIBN at various temperature: $[TrMA]_0 = [MAA]_0 = 0.50$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM in toluene at 80 (red), 60 (green), or 40 °C (blue). SEC curves: poly(MMA) converted from the obtained copolymers.

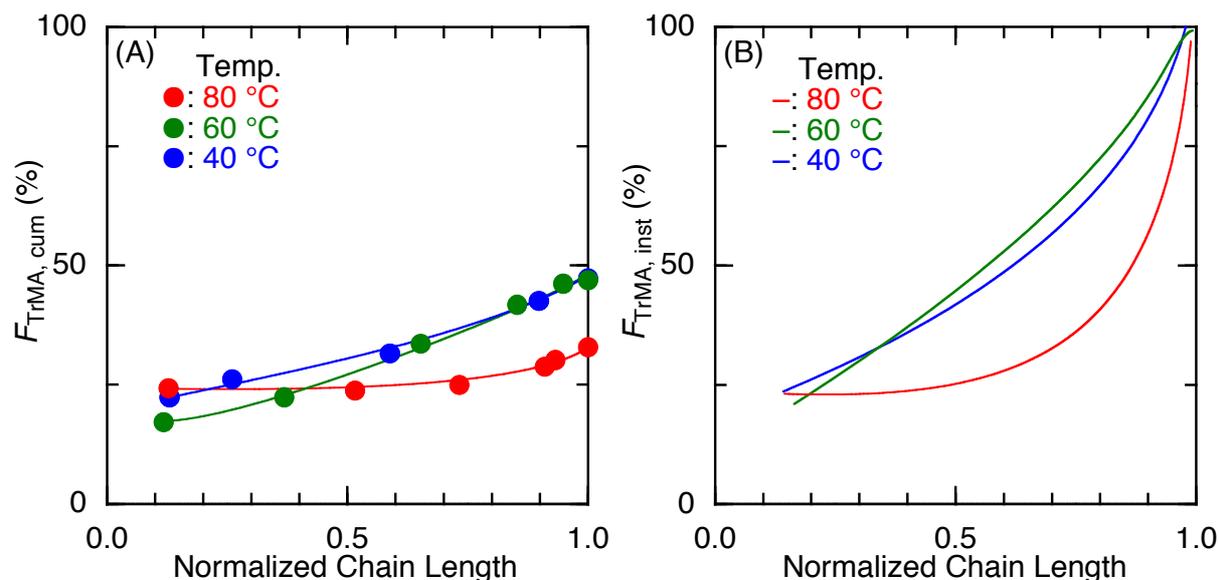


Figure S5. Effects of polymerization temperature on the dependences of cumulative (A) and instantaneous (B) TrMA contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN at various temperature: $[\text{TrMA}]_0 = [\text{MAA}]_0 = 0.50 \text{ M}$; $[\text{CDB}]_0 = 10 \text{ mM}$; $[\text{AIBN}]_0 = 5.0 \text{ mM}$ in toluene at 80 (red), 60 (green), or 40 °C (blue).

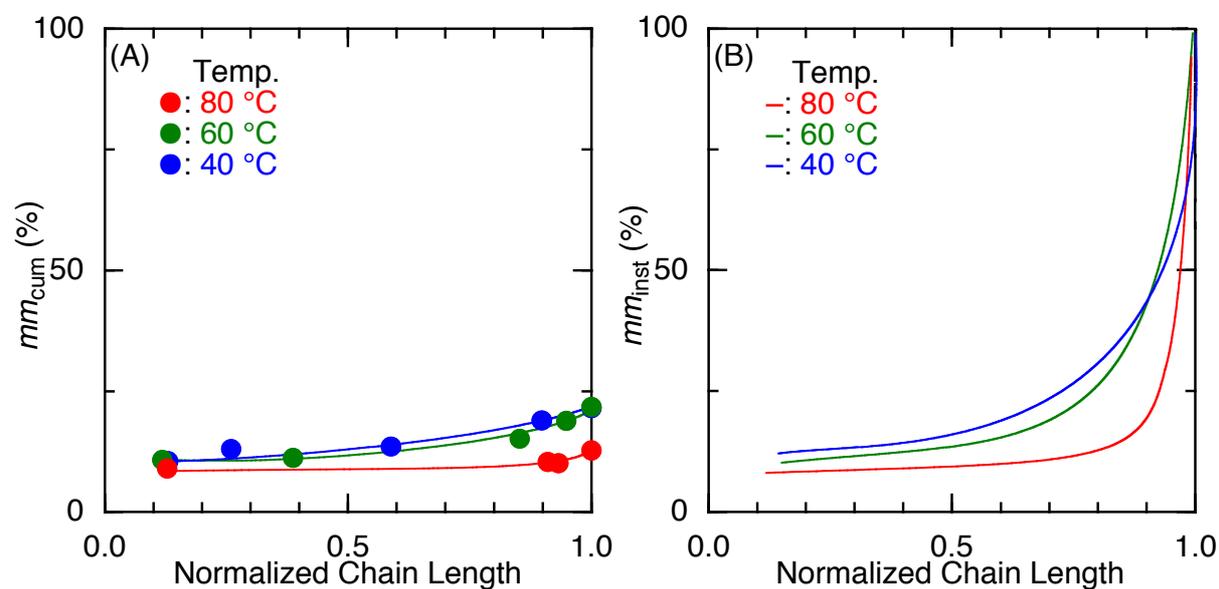


Figure S6. Effects of polymerization temperature on the dependences of cumulative (A) and instantaneous (B) *mm* contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN at various temperature: $[\text{TrMA}]_0 = [\text{MAA}]_0 = 0.50 \text{ M}$; $[\text{CDB}]_0 = 10 \text{ mM}$; $[\text{AIBN}]_0 = 5.0 \text{ mM}$ in toluene at 80 (red), 60 (green), or 40 °C (blue).

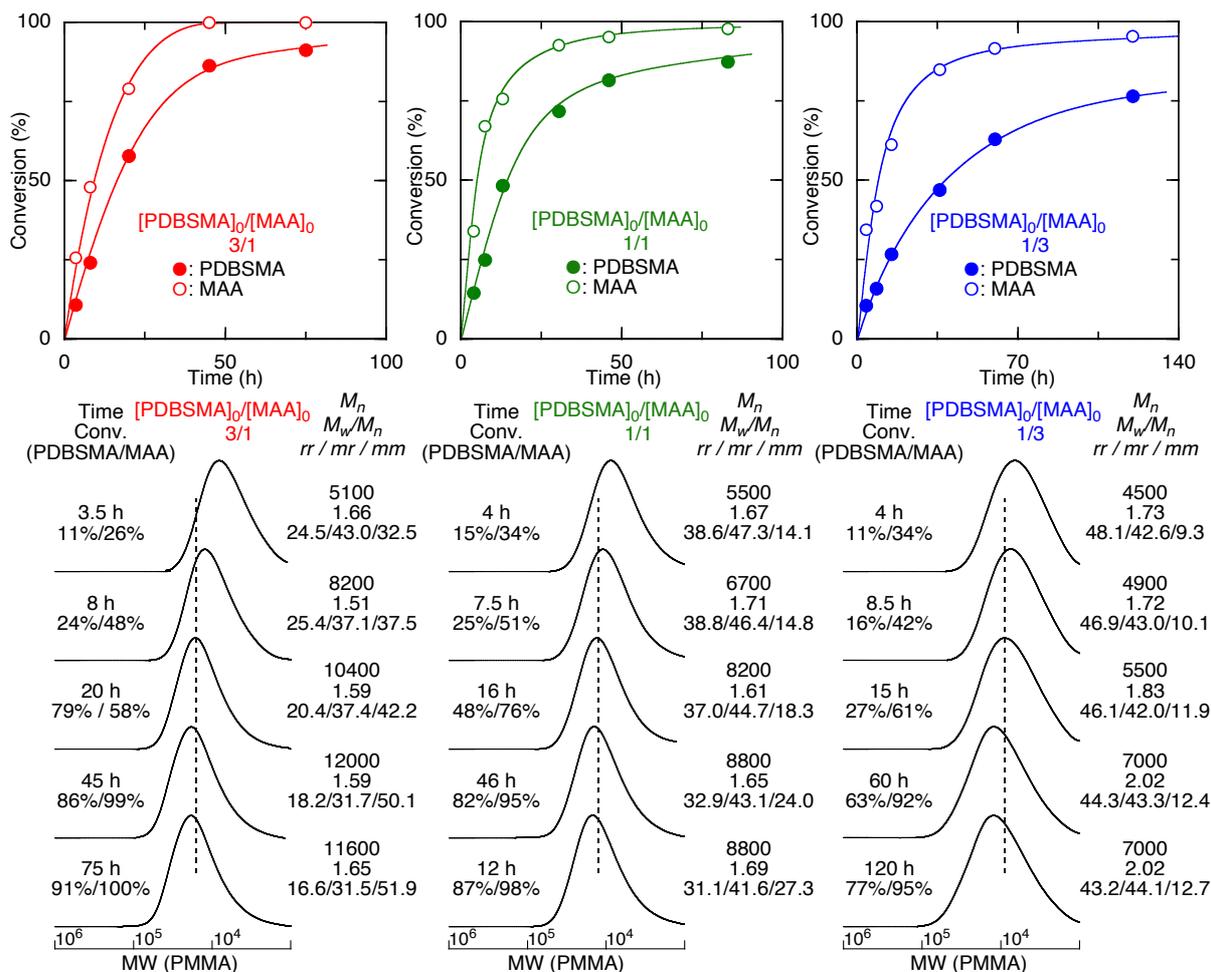


Figure S7. Effects of initial charge ratio of PDBSMA and MAA on the RAFT copolymerization of PDBSMA and MAA with CDB/AIBN in toluene at 60 °C: $[PDBSMA]_0 + [MAA]_0 = 0.60$ M; $[CDB]_0 = 6.0$ mM; $[AIBN]_0 = 3.0$ mM; $[PDBSMA]_0/[MAA]_0 = 3/1$ (red), $1/1$ (green), or $1/3$ (blue). SEC curves: poly(MMA) converted from the obtained copolymers.

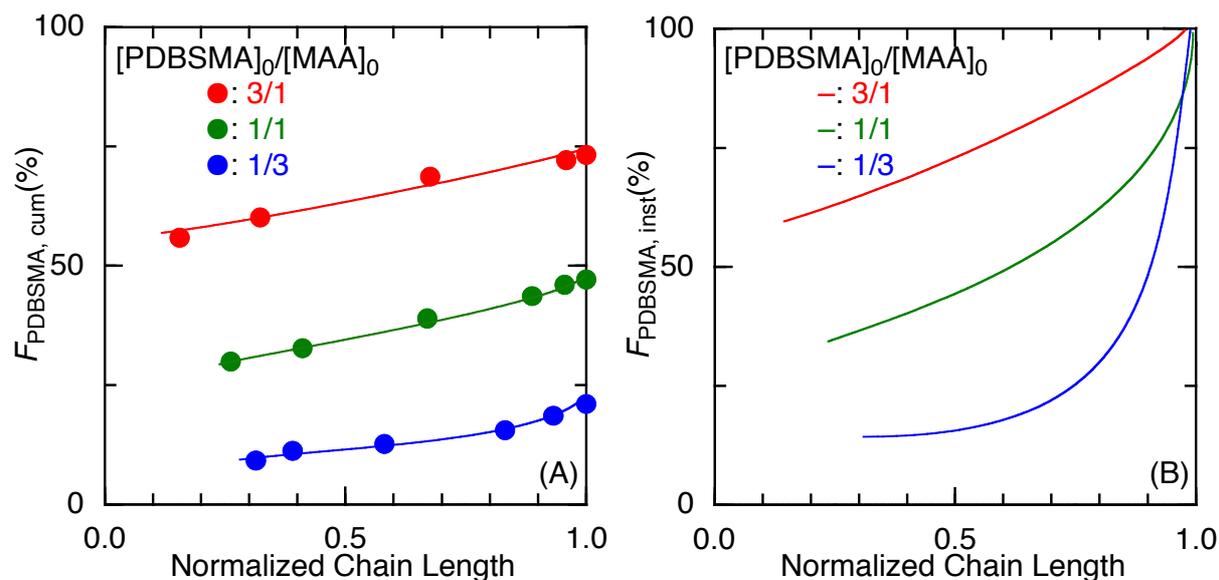


Figure S8. Effects of initial charge ratio of PDBSMA and MAA on the dependences of cumulative (A) and instantaneous (B) PDBSMA contents on the normalized chain length in the RAFT copolymerization of PDBSMA and MAA with CDB/AIBN in toluene at 60 °C: $[\text{PDBSMA}]_0 + [\text{MAA}]_0 = 0.60 \text{ M}$; $[\text{CDB}]_0 = 6.0 \text{ mM}$; $[\text{AIBN}]_0 = 3.0 \text{ mM}$; $[\text{PDBSMA}]_0 / [\text{MAA}]_0 = 3/1$ (red), $1/1$ (green), or $1/3$ (blue).

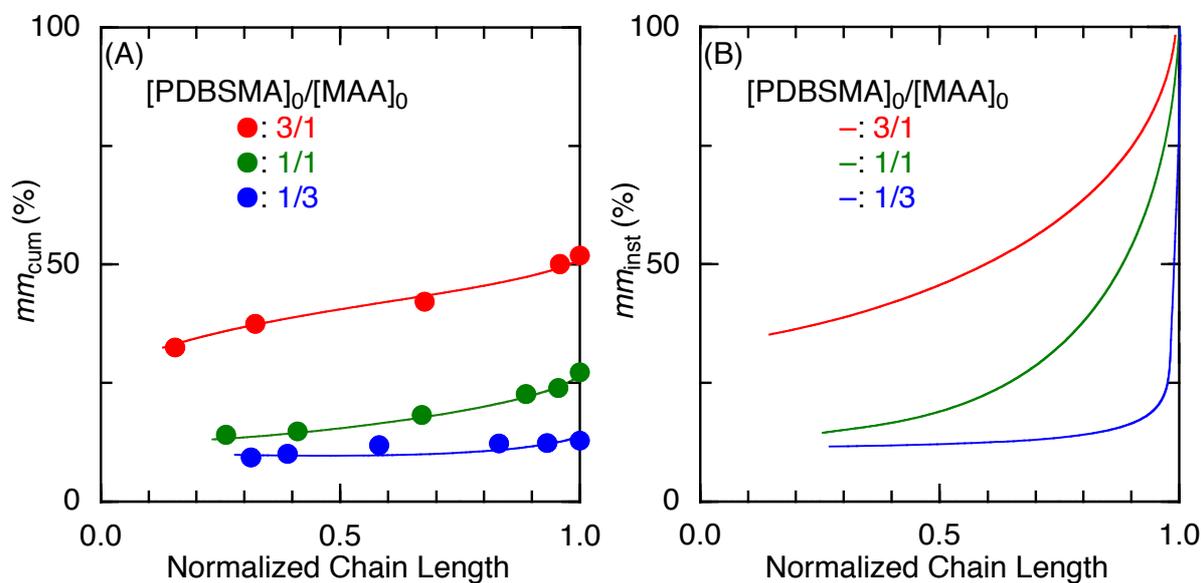


Figure S9. Effects of initial charge ratio of PDBSMA and MAA on the dependences of cumulative (A) and instantaneous (B) *mm* contents on the normalized chain length in the RAFT copolymerization of PDBSMA and MAA with CDB/AIBN in toluene at 60 °C: $[\text{PDBSMA}]_0 + [\text{MAA}]_0 = 0.60 \text{ M}$; $[\text{CDB}]_0 = 6.0 \text{ mM}$; $[\text{AIBN}]_0 = 3.0 \text{ mM}$; $[\text{PDBSMA}]_0 / [\text{MAA}]_0 = 3/1$ (red), $1/1$ (green), or $1/3$ (blue).