Supporting Information

A Thermodynamic Polymer Cross-linking System Based on Radically Exchangeable Covalent Bonds

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Scheme S1. Synthesis of alkoxyamine 1 and poly(methacrylic ester) 2
Scheme S2. Synthesis of alkoxyamine 3 and 4
Scheme S3. Synthesis of alkoxyamine 5
Scheme S4. Synthesis of poly(methacrylic ester) 6

Figure S1. The ln([M]_0/[M]_t) vs. time plots for solution copolymerization of MMA and 5 in anisole (50 wt%) at 50 °C.

Figure S2. Evolution of $M_n$ and $M_w/M_n$ of the polymers as a function of monomer conversion for solution copolymerization of MMA and 5 in anisole (50 wt%) at 50 °C.
Scheme S1. Synthesis of alkoxyamine 1 and poly(methacrylic ester) 2

The detailed synthetic procedures are described in the following paper.

Scheme S2. Synthesis of alkoxyamine 3 and 4

Scheme S3. Synthesis of alkoxyamine 5
Scheme S4. Synthesis of poly(methacrylic ester) 6
Figure S1. The $\ln([M]_o/[M]_t)$ vs. time plots for solution copolymerization of MMA and 5 in anisole (50 wt%) at 50 °C: $[\text{MMA}]_o/[5]_o/[2-(\text{EiB})\text{Br}]_o/[\text{Cu(I)Br}]_o/[\text{Sp}]_o = 190.5/9.5/1/1/2$.

Figure S2. Evolution of (circle) $M_n$ and (triangle) $M_w/M_n$ of the polymers as a function of monomer conversion for solution copolymerization of MMA and 5 in anisole (50 wt%) at 50 °C: $[\text{MMA}]_o/[5]_o/[2-(\text{EiB})\text{Br}]_o/[\text{Cu(I)Br}]_o/[\text{Sp}]_o = 190.5/9.5/1/1/2$. The calculated molecular weights are shown as a dashed line.