Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Is it ATRP or SET-LRP? I. Cu^0&Cu^{II}/PMDETA-mediated reversible - deactivation radical polymerization with PMDETA.

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Experimental details

Materials: methyl acrylate (MA, 99%, Aldrich), ethyl α-bromoisobutyrate (EBriB, 98%, Aldrich), ethyl 2-bromopropionate ($CuBr_2$, 99%, Aldrich), tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 97%, Aldrich), and pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were used as received. Cu(0)-wire (diameter 1 mm) was purchased from Sigma-Aldrich and was treated by immersion in conc. HCl prior to use. Solvents were purchased from Fisher Scientific and used as received.

Synthesis of PMA catalyzed by Cu^0/Me_6TREN: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water before used. The solution was stirred at 600 rpm and the polymerization was conducted at 25 ℃ in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu^0/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water. The solution was stirred at 600 rpm and the polymerization was conducted at 25 ℃ in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu^I/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv), pretreated CuCl (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. The solution was stirred at 600 rpm and the polymerization was conducted at 25 ℃ in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu^{II}/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv), $CuBr_2$ (0.05 mmol, 0.05 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. The solution was stirred at 600 rpm and the polymerization was conducted at 25 ℃ in an oil bath for the desired reaction time.

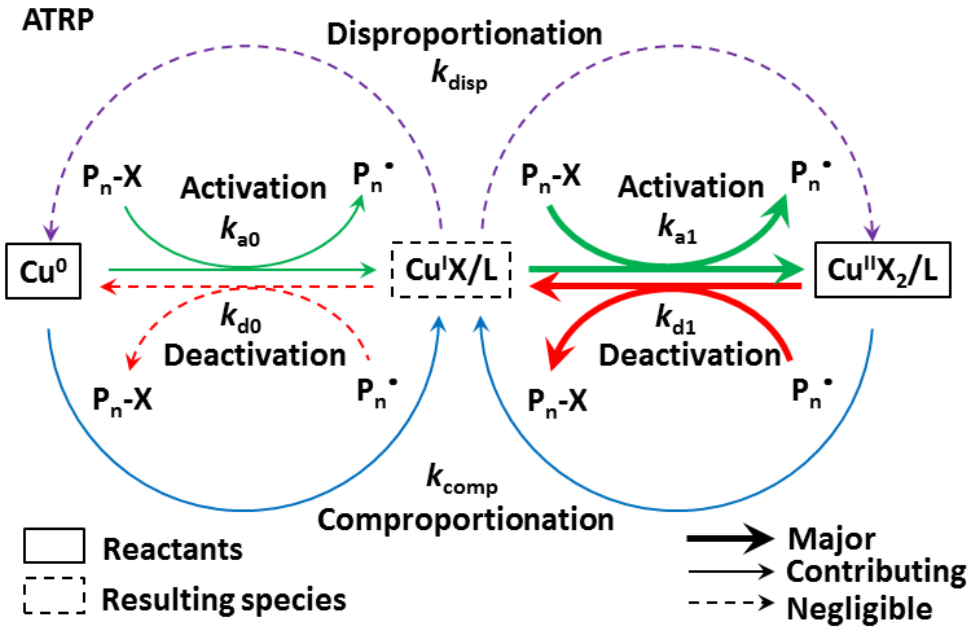
Synthesis of PMA catalyzed by Cu^0&Cu^{II}/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv), $CuBr_2$ (0.05 mmol, 0.05 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water. The solution was stirred at 600 rpm and the polymerization was conducted at 25 ℃ in an

oil bath for the desired reaction time.

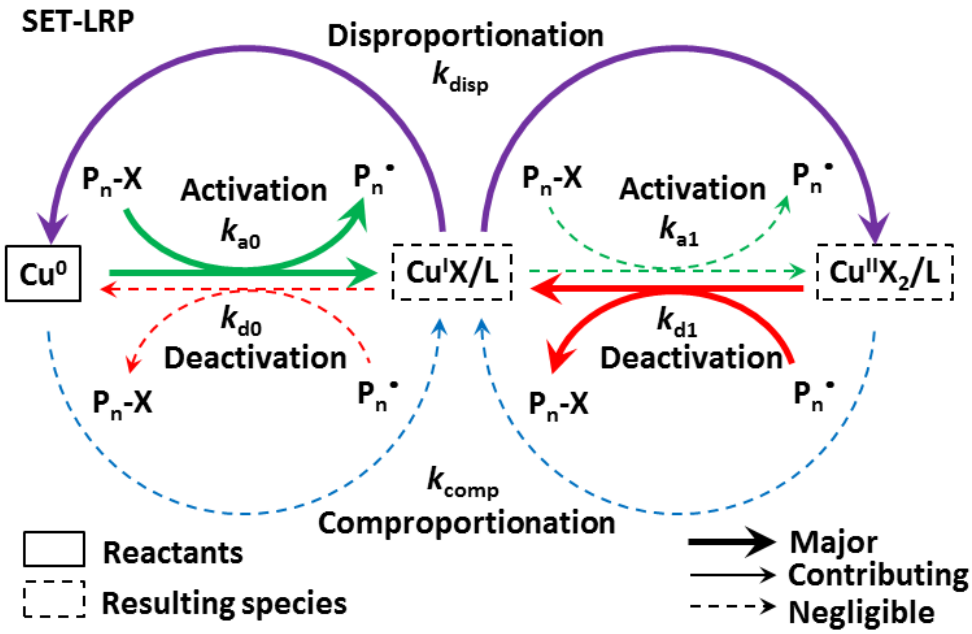
Size exclusion chromatography (SEC) characterizations: Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity (M_w/M_n) were obtained by SEC (Varian 920-LC) equipped with an RI and an LS detector. The columns (30 cm PLgel Mixed-C, two in series) were eluted using tetrahydrofuran (THF) and calibrated using a series of 12 near-monodisperse PMMA standards (M_p from 690 to 1,944,000 g/mol). The polymers were analyzed in THF at a concentration of 5.0 mg/ml. All calibrations and analyses were performed at 40 ^oC and a flow rate of 1 ml/min.

^{1}H NMR characterizations: ^{1}H NMR analysis was carried out on a S4 300 MHz Bruker NMR with JEOL Delta v5.0.1 processing software.

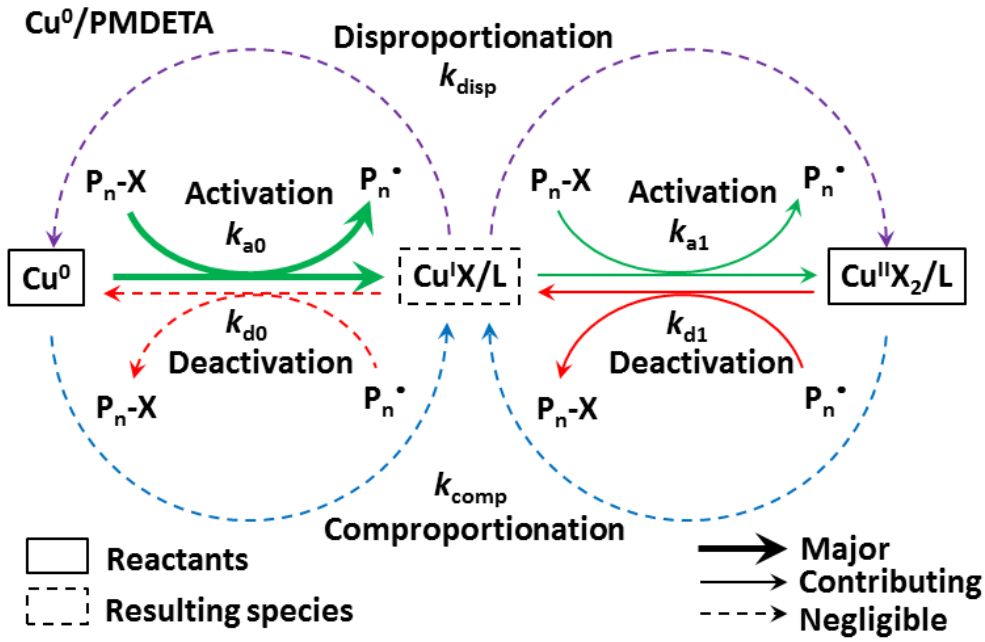
Scheme S1. The SARA ATRP mechanism[1]



Scheme S2. The SET-LRP mechanism[1]



Scheme S3. The mechanism of Cu^0/PMDETA catalyzed polymerization



Scheme S4. The mechanism of Cu^{I}/PMDETA catalyzed polymerization

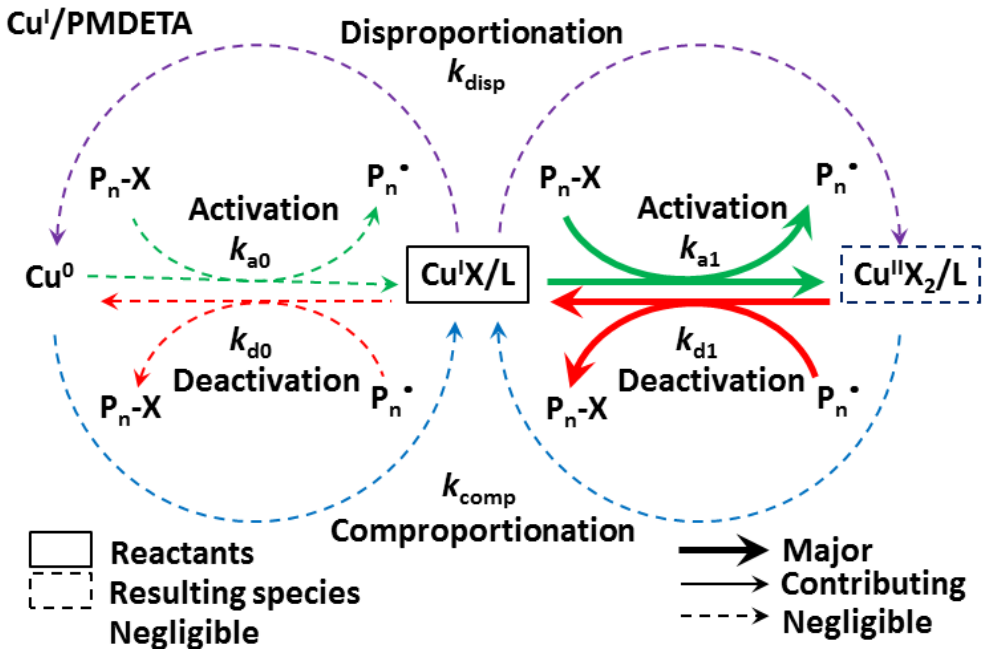


Figure S1. SEC trace of Cu^0 /Me_6TREN catalyzed polymerization (entry 1-5 in Table 1)

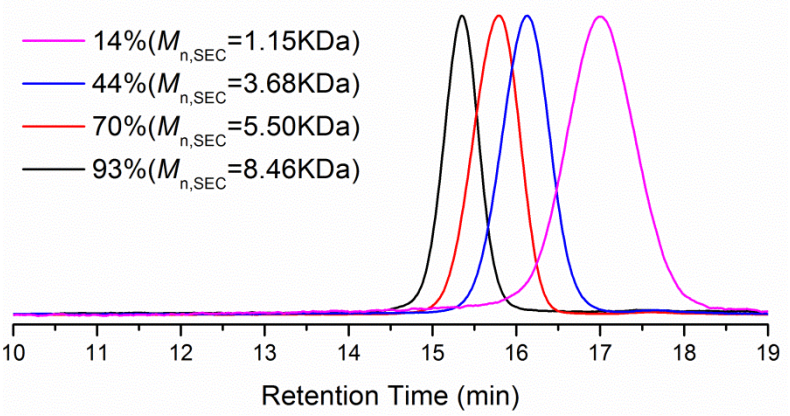


Figure S2. SEC trace of Cu^0/PMDETA catalyzed polymerization (entry 6-9 in Table 1)

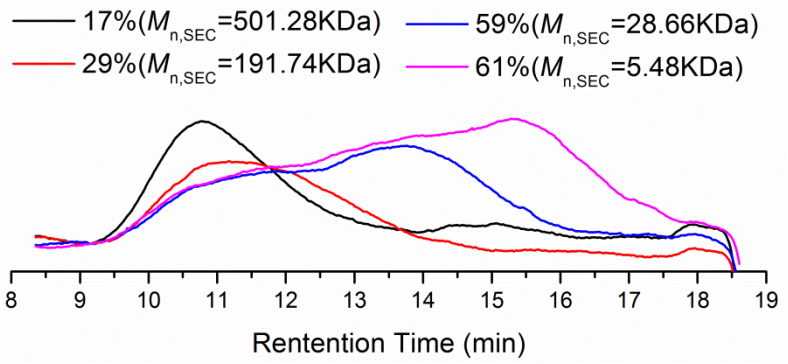


Figure S3. SEC trace of Cu^{I}/PMDETA catalyzed polymerization (entry 10-15 in Table 1)

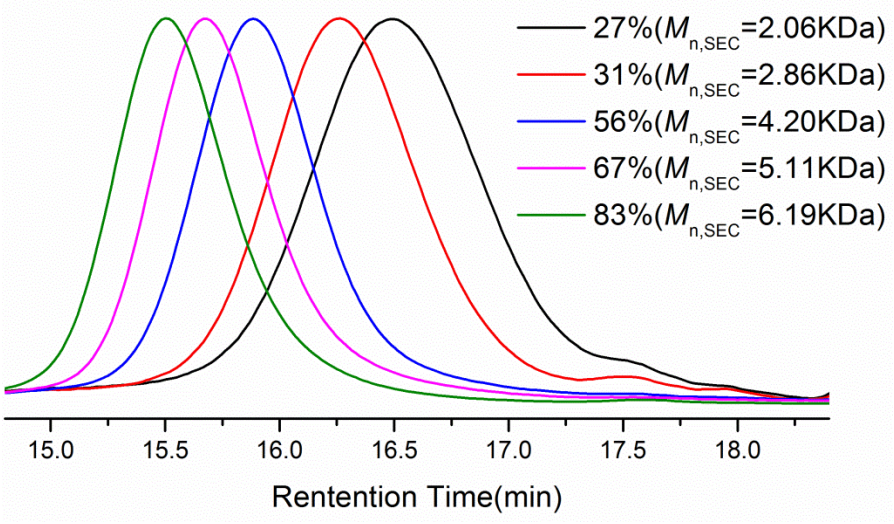


Figure S4. ^{1}H NMR results for PMA catalyzed by Cu^{0}/Me_6TREN

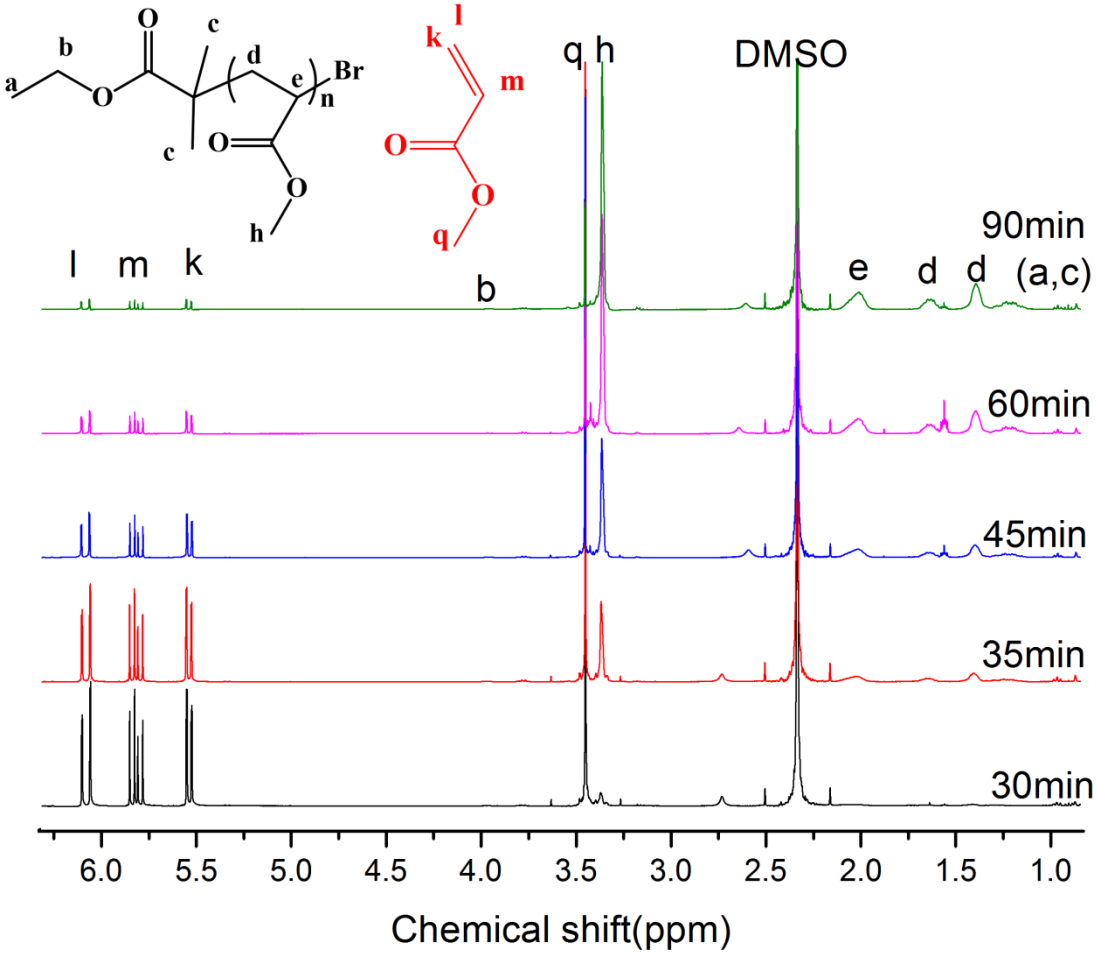


Figure S5. ^{1}H NMR results for PMA catalyzed by Cu^{0}/PMDETA

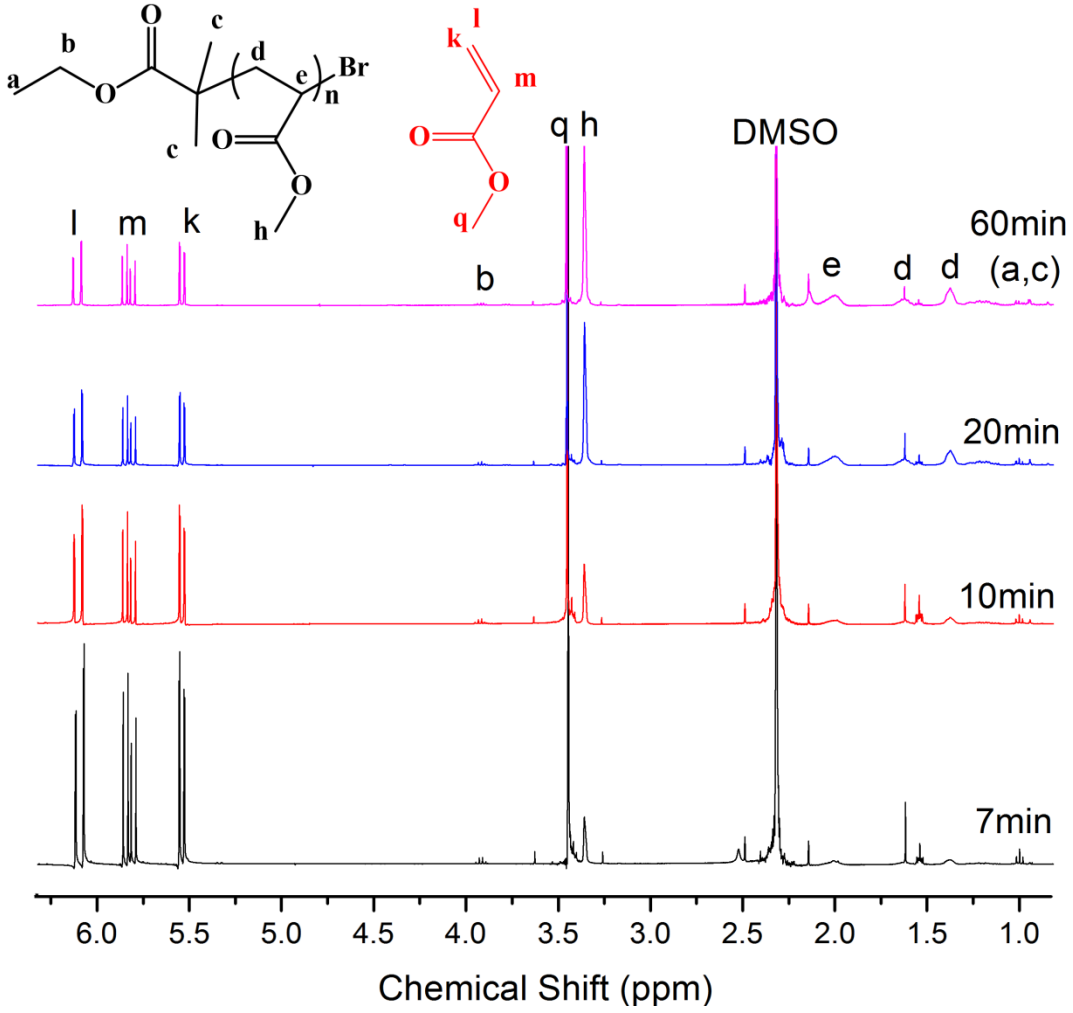


Figure S6. ^{1}H NMR results for PMA catalyzed by Cu^{I}/PMDETA

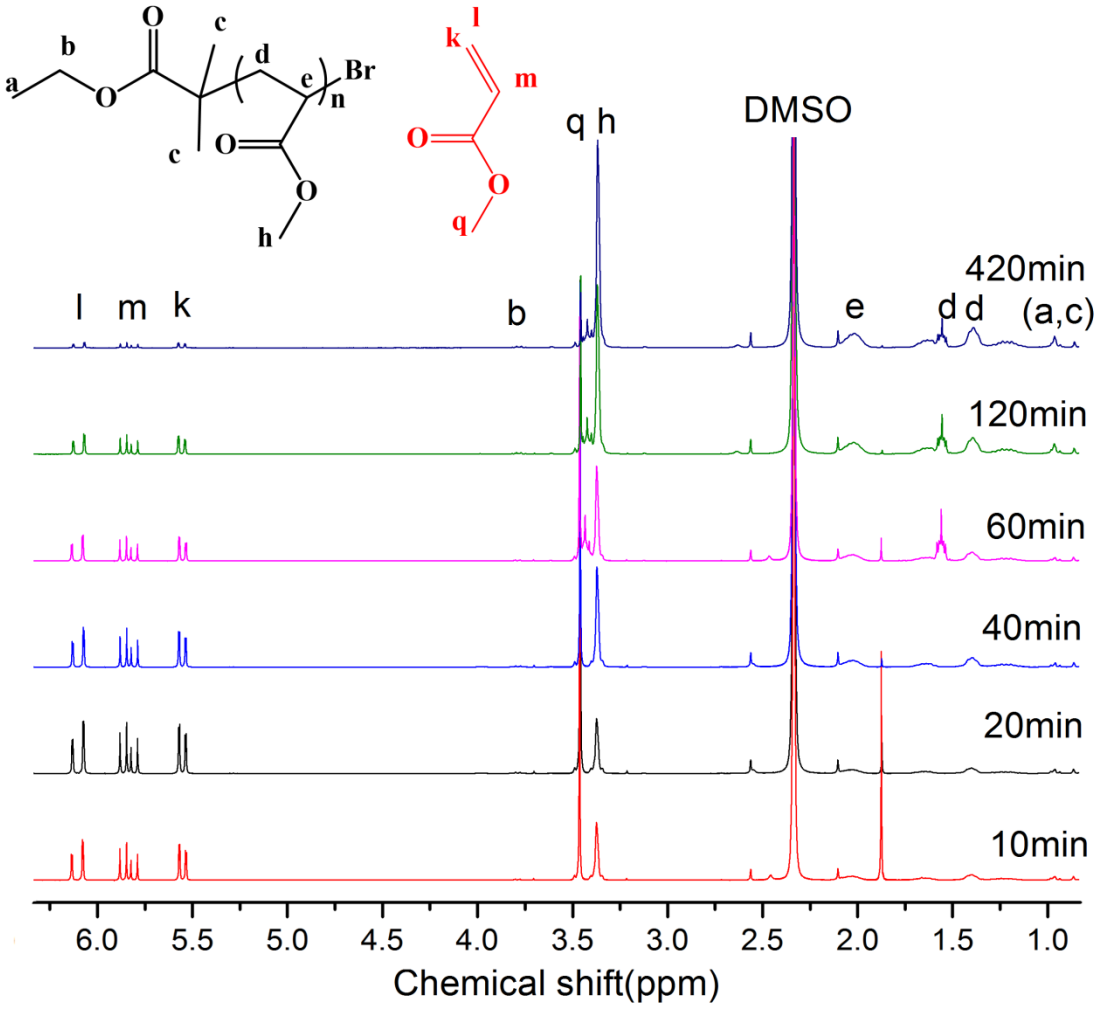
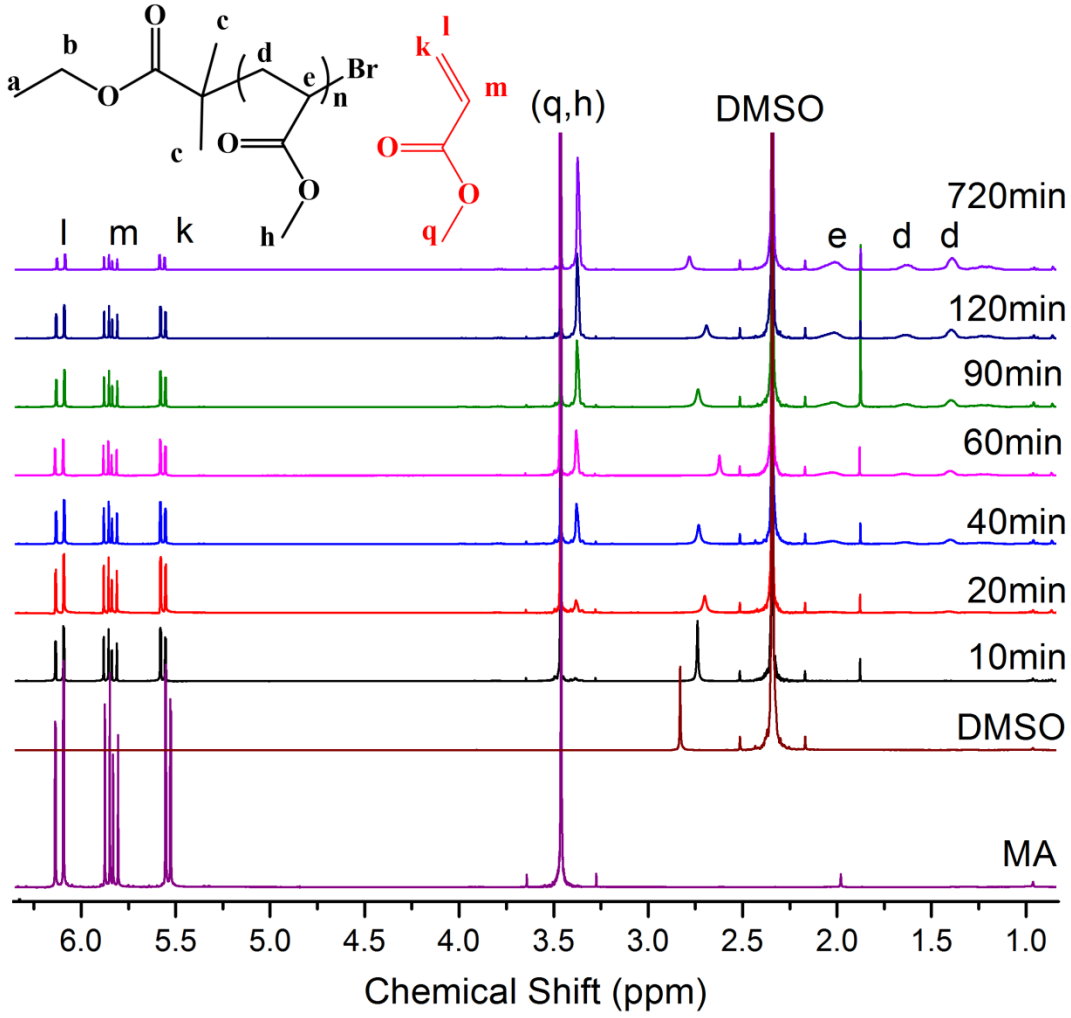


Figure S7. ^{1}H NMR results for PMA catalyzed by Cu^{0}&Cu^{II}/PMDETA



Equation S1.

$$\text{Vinyl conversion} = \frac{consumed\ vinyl\ groups}{original\ vinyl\ groups} = 1 - \frac{current\ vinyl\ groups}{original\ vinyl\ groups} = 1 - \frac{integrals\ of\ k}{integrals\ of\ (h+q)/3}$$

Reference

1 D. Konkolewicz, Y. Wang, M Zhong, P. Krys, A. A. Isse, A. Gennaro, K. Matyjaszewski, Macromolecules, 2013, 46, 8749–8772.