Electronic Supplementary Information

For

PPM Amount of Fe (III)-mediated ATRP of MMA with Phosphorus Containing Ligands in the Absence of Any Additives

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Experimental section

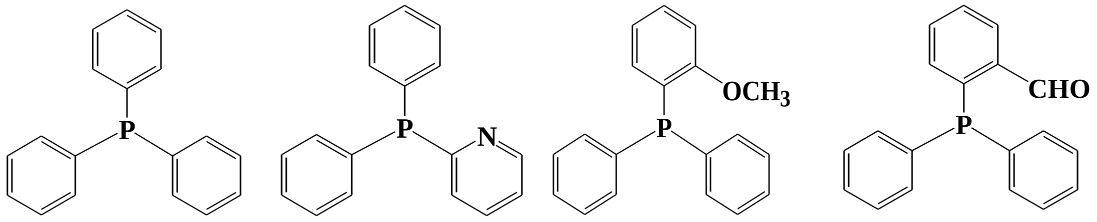
Methyl methacrylate (MMA, 99%, Aldrich) was passed through a column filled with neutral alumina, dried over CaH_2, distilled under reduced pressure, and stored in a freezer under nitrogen. Tetrahydrofuran (THF, HPLC grade, Fisher) and toluene (certified grade, Fisher) were freshly distilled from Na/K alloy with benzophenone (99%, Aldrich) and stored under nitrogen. 2-(Diphenylphosphino)pyridine (DPPP, 97%, Aldrich), triphenylphosphine(TPP, 99%, Aldrich), diphenyl-(2-methoxyphenyl) phosphine (DPMPP,99%,Aldrich) and 2-(diphenylphosphino) benzaldehyde (DPPB, 97%, Aldrich), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 99%, Aldrich), FeBr3 (98%, Aldrich), ethyl 2-bromoisobutyrate (EBriB, 99%, Aldrich), anisole (99%, Aldrich), methanol (MeOH, 99.9+%, Aldrich), and all other solvents were used without further purification.

Polymerization Experiments

The polymerization reaction was conducted using the following procedure: (targeted number-average degree of polymerization (DPn)=10000; 10 ppm Fe catalyst): A Schlenk flask was charged with $FeBr_3$ (6 mg, 0.001865 mmol) and the DPMPP ligand (1.0829 mg, 0.00373 mmol). The flask was sealed with a rubber septum and was cycled three times between vacuum and nitrogen to remove the oxygen. The degassed solvent (20 mL) (in solution polymerization), anisole (1 mL), and MMA (20 mL,186.5 mmol) were then added to the flask by using degassed syringes. The solution was stirred for 20 min at room temperature and then EBriB (0.006 mL, 0.00373 mmol) was added. The flask was sealed with a new rubber septum and degassed by three freeze/pump/thaw cycles to remove the oxygen. The flask was immersed in a thermostated oil bath. At timed intervals, samples were withdrawn from the flask with a degassed syringe, diluted with THF, and then filtered through a column filled with neutral aluminum oxide to remove the iron catalyst. Parts of the polymer solution were used for gas chromatography (GC) measurements to determine the monomer conversions. Other parts of the PMMA solution were then precipitated by using an excess of n-hexane, and these polymers were dried under vacuum for 24 h in preparation for gel permeation chromatography (GPC) measurements to determine the molecular weights of the polymers.

Characterization

The monomer conversion was determined in THF solvent with anisole as an internal standard with HP 6890 gas chromatography equipped with FID detector and J&W Scientific 30 m DB WAX Mega bore column. The injector and detector temperatures were kept at 250^0C. The analysis was run isothermally at 40^0C for 1 min, following which the temperature was increased to 120^{0}C at heating rate of 20^{0}C/min. The number average molecular weight (Mn) and molecular weight distribution (Mw/Mn) was determined by GPC using Waters columns (Styragel, HR 5E) equipped with the Water 515 pump and Waters 2410 differential refract-tometer using diphenyl ether as internal standard. THF was used as the eluent at the flow rate of 1mL/min. linear polystyrene standard were used for the calibration.



TPP **DPPP** **DPMPP** **DPPB**

Figure S1. The structures of phosphorus-containing ligands.

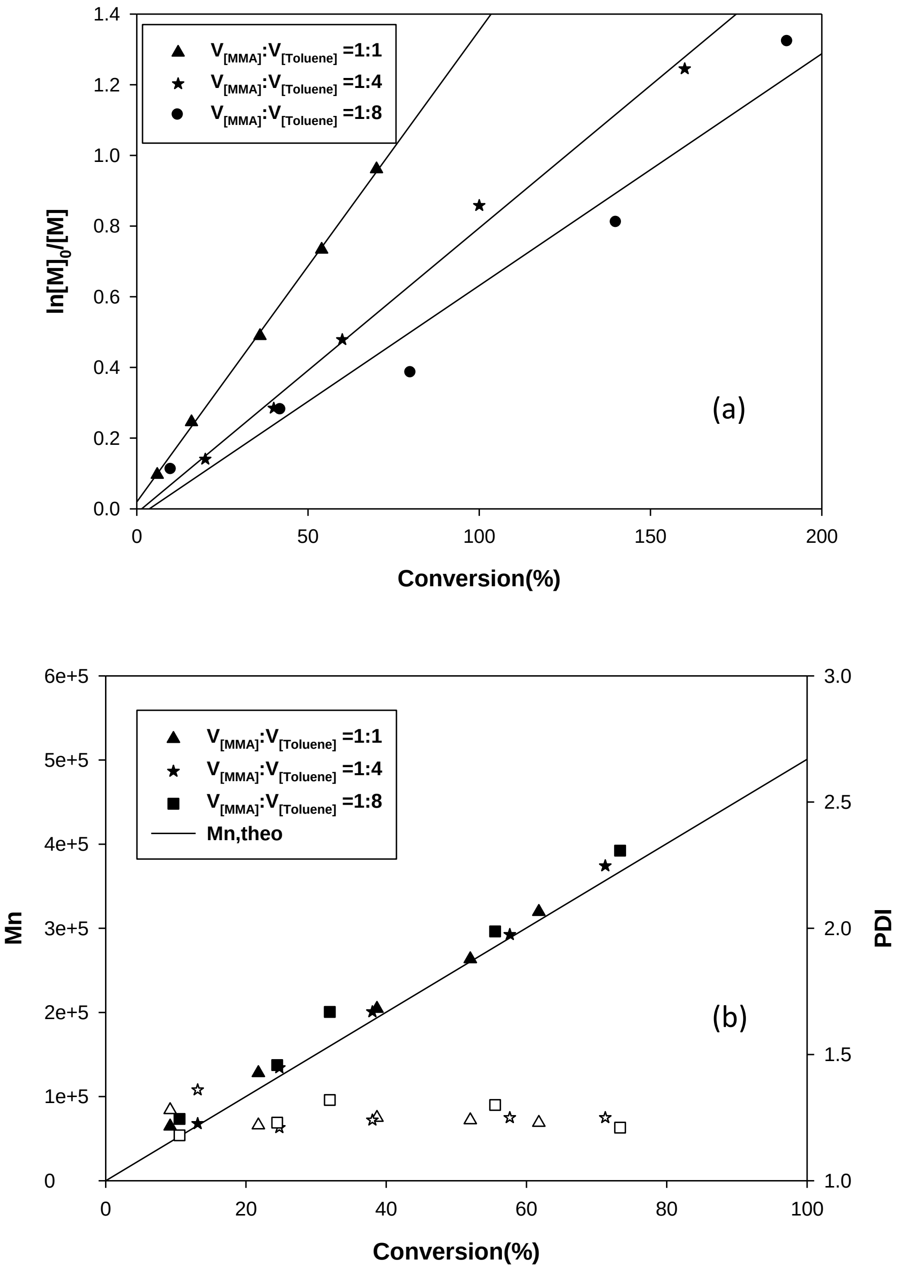


Figure S2. (a) Kinetics plots of ln[M]$_0$/[M] versus reaction time and (b)dependence of molecular weights, *M*n (filled symbols), and molecular weight distributions, M_w/M_n (open symbols), on the monomer conversion for the ATRP of MMA in different solvent amount systems at 80 °C.[MMA]$_0$ =186.5 M; [MMA]$_0$/[EBriB]$_0$/[FeBr$_3$]$_0$/[DPMPP]$_0$ = 200:0.04:0.002:0.04.

To understand the mechanism of polymerization of MMA initiated by MMA/$FeBr_3$/DPMPP, a radical scavenger (TEMPO) was added to the reaction system after 40hrs and 70hrs there were no change in the molecular weight and PDI remained narrow even after 70hrs of reaction. Figure S3 indicated that the polymerization was immediately terminated by the radical scavenger. Therefore, we can conclude that Fe (III)/DPMPP catalyzed polymerization of MMA was preceded by radical mechanism.

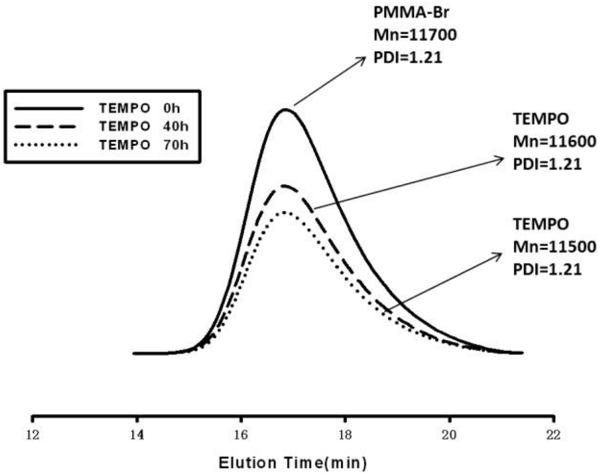


Figure S3. GPC traces of the reaction PMMA before and after TEMPO addition experiment with MMA/$FeBr_3$/DPMPP at 80^0C in bulk.

End-group Analysis of PMMA-Br. The end-group analysis of ATRP polymers is important, because polymer chains with halogen end groups act as a macroinitiator. It can be reactivated in the presence of the ATRP catalyst system so as to initiate the polymerization of the second monomer to form block, graft or star polymers, depending on the position and number of initiation sites.

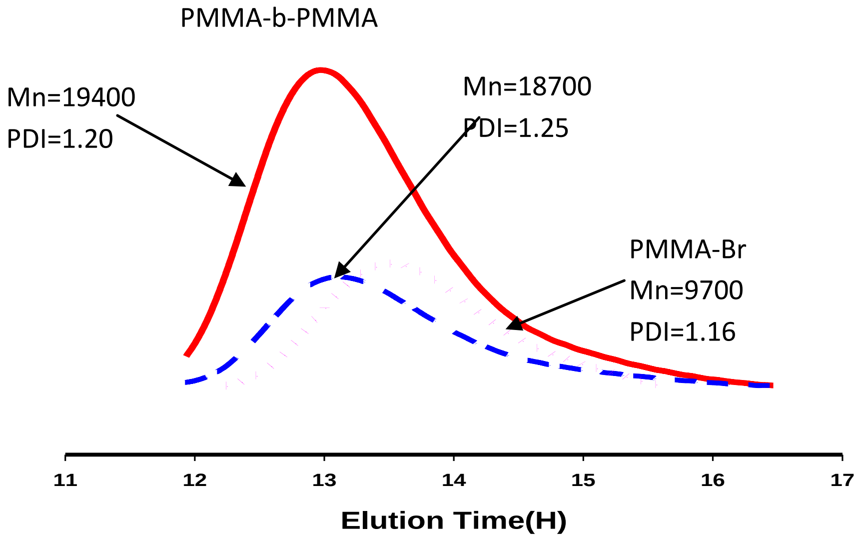


Figure S4. GPC traces of the macroinitiator (PMMA-Br) and its chain extended polymers (PMMA-*b*-PMMA) obtained at 6h and 8 h, respectively.

The chain extension experiment of MMA with PMMA-Br ($M_{n,GPC}$ = 9700, Mw/Mn=1.16) as macroinitiator to initiate the polymerization of fresh MMA was carried out in bulk at 80^0C using $FeBr_3$/DPMPP as the catalyst. The experiment was conducted using a ratio of $[MMA]_0/[macroinitiator]_0/[FeBr_3]_0/[DPMPP]_0$ = 200:1:0.01:2. After the chain extension reaction, the $Mn,_{GPC}$ of PMMA increased and the polydispersities of the final polymers kept quite narrow. These results clearly establish that the PMMA obtained by ATRP with $FeBr_3$/DPMPP catalyst system is living polymer.