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Supporting Information

A Complexed Initiating System $AlCl_3$·Phenetole/$TiCl_4$·H_2O with Dominant Synergistic Effect for Efficient Synthesis of High Molecular Weight Polyisobutylene

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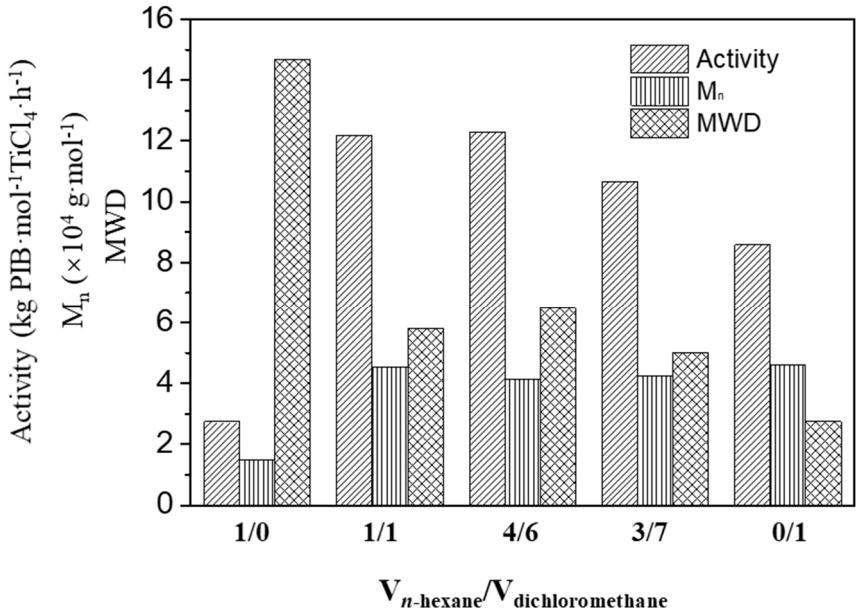

Figure S1. The effect of solvent polarity on $TiCl_4/H_2O$ for IB polymerization ([IB] = 2.9 mol·L^{-1}; [H_2O] = 20 mmol·L^{-1}; [$TiCl_4$] = 30 mmol·L^{-1}; t_p=30 min; T_p = −60 °C.).

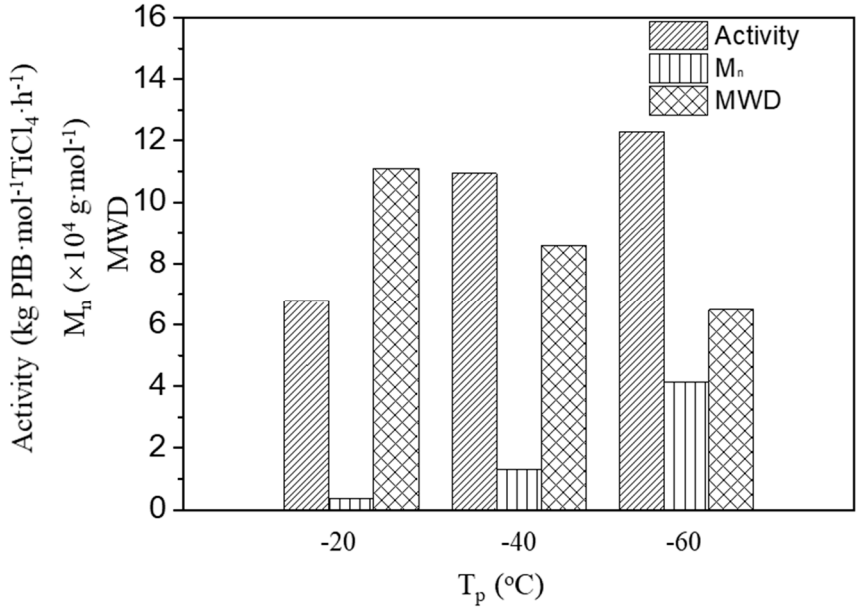

Figure S2. The effect of T_P on $TiCl_4/H_2O$ for IB polymerization ([IB] = 2.9 mol·L^{-1}; [H_2O] = 20 mmol·L^{-1}; [$TiCl_4$] = 30 mmol·L^{-1}; 60 mL $C_2H_2Cl_2$;40 mL n-hexane; t_P = 30 min)

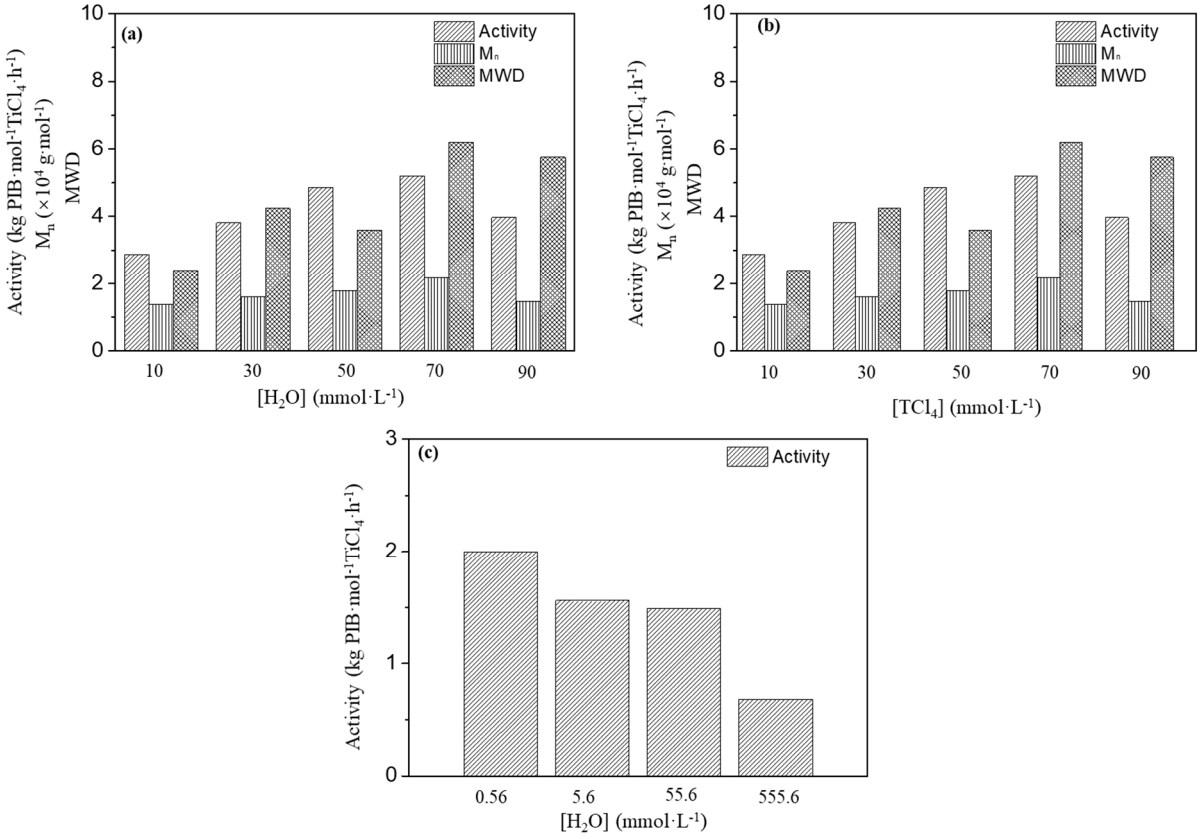

Figure S3. The effect of [H_2O] and [$TiCl_4$] on IB polymerization ((**a**) [$TiCl_4$] = 50 mmol·L^{-1}; (**b**) [H_2O] = 40 mmol·L^{-1}; (**c**) [$TiCl_4$] = 4.56 mmol·L^{-1}; Other conditions: [IB] = 2.9 mol·L^{-1}; 60 mL $C_2H_2Cl_2$; 40 mL n-hexane; t_P = 30 min; T_P = −60 °C.).

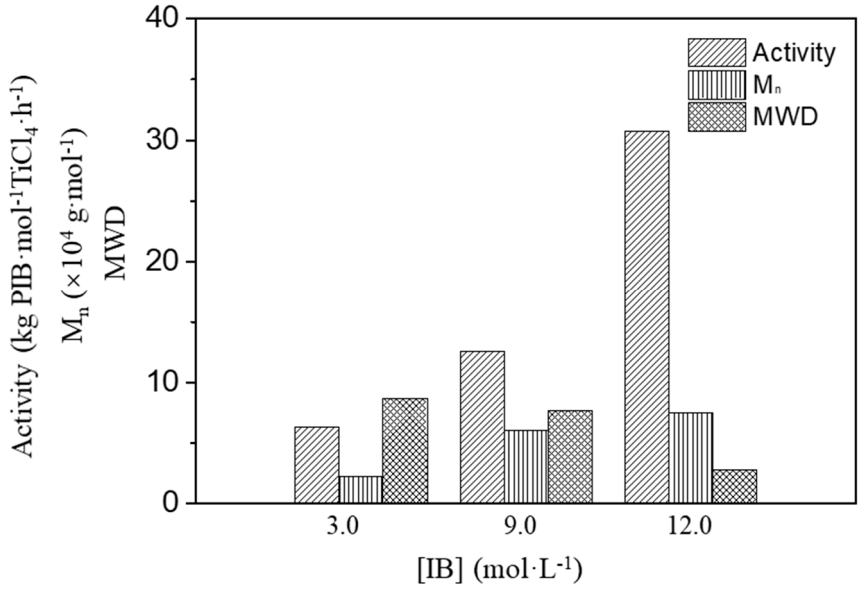

Figure S4. The effect of monomer concentration on $TiCl_4/H_2O$ for IB polymerization ([H_2O] = 30 mmol·L^{-1}; [$TiCl_4$] = 20 mmol·L^{-1}; 60 mL $C_2H_2Cl_2$; 40 mL n-hexane; t_p = 30 min; T_p = −60 °C).

The effect of various reaction conditions on the polymerization behaviors of $TiCl_4/H_2O$ were investigated as well (see **Figure S1-S4**). The results indicated that $TiCl_4/H_2O$ was good at producing high or medium molecular weight polyisobutylene with M_n=1~6 × 10^4 g·mol^{-1} and the MWD of the polymer was relatively broad. In addition, this initiating system showed low efficiency, and activity≈10 kg PIB·$mol^{-1}TiCl_4$·h^{-1} could be observed in most cases, thus a much higher catalyst concentration was needed to achieve a reasonable monomer conversion. This was also in accordance with the reported work that the dimer of $TiCl_4$ was the active coinitiator for cationic polymerization, and a relatively high concentration of $TiCl_4$ was needed for achieving reasonable polymerization rate [S1].

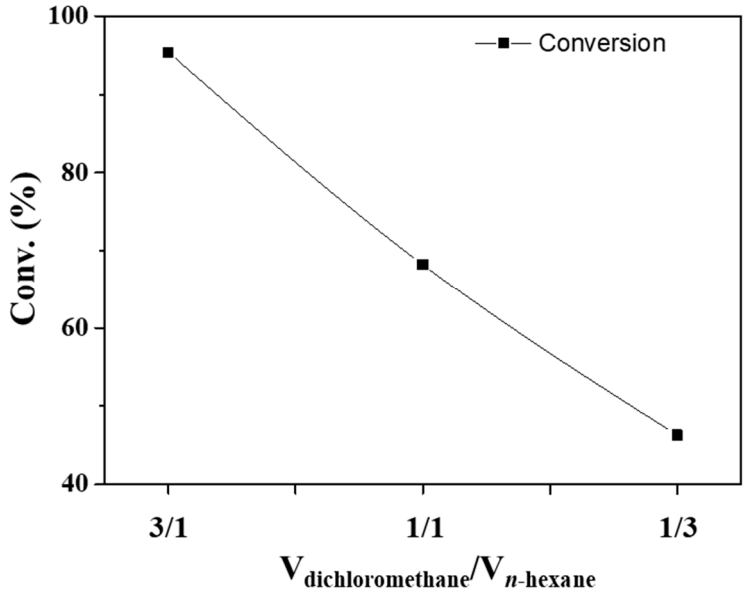

Figure S5. The effect of solvent polarity on monomer conversion with $AlCl_3$/phenetole initiating system *(*[IB] = 4 mol·L^{-1}; $V_{dichloromethane}$ + $V_{n\text{-}hexane}$ = 100 mL; T_p = −60 °C; t_p = 30 min; [$AlCl_3$]/[phenetole] = 1/1.*)*.

According to **Figure S5**, a relatively stronger polarity of the solvent was more favored by the $AlCl_3$/phenetole initiating system to achieve high monomer conversion, as more polar conditions could possibly help to produce more active ion pairs for IB polymerization [S2].

References

[S1] M. Tawada, R. Faust. *Macromolecules* **2005,** *38*, 4989.

[S2] L. Sipos, P. De, R. Faust. *Macromolecules* **2003,** *36*, 8282.