

# Supporting Information

for

## Controlled Divinyl Monomer Polymerization Mediated By Lewis Pairs: A Powerful Synthetic Strategy for Functional Polymers

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### Experiment section

**Materials, Reagents and Methods** All syntheses and manipulations of air- and moisture sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an inert gas (Ar or N<sub>2</sub>)-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. Vinyl methacrylate (VMA), allyl methacrylate (AMA) were purchased from the Aldrich Chemical Co., Ltd. These monomers were dried with CaH<sub>2</sub> over night, followed by vacuum distillation. The 4-vinylbenzyl methacrylate (VBMA) was synthesized according to the literature<sup>1</sup>. The purified monomers were stored in brown bottles inside a glovebox freezer at -30 °C.  $\alpha,\alpha$ -Azobis(isobutyronitrile) (AIBN) (Kishida, 99%) was purified by recrystallization from methanol before use. Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was prepared by ligand exchange reactions between B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and AlEt<sub>3</sub> in toluene.<sup>2</sup> *t*-Bu<sub>3</sub>P, Ph<sub>3</sub>P, hydroxytoluene (BHT-H, 2,6-di-tert-butyl-4-methylphenol) were purchased from Aladdin reagent and recrystallization prior to use. 1,3-bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene (<sup>Mes</sup>NHC) was prepared according to the literature.<sup>3</sup> 2,6-diisopropylphenyl-2,3-dihydro-1H-imidazole (IPr=CH<sub>2</sub>), 1-(2,6-diisopropylphenyl)-2-methylene-2,3-dihydro-1H-imidazole (Dip-IPr=CH<sub>2</sub>) was prepared according to the literature.<sup>4</sup>

**Polymer characterizations.** Polymer number-average molecular weights ( $M_n$ ) and molecular weight distributions (PDI) were measured by gel permeation chromatography (GPC) analysis carried out at 35 °C and a flow rate of 1.0 mL min<sup>-1</sup>, with THF (for PVBMA) and CHCl<sub>3</sub> (for PVMA and PAMA) as the eluent, on a Agilent 1260 instrument coupled with a Agilent RI detector and equipped with four PL gel 5  $\mu$ m mixed-C columns. The sample concentration was about 0.1%, and the injection volume was 50  $\mu$ L. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 to 460000 g/mol. Low-molecular-weight PVBMA produced by IPr=CH<sub>2</sub> and Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene was analyzed by Electrospray Ionization Mass Spectrometry (ESI-MS) in positive mode, using a Agilent 6224 TOF LC/MS or matrix-assisted laser.

### **Lewis pair Polymerization**

Polymerizations were performed in 10 mL oven-dried glass reactors inside the glovebox under ambient conditions (ca. 25 °C). A certain amount of a Lewis acid,  $\text{Al}(\text{C}_6\text{F}_5)_3$  (2 equiv) was first dissolved in the vinyl monomer (100-1600 equiv) and 3 mL of toluene inside a glovebox. The polymerization was started by rapid addition of a solution of Lewis base (1 equiv) in 2 mL of toluene *via* a gastight syringe to the above  $\text{Al}(\text{C}_6\text{F}_5)_3$ /monomer solution under vigorous stirring. In all procedures, after the measured time interval, a 0.2 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4 mL vial containing 0.6 mL of undried “wet”  $\text{CDCl}_3$  stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by  $^1\text{H}$  NMR to obtain the percent monomer conversion data. Polymerization was immediately quenched after the removal of the aliquot by addition of 5 mL 5% HCl-acidified methanol. The quenched mixture was precipitated into 100 mL of methanol, stirred for 1 h, filtered, washed with methanol, and vacuum-dried to give the product polymers.

### **Radical polymerization with AIBN as initiator**

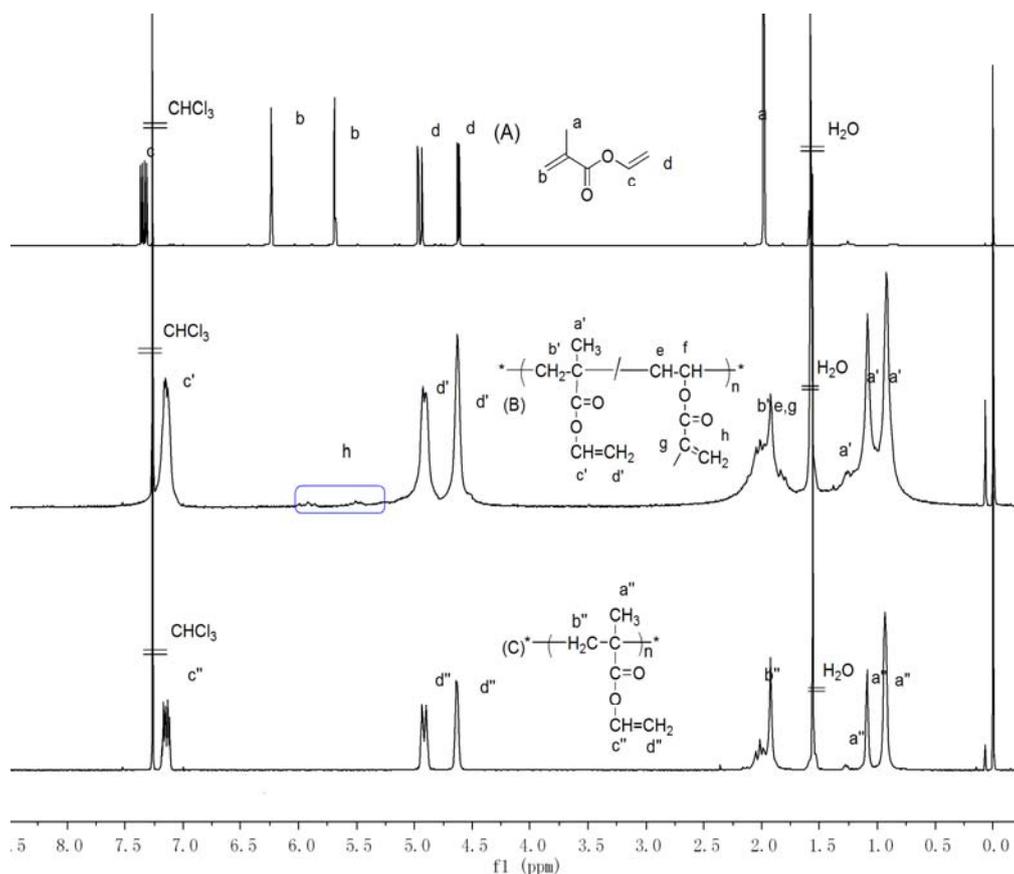
In a 50 mL round-bottomed flask, vinyl monomers and AIBN was dissolved in toluene (4.52 mL) at room temperature. The flask was immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by methanol (0.2 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with n-hexane as an internal standard. The quenched reaction mixture was diluted with toluene (10 mL), washed with dilute hydrochloric acid, aqueous sodium hydroxide solution respectively. Then water was added to dissolve remove initiator residues. After filtered, the resulted solid was further dried under reduced pressure, and vacuum-dried to give the product polymers.

### **Anion polymerization of VBMA with n-BuLi as initiator**

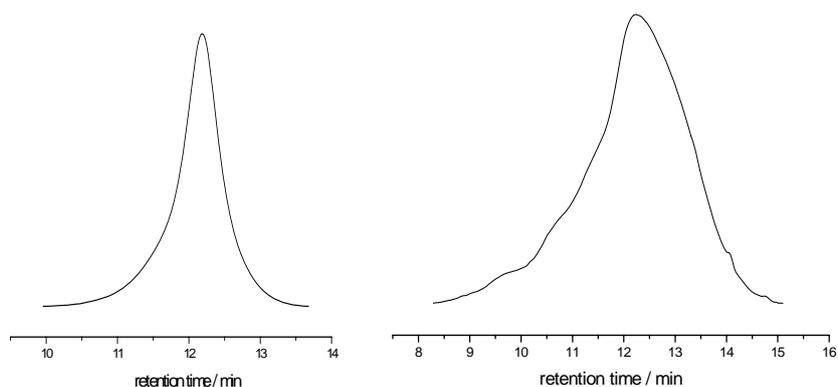
The polymerizations were carried out in a flamed glass reactor under a pure nitrogen atmosphere. Solvent, initiator, (4-vinylbenzyl methacrylate) (VBMA) in THF were transferred by syringe. n-BuLi solution was added drop by drop until a persistent red color was observed. Subsequently, the required amount of the initiator was added and the reactor was brought to a  $-78^\circ\text{C}$ . The reaction was terminated after 60 min with degassed methanol. Poly(4-vinylbenzyl methacrylate) (PVBMA) were recovered by stripping off the solvent, dissolving the residue in a small amount of benzene (10 mL), and freeze-drying at  $0^\circ\text{C}$ .

### **Thiol-ene click reaction**

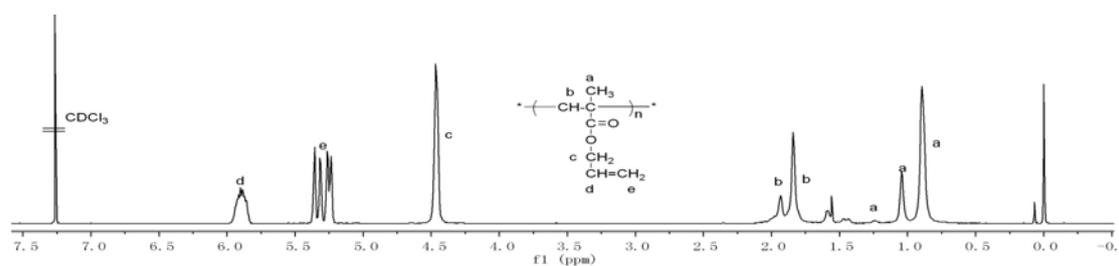
A typical procedure was started with the ratio of reagents  $[\text{C}=\text{C}]/[\text{benzyl mercaptan}]/[\text{AIBN}] = 1/40/0.33$ . Thiol-ene click reaction between PVBMA (150 mg, 1.19 mmol of  $\text{C}=\text{C}$  group) and benzyl mercaptan (5.6 g, 47.6 mmol) was conducted in a 25 mL Schlenk flask under nitrogen atmosphere with 10 mL THF as solvent and AIBN (64.4 mg, 0.39 mmol) as initiator. The reaction mixture was allowed to stir for 24 h at  $70^\circ\text{C}$ . After filtration, the solvent was removed by rotary evaporation. The crude product was dissolved into THF and precipitated in toluene. The product was reprecipitated for several times and dried by vacuum.



**Figure S1.** The  $^1\text{H}$  NMR spectra of the VMA before and after polymerization. (A) VMA, (B) PVMA produced by radical polymerization with AIBN as initiator, (C) PVMA produced by Lewis pair  $[\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2]$  polymerization.



**Figure S2.** The Gel permeation chromatography (GPC) traces of PVMA produced by Lewis pair  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$  with the ratio 400:1 (left) and radical polymerization with AIBN as initiator with the ratio of monomer to initiator at 200:1 (right).



**Figure S3.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C) of PAMA produced by Lewis pair  $[\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2]$  polymerization



**Figure S4.** The  $\text{CH}_2\text{Cl}_2$  solution of PAMA resulted from radical polymerization with AIBN as initiator (left) and by Lewis pair polymerization with  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$  as catalyst (right).

**Reference:**

- (1) Mohan, Y. M.; Raghunadh, V.; Sivaram, S.; Baskaran, D. *Macromolecules* **2012**, *45*, 3387–3393.
- (2) Feng, S.; Roof, G. R.; Chen, E. Y. -X. *Organometallics* **2002**, *21*, 832-839.
- (3) Arduengo III, A. J.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523-14534.
- (4) Jia, Y. B.; WANG, Y. B.; Ren, W. M.; Xu, T.Q.; Wang, J.; Lu, X. B. *Macromolecules* **2014**, *47*, 1966-1972.