

## Electronic Supplementary Information

for

Room temperature cationic polymerization of  $\beta$ -pinene using modified  $\text{AlCl}_3$   
catalyst: toward sustainable plastics from renewable biomass resources

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coinitiators

## 1. Experimental section

### *Materials*

(-)- $\beta$ -Pinene (Aldrich, 99 %) was distilled from CaH<sub>2</sub> under reduced pressure. CH<sub>2</sub>Cl<sub>2</sub> (Sigma–Aldrich, >99.5%), *n*-hexane (Sigma–Aldrich, >95%) were treated with sulphuric acid, washed with aqueous sodium bicarbonate, dried over CaCl<sub>2</sub> and distilled twice from CaH<sub>2</sub> under an inert atmosphere. Toluene (Sigma–Aldrich, 99.8%) was dried by refluxing with Na/benzophenone, distilled and stored under dry argon atmosphere.  $\alpha,\alpha,\alpha$ -Trifluorotoluene (TFT, Aldrich, 99%), ethyl acetate (Aldrich, 99.5 %), dibutyl ether (Sigma–Aldrich, 99.3%) were distilled from CaH<sub>2</sub> under an inert atmosphere prior to use. Diphenyl ether (Aldrich,  $\geq$ 99 %) was distilled from CaH<sub>2</sub> under reduced pressure. AlCl<sub>3</sub> (Aldrich, 99.999%), ethanol (Sigma–Aldrich,  $\geq$ 96%) and CDCl<sub>3</sub> (Euriso-top<sup>®</sup>) were used as received.

### *Methods*

Size-exclusion chromatography (SEC) was performed on a Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7,7 column thermostated at 30 °C. The detection was achieved by a differential refractometer and tetrahydrofuran (THF) was eluted at a flow rate of 1.0 mL/min. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany). <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100.6 MHz) spectra were recorded in CDCl<sub>3</sub> at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the solvent peak in reference to tetramethylsilane standard (<sup>1</sup>H NMR). DSC measurements were performed on a NETZSCH STA 449C instrument calibrated with indium. Samples of poly( $\beta$ -pinene) (10-15 mg) were analyzed using the following steps: heating at 20°C/min from 20°C to 220°C and, after 5 minutes at 220°C isothermally, cooling at 20°C/min from 220°C to -40°C, and, finally, heating at 20°C/min from -40°C to 220°C to obtain the glass transition temperature (T<sub>g</sub>). Thermogravimetric analysis (TGA) was performed on a TGA51 TA Instruments apparatus between 20 and 550 °C under nitrogen at heating rate 10 °C min<sup>-1</sup>

### *Procedures*

(a) *Synthesis of AlCl<sub>3</sub> complexes.* The complexes of AlCl<sub>3</sub> with different electron donors (Bu<sub>2</sub>O, EtOAc and Ph<sub>2</sub>O) were prepared under argon atmosphere in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. As a typical example, the synthesis of AlCl<sub>3</sub>OPh<sub>2</sub> complex is given below: Ph<sub>2</sub>O (3.6 mL, 2.25×10<sup>-2</sup> mol) was added dropwise to the slurry of AlCl<sub>3</sub> (3 g, 2.25×10<sup>-2</sup> mol) in 18.7 mL of CH<sub>2</sub>Cl<sub>2</sub> during 5-10 min. The reaction was allowed to stir for 30–60 min up to complete dissolving of AlCl<sub>3</sub> to give a complex (AlCl<sub>3</sub>OPh<sub>2</sub>) solution in CH<sub>2</sub>Cl<sub>2</sub> (1 M). The concentration of complex was determined by back titration of Al with EDTA by ZnSO<sub>4</sub> with diphenylthiocarbazon as an indicator.

(b) *Polymerization.* The polymerization reactions were carried out in glass tubes under argon atmosphere at different temperatures (from –60 to 20 °C). As an example of a typical procedure, polymerization was initiated by adding a solution of AlCl<sub>3</sub>OPh<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (0.07 mL, 1 M) to a mixture of total volume 26.8 mL consisting of β-pinene (1.76 mL, 1.49×10<sup>-2</sup> M), CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and *n*-hexane (10 mL). After a predetermined time, 3–5 mL aliquots were withdrawn and poured into ethanol. The precipitated polymer was separated from the solution by centrifugation and dried in vacuum. Monomer conversions were determined gravimetrically.

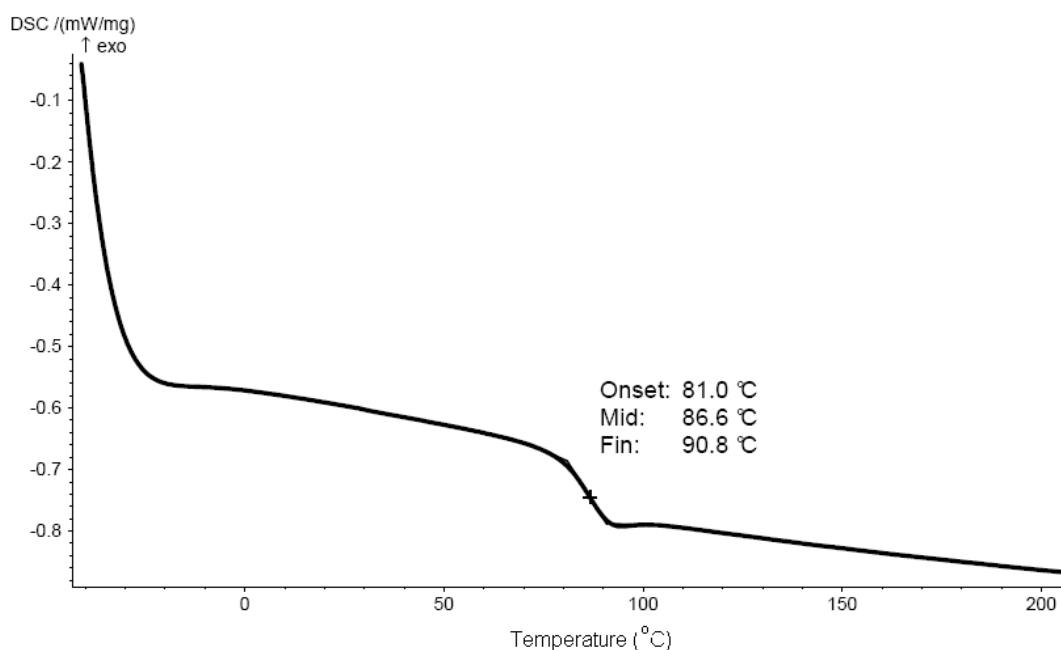
## 2. Influence of electron donor nature (Ph<sub>2</sub>O, EtOAc, Bu<sub>2</sub>O) on the cationic polymerization of $\beta$ -pinene

**Table S1.** Cationic polymerization of  $\beta$ -pinene cointiated by AlCl<sub>3</sub>ED (ED=Ph<sub>2</sub>O, Bu<sub>2</sub>O, EtOAc)<sup>a</sup>

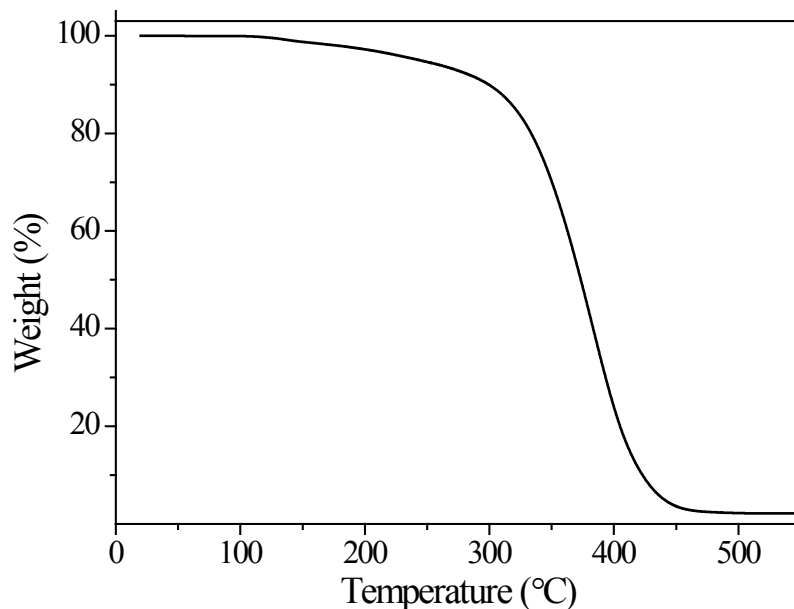
Entry	Temperature (°C)	Coinitiator	pK <sub>a</sub> <sup>c</sup>	Time (min)	Conv (%)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	T <sub>g</sub>
1	-60	AlCl <sub>3</sub> OPh <sub>2</sub>	-6.54 <sup>d</sup>	0.5	99	13140	2.04	88.7
2	-60	AlCl <sub>3</sub> OBu <sub>2</sub>	-3.59	90	25	6450	1.65	–
3 <sup>b</sup>	-60	AlCl <sub>3</sub> 0.8EtOAc	-6.5	0.5	100	18050	1.92	91.0
4	-20	AlCl <sub>3</sub> OBu <sub>2</sub>	-3.59	30	98	2700	2.17	67.4

<sup>a</sup> Conditions: [AlCl<sub>3</sub>ED]=13 mM; [M]=0.55 M; Solvent: CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 60/40 v/v; reaction time: 0.5 min. <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 40/60 v/v. <sup>c</sup> pK<sub>a</sub> values for corresponding electron donors. <sup>d</sup> This value is for anisole.

### 3. Thermal properties of obtained poly( $\beta$ -pinene)s

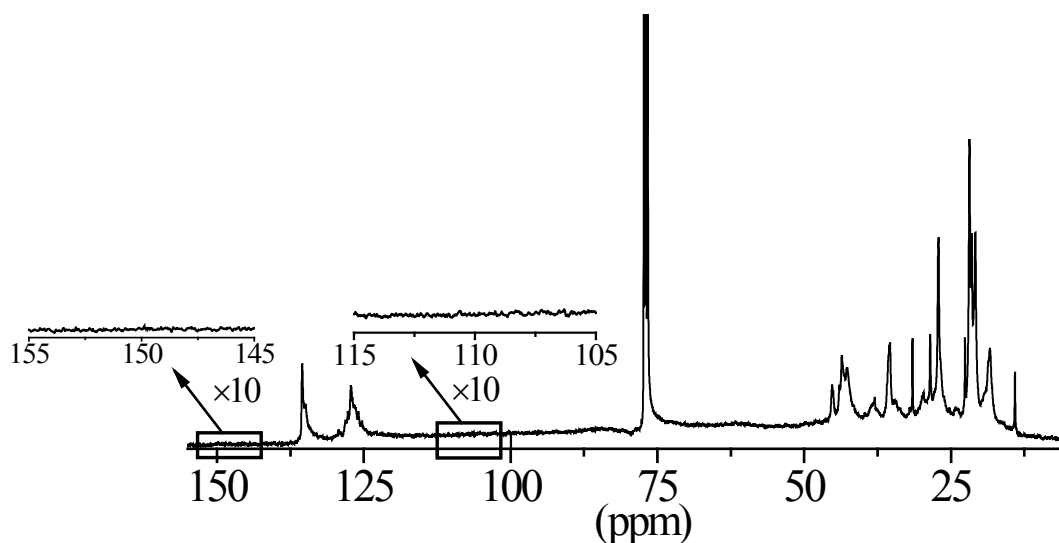


**Fig. S1** Representative DSC thermogram of poly( $\beta$ -pinene) synthesized with  $\text{H}_2\text{O}/\text{AlCl}_3\text{OPh}_2$  initiating system at 0 °C in  $\text{CH}_2\text{Cl}_2/\text{n-hexane}$  60/40 v/v mixture:  $[\text{AlCl}_3\text{OPh}_2]=2.5$  mM;  $[\text{M}]=0.55$  M (run 6 in Table 1).

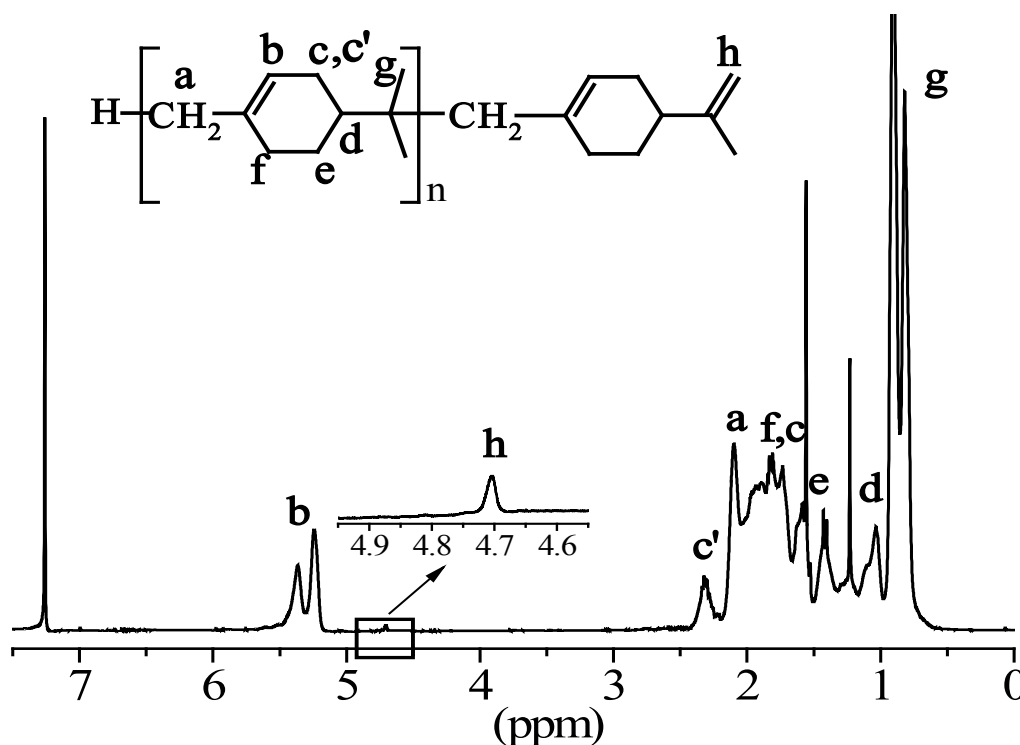


**Fig. S2** Representative TGA thermogram of poly( $\beta$ -pinene) synthesized with  $\text{H}_2\text{O}/\text{AlCl}_3\text{OPh}_2$  initiating system at 0 °C in  $\text{CH}_2\text{Cl}_2/\text{n-hexane}$  60/40 v/v mixture:  $[\text{AlCl}_3\text{OPh}_2]=2.5$  mM;  $[\text{M}]=0.55$  M (run 6 in Table 1).

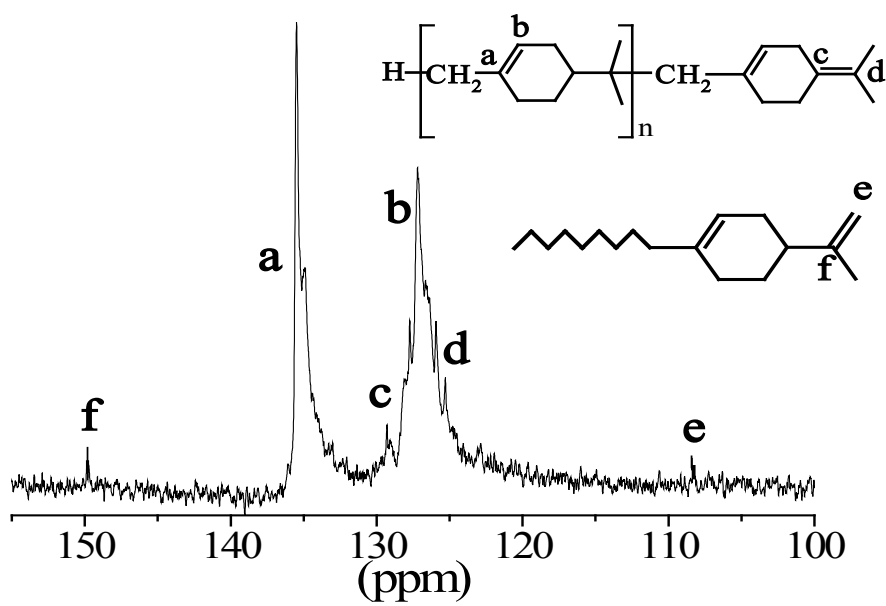
#### 4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of poly( $\beta$ -pinene)s obtained with $\text{AlCl}_3\text{OPh}_2$ and $\text{AlCl}_3\text{OBu}_2$ as coinitiators



**Fig. S3**  $^{13}\text{C}$  NMR spectrum of poly( $\beta$ -pinene) obtained with  $\text{H}_2\text{O}/\text{AlCl}_3\text{OPh}_2$  initiating system at 20  $^\circ\text{C}$  (entry 11, Table 1).



**Fig. S4**  $^1\text{H}$  NMR spectrum of poly( $\beta$ -pinene) obtained with  $\text{H}_2\text{O}/\text{AlCl}_3\text{OBu}_2$  initiating system at 20  $^\circ\text{C}$  (entry 15, Table 1). The content of *exo*-olefin terminal groups is 19.5 %.



**Fig. S5** Olefinic part of  $^{13}\text{C}$  NMR spectrum of poly( $\beta$ -pinene) obtained with  $\text{H}_2\text{O}/\text{AlCl}_3\text{OBu}_2$  initiating system at 20 °C (entry 15, Table 1).