Electronic Supplementary Information

for

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

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1. Experimental section

Materials

(–)-β-Pinene (Aldrich, 99 %) was distillated from CaH₂ under reduced pressure. CH₂Cl₂ (Sigma–Aldrich, >99.5%), n-hexane (Sigma–Aldrich, >95%) were treated with sulphuric acid, washed with aqueous sodium bicarbonate, dried over CaCl₂ and distilled twice from CaH₂ under an inert atmosphere. Toluene (Sigma–Aldrich, 99.8%) was dried by refluxing with Na/benzophenone, distilled and stored under dry argon atmosphere. α,α,α-Trifluorotoluene (TFT, Aldrich, 99%), ethyl acetate (Aldrich, 99.5 %), dibutyl ether (Sigma–Aldrich, 99.3%) were distilled from CaH₂ under an inert atmosphere prior to use. Diphenyl ether (Aldrich, ≥99 %) was distilled from CaH₂ under reduced pressure. AlCl₃ (Aldrich, 99.999%), ethanol (Sigma–Aldrich, ≥96%) and CDCl₃ (Eurisotop®) 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). ¹H NMR (400 MHz) and ¹³C NMR (100.6 MHz) spectra were recorded in CDCl₃ at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the solvent peak in reference to tetramethylsilane standard (¹H NMR). DSC measurements were performed on a NETZSCH STA 449C instrument calibrated with indium. Samples of poly(β-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 (Tₙ). Thermogravimetric analysis (TGA) was performed on a TGA51 TA Instruments apparatus between 20 and 550 °C under nitrogen at heating rate 10 °C min⁻¹.
Procedures

(a) Synthesis of AlCl₃ complexes. The complexes of AlCl₃ with different electron donors (Bu₂O, EtOAc and Ph₂O) were prepared under argon atmosphere in CH₂Cl₂ solution at room temperature. As a typical example, the synthesis of AlCl₃OPh₂ complex is given below: Ph₂O (3.6 mL, 2.25×10⁻² mol) was added dropwise to the slurry of AlCl₃ (3 g, 2.25×10⁻² mol) in 18.7 mL of CH₂Cl₂ during 5-10 min. The reaction was allowed to stir for 30–60 min up to complete dissolving of AlCl₃ to give a complex (AlCl₃OPh₂) solution in CH₂Cl₂ (1 M). The concentration of complex was determined by back titration of Al with EDTA by ZnSO₄ with diphenylthiocarbazone 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 AlCl₃OPh₂ in CH₂Cl₂ (0.07 mL, 1 M) to a mixture of total volume 26.8 mL consisting of β-pinene (1.76 mL, 1.49×10⁻² M), CH₂Cl₂ (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$_2$O, EtOAc, Bu$_2$O) on the cationic polymerization of $\beta$-pinene

Table S1. Cationic polymerization of $\beta$-pinene coinitiated by AlCl$_3$ED (ED=Ph$_2$O, Bu$_2$O, EtOAc)$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Coinitiator</th>
<th>pK$_a$</th>
<th>Time (min)</th>
<th>Conv (%)</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>$T_g$</th>
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<tr>
<td>1</td>
<td>–60</td>
<td>AlCl$_3$OPh$_2$</td>
<td>–6.54$^d$</td>
<td>0.5</td>
<td>99</td>
<td>13140</td>
<td>2.04</td>
<td>88.7</td>
</tr>
<tr>
<td>2</td>
<td>–60</td>
<td>AlCl$_3$OBu$_2$</td>
<td>–3.59</td>
<td>90</td>
<td>25</td>
<td>6450</td>
<td>1.65</td>
<td>–</td>
</tr>
<tr>
<td>3$^b$</td>
<td>–60</td>
<td>AlCl$_3$0.8EtOAc</td>
<td>–6.5</td>
<td>0.5</td>
<td>100</td>
<td>18050</td>
<td>1.92</td>
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</tr>
<tr>
<td>4</td>
<td>–20</td>
<td>AlCl$_3$OBu$_2$</td>
<td>–3.59</td>
<td>30</td>
<td>98</td>
<td>2700</td>
<td>2.17</td>
<td>67.4</td>
</tr>
</tbody>
</table>

$^a$ Conditions: [AlC$_3$ED]=13 mM; [M]=0.55 M; Solvent: CH$_2$Cl$_2$/n-hexane 60/40 v/v; reaction time: 0.5 min. $^b$ CH$_2$Cl$_2$/n-hexane 40/60 v/v. $^c$ pK$_a$ values for corresponding electron donors. $^d$ This value is for anisole.
3. Thermal properties of obtained poly(β-pinene)s

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

**Fig. S2** Representative TGA thermogram of poly(β-pinene) synthesized with H$_2$O/AlCl$_3$OPh$_2$ initiating system at 0 °C in CH$_2$Cl$_2$/n-hexane 60/40 v/v mixture: [AlCl$_3$OPh$_2$]=2.5 mM; [M]=0.55 M (run 6 in Table 1).
4. $^1$H and $^{13}$C NMR spectra of poly($\beta$-pinene)s obtained with AlCl$_3$OPh$_2$ and AlCl$_3$OBu$_2$ as coinitiators

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

**Fig. S4** $^1$H NMR spectrum of poly($\beta$-pinene) obtained with H$_2$O/AlCl$_3$OBu$_2$ initiating system at 20 °C (entry 15, Table 1). The content of exo-olefin terminal groups is 19.5 %.
**Fig. S5** Olefinic part of $^{13}$C NMR spectrum of poly($\beta$-pinene) obtained with H$_2$O/AlCl$_3$OBu$_2$ initiating system at 20 °C (entry 15, Table 1).