

## Electronic Supplementary Information (ESI)

### **A Novel Tin-based Imidazolium-modified Montmorillonite Catalyst for the Preparation of Poly(butylene terephthalate)-based Nanocomposites Using *in situ* Entropically-driven Ring-opening Polymerization**

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Note that formulae keep the same numbers as in the main paper.

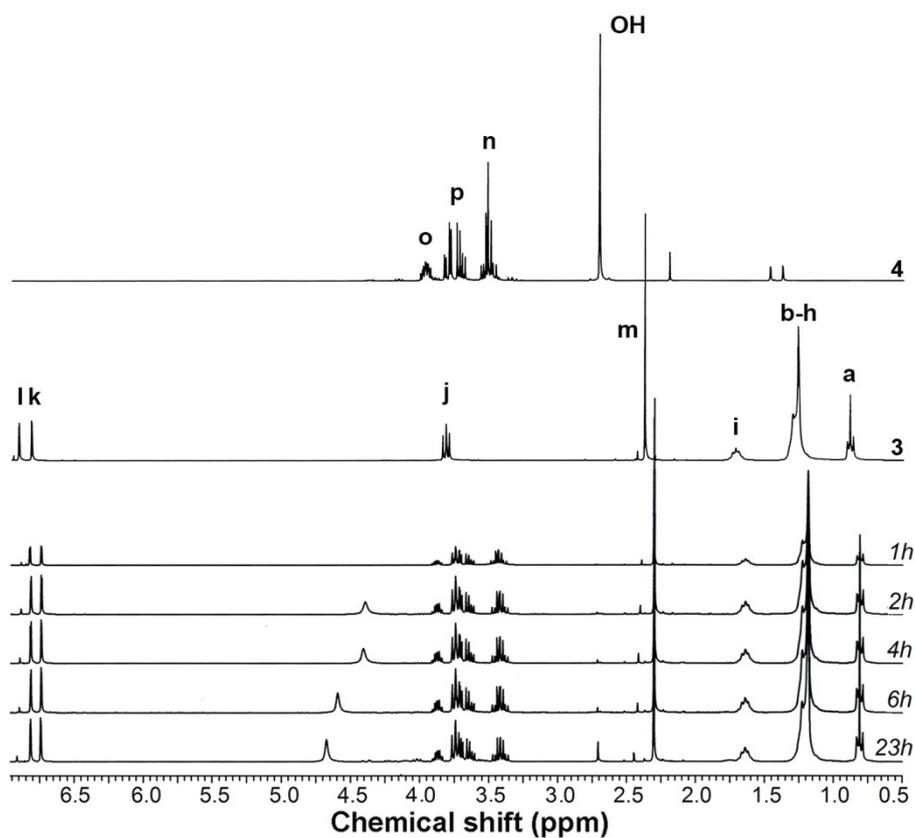
#### **1. Synthesis of imidazolium salts **5** and **6**: <sup>1</sup>H-NMR characterization**

The formation of imidazolium salts **5** and **6** through the reactions described in Scheme 2 was followed by <sup>1</sup>H-NMR spectroscopy. Spectra of the reagents were also recorded for reference purposes.

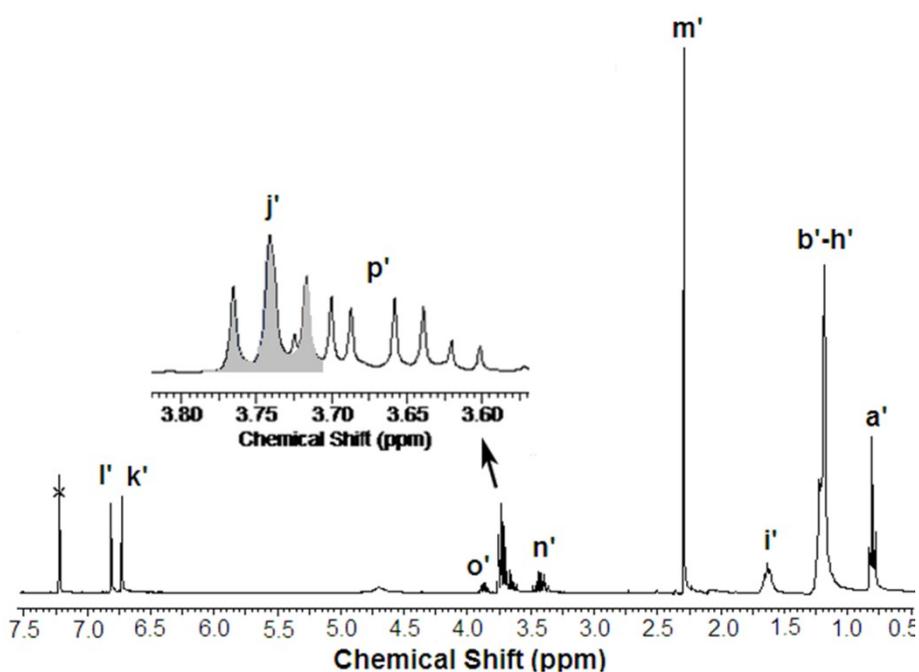
Fig. S1 shows the <sup>1</sup>H-NMR spectra of reagents (**3** and **4**) and reaction mixtures withdrawn at different times throughout the preparation of **5** as described in the full paper.

Already after 1 h of reaction time, the signals of imidazole **3**, corresponding to the **k** and **l** protons on the ring (see Table 1 and Fig. S1), and those of the aliphatic protons **i**, **j**, and **m**, closest to the ring, are shifted towards lower ppm, as expected for the conversion of an imidazole ring to its imidazolium salt. Further evidence for the addition of diol **4** to the imidazole ring of **3** is the appearance, in the spectra of mixtures withdrawn after 2 h reaction time, of a broad peak at about 4.35 ppm, with integration value roughly corresponding to two protons, that can be assigned to the vicinal –OH groups of the diol moiety. The formation of the imidazolium **5** appears to be complete after 4 h reaction time.

On the base of these indications, the reaction was repeated using the same experimental conditions, but with an excess of **3** and a time reaction of 4 h. The excess of **3** was used to avoid, in the subsequent step, the presence of unreacted diol **4**, which might give rise to formation of a catalytic species non-supportable on the **MMT**. The resultant product **5** is a yellow oil and its yield is essentially quantitative. All the peaks observed in its <sup>1</sup>H-NMR spectrum were assigned, as shown in Table 1 and Fig. S2.

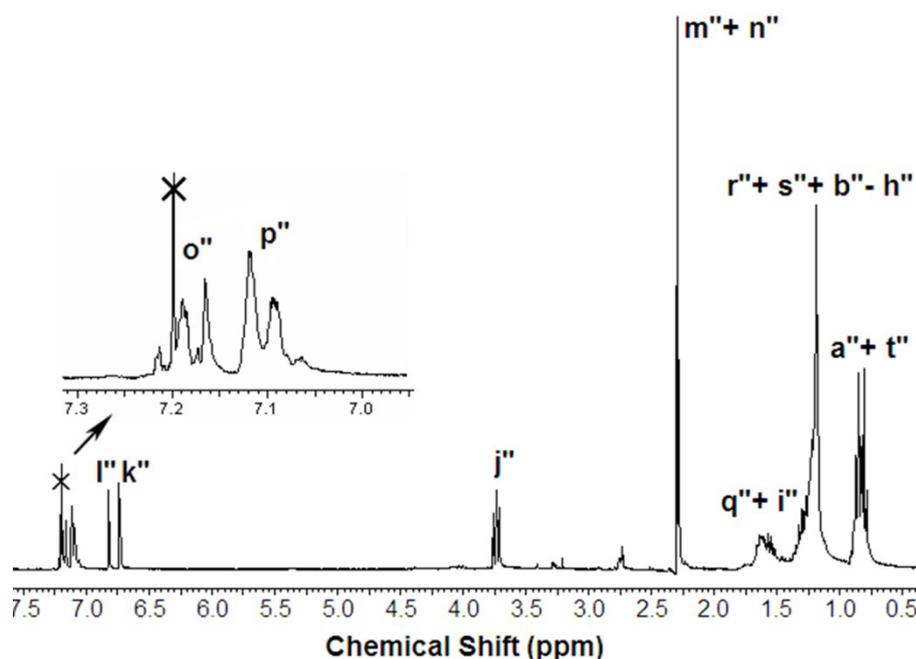


**Fig. S1** <sup>1</sup>H-NMR spectra in CDCl<sub>3</sub> of reagents (**3** and **4**) and reaction mixtures withdrawn at different times during formation of the imidazolium salt **5**.



**Fig. S2** <sup>1</sup>H-NMR spectrum in CDCl<sub>3</sub> of the imidazolium salt **5**.

In the second reaction the diol moiety of the imidazolium salt **5** was reacted with  $\text{Bu}_2\text{Sn}(\text{OMe})_2$  to obtain the 1,3-dioxa-2-stannolane **6**, able in principle of polymerizing macrocyclic oligomers of PBT. All the peaks observed in the  $^1\text{H-NMR}$  spectrum of the obtained product (Fig. S3) were assigned (Table 1) and correspond to the expected structure **6**, indicating that the reaction is complete after 2 h reaction time. In particular, with respect to **5**, the signal of the protons **o'** and **p'** shift above 7 ppm, while that of protons **n'** overlaps to that of protons **m'**, due to the changes in their electronic environment. Product **6** appears as a brownish viscous oil and its yield is essentially quantitative.



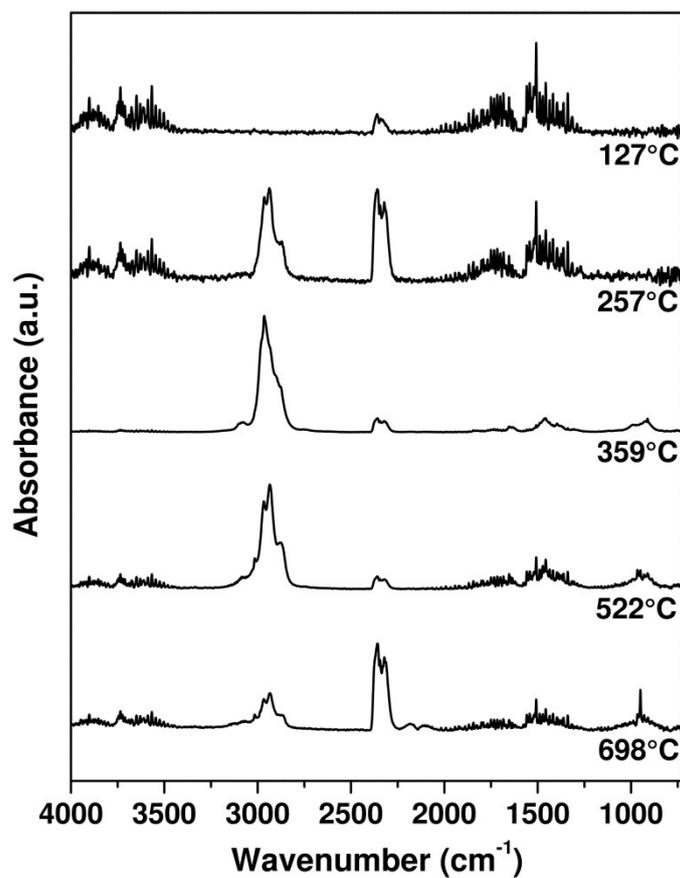
**Fig. S3**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the 1,3-dioxa-2-stannolane **6**.

## 2. TGA-FTIR analysis of 6-MMT

A combined TGA-FTIR analysis was carried out on **6-MMT** to investigate the volatiles being produced during the two-step degradation process. A PerkinElmer Pyris 1 TGA instrument and a PerkinElmer Spectrum 100 spectrophotometer coupled with a TL8000 balanced flow interface (transfer line and cell thermostated at  $280^\circ\text{C}$ ; 10 cm internal cell with KBr optics) were used. The  $\text{N}_2$  purge gas carried the decomposition products through the inner SilcoSteel transfer line to the gas cell for infrared detection.

Selected infrared spectra recorded at increasing temperatures during the TGA heating ramp are shown in Fig. S4. The water adsorbed onto clay surface (signals from  $4000$  to  $3480\text{ cm}^{-1}$  and from  $2000$  to  $1250\text{ cm}^{-1}$ ) was released at temperatures up to  $200^\circ\text{C}$ . The evolution of various hydrocarbons, such as methane, butane and 1-butene, was observed in the range  $200$ - $385^\circ\text{C}$  (signals

from 3100 and 2800  $\text{cm}^{-1}$  and from 2400 to 2250  $\text{cm}^{-1}$ ). At temperatures higher than 350°C, it was also observed the presence of ammonia (signals from 1100 and 800  $\text{cm}^{-1}$ ) deriving from the decomposition of imidazolium ring. The whole process was practically complete at 700°C.



**Fig. S4** FTIR spectra recorded at increasing temperatures of the volatiles produced during dynamic TGA of **6-MMT** under  $\text{N}_2$ .