

# Supplementary Materials

## Zirconium (IV) acetylacetonate – ring-opening initiator mediating one-step synthesis of biodegradable polyacids

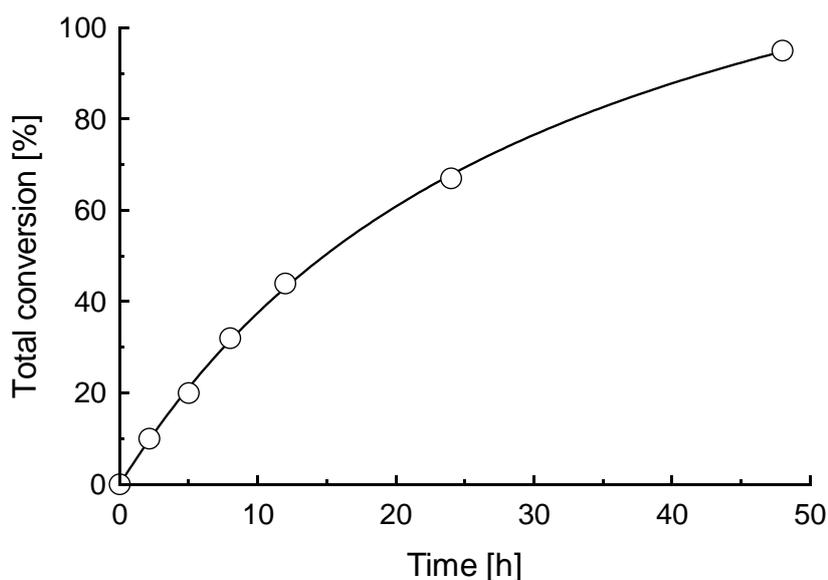
Piotr Dobrzyński, Małgorzata Pastusiak, Joanna Jaworska, Bożena Kaczmarczyk, Michał Kwiecień, Michał Kawalec\*

*Centre of Polymer and Carbon Materials, Polish Academy of Sciences; 34, M. Curie-Skłodowska Str., 41-819 Zabrze, Poland*

\* e-mail: [michal.kawalec@cmpw-pan.edu.pl](mailto:michal.kawalec@cmpw-pan.edu.pl)

### Comonomers conversion during bulk synthesis of P(LA-co-MTC-COOH)

Conversion of the monomers was monitored with  $^1\text{H}$  NMR technique.



*Figure S1.* Time-dependent comonomers conversion mediated with zirconium complex during bulk synthesis of P(LA-co-MTC-COOH) carried out at 120 °C

## P(LA-co-MTC-COOH) Analyses

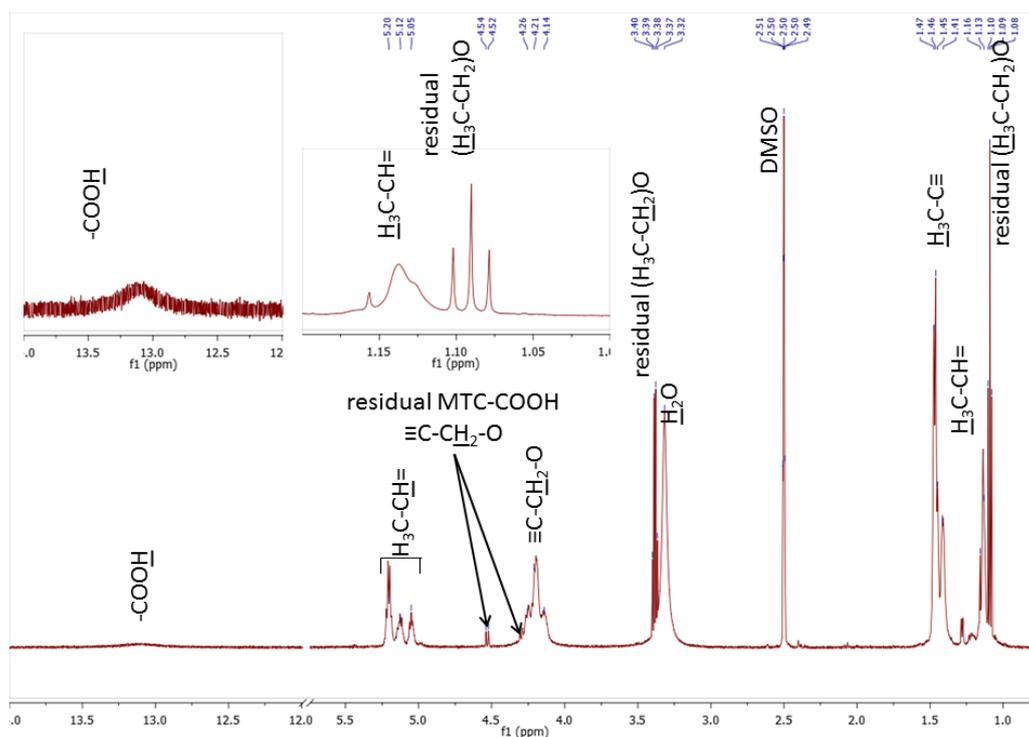


Figure S2.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-d}_6$ ) spectrum of purified P(LA-co-MTC-COOH) obtained in presence of zirconium complex at  $120^\circ\text{C}$

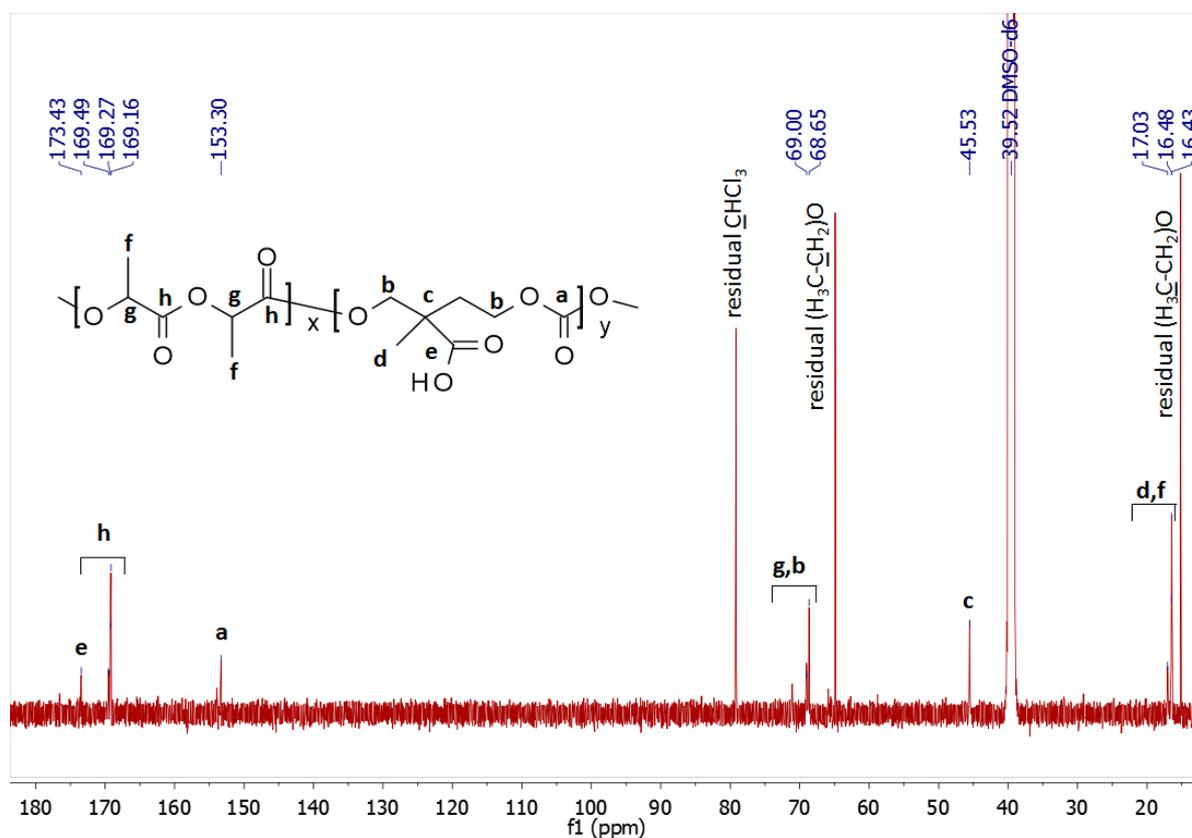


Figure S3.  $^{13}\text{C}$  NMR inverse-gated (150 MHz,  $\text{DMSO-d}_6$ ) spectrum of purified P(LA-co-MTC-COOH) obtained in presence of zirconium complex at  $120^\circ\text{C}$

FTIR analysis of the purified P(LA-co-MTC-COOH) revealed two bands recorded at 3505  $\text{cm}^{-1}$  and 3234  $\text{cm}^{-1}$  corresponding to stretching vibrations of the OH groups (Fig. S4). Generally, the bands attributed to the stretching vibrations of the OH carboxyl groups are observed in the range of 3600-2600  $\text{cm}^{-1}$ . Free OH groups absorb at higher wavenumbers of this region while hydrogen bonds between OH and C=O groups, especially strong in the case of carboxyl groups, cause shift of the bands towards lower wavenumbers of this region. The bands observed herein correspond to vibrations of free and bonded OH groups, respectively. In the region attributed to the stretching vibrations of C=O groups a band with maximum at 1753  $\text{cm}^{-1}$  was detected owing to vibrations of this band in the ester groups from polylactide and in carbonate groups from polycarbonate. Additionally, observed two shoulders at about 1714  $\text{cm}^{-1}$  and 1628  $\text{cm}^{-1}$  were originated from vibrations of free and bonded C=O groups in carboxylic groups. MTC-COOH monomer was used as a reference sample. Its spectrum revealed a broad band in the range of 3300-2700  $\text{cm}^{-1}$  indicating the presence of bonded hydroxyl groups. These bands strongly overlapped the bands arising from stretching vibrations of aliphatic groups (2900-2800  $\text{cm}^{-1}$ ). In the region attributed to the stretching vibrations of C=O groups, *i.e.* 1800-1600  $\text{cm}^{-1}$ , two bands were detected: the first, relatively sharp, at 1743  $\text{cm}^{-1}$  and the second, broad band, at 1688  $\text{cm}^{-1}$ , corresponding to these vibrations in carbonate and carboxylic groups, respectively. Additionally, in the case of the band at 1688  $\text{cm}^{-1}$  the shoulders at about 1665 and 1622  $\text{cm}^{-1}$  were seen, proving the presence of inter- and intramolecular hydrogen bonding, respectively.

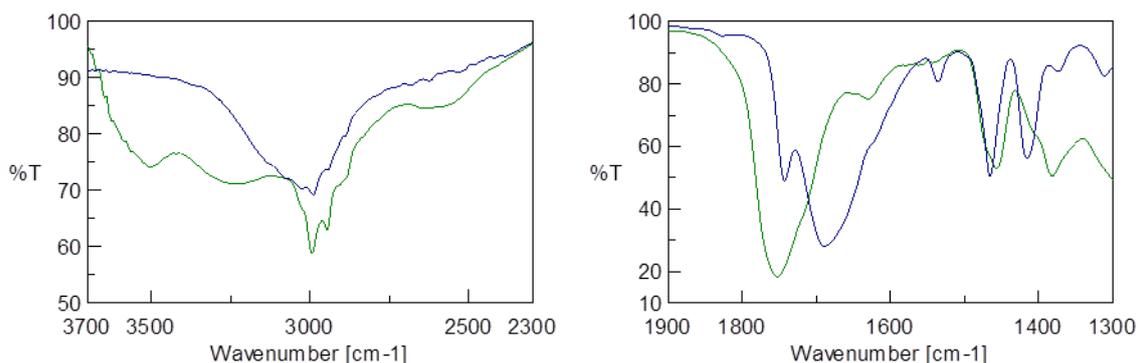


Figure S4. FTIR spectra of MTC-COOH (blue) and purified P(LA-co-MTC-COOH) (green) in the region of 3700-2300  $\text{cm}^{-1}$  and 1900-1300  $\text{cm}^{-1}$

ESI-MS Analysis. Sample of MTC-COOH/ LA reacting mixture after 2.25h of polymerization at 120 °C and conversion *ca.* 10 % (conversion determined by <sup>1</sup>H NMR) was analyzed with ESI-MS technique.

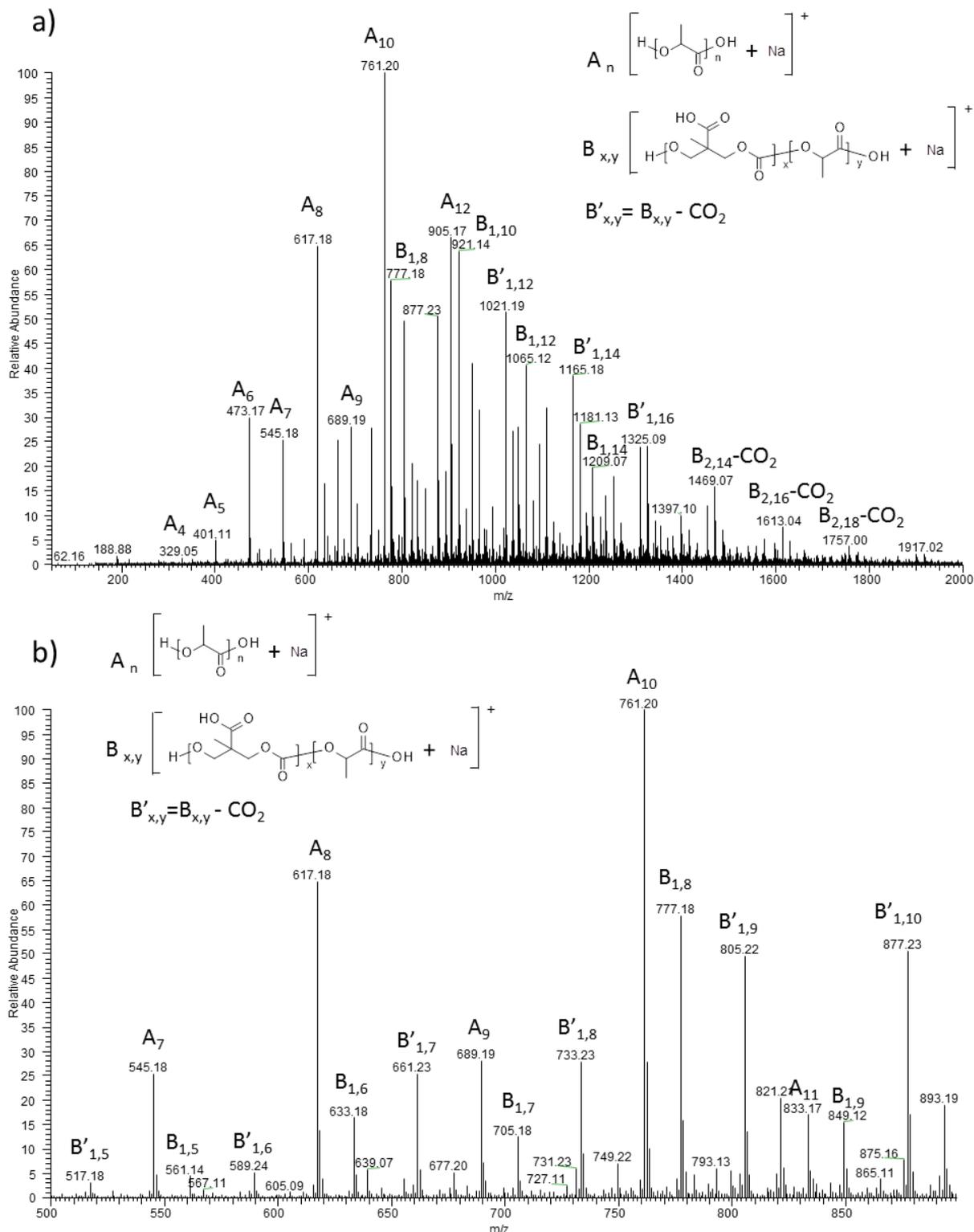


Figure S5. ESI-MS (positive ion mode) spectrum of reacting mixture Table 1, Entry 1 (total conversion 10%)

More intense series (A) of LA homooligomer adducts with sodium cation dominates in lower *m/z* region although expanded region (Figure S5b) depicts existence of LA-co-MTC-COOH

oligomers even in the lower  $m/z$  range. One can also notice that the LA oligomers differ of 72 Th (lactil unit) which correlates with previously reported transesterification phenomenon observed during ROP of cyclic esters mediated with Zr complex. Importantly, ions ascribed to copolymeric structures were also identified (B series) during early course of the polymerization. Despite the B series ions in the spectrum there were noticed also ions with  $m/z$  44 Th lower (B' series) which correlate to loss of carbon dioxide. The most probably macromolecules were formed in consequence of mixed carboxylic – carbonic anhydride pyrolysis. Therefore the series should correspond to macromolecules starting with opened carbonate unit in contrast to B series containing molecules starting with opened lactide. Apparently, the explanation clarifies also fact that no benzoic acid derivative was found during ESI-MS analysis of PTMC obtained in presence of zirconium complex and BA (compare Figure 2 and Figure S6).

## TMC homopolymerization

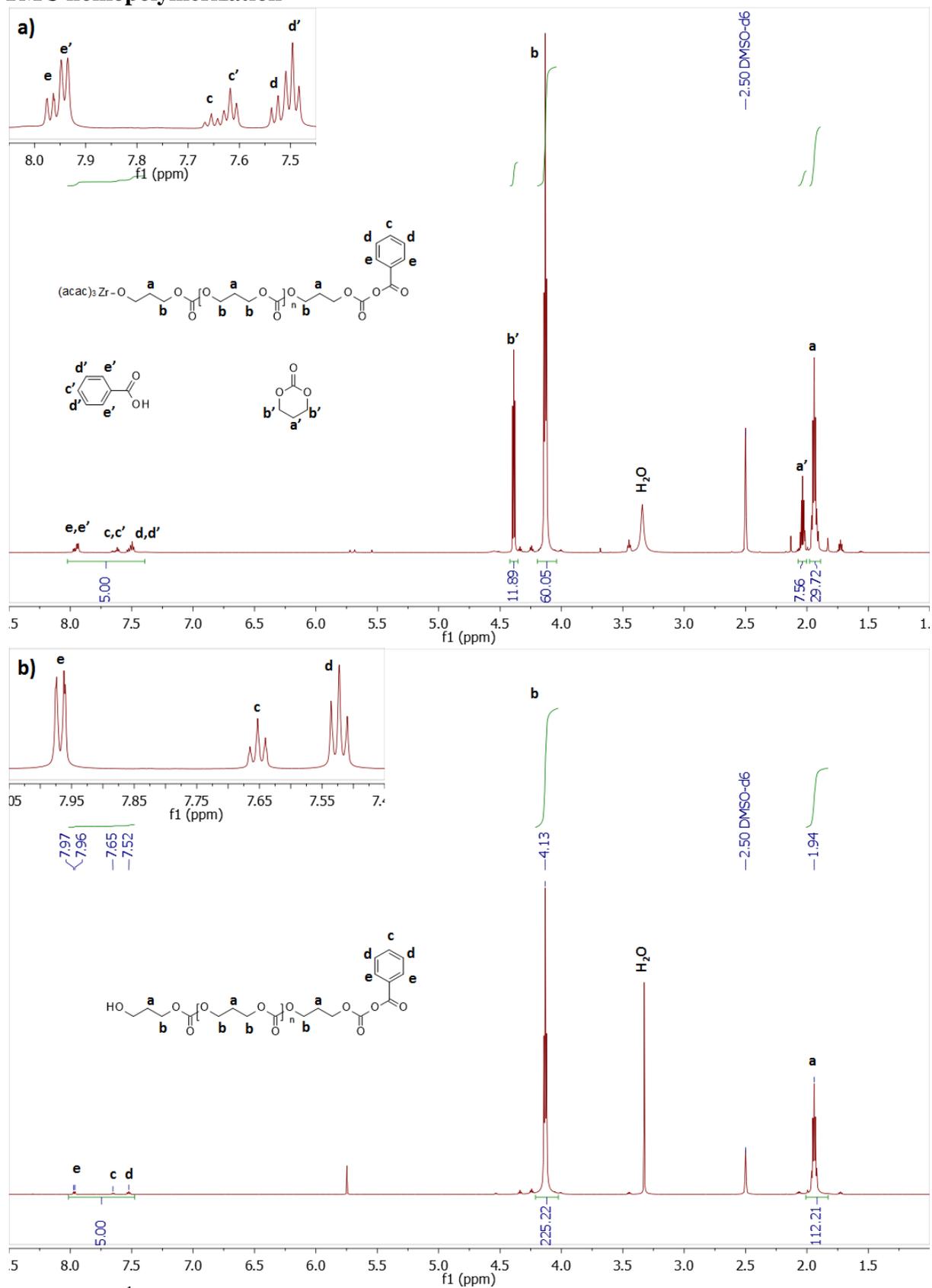


Figure S6.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-d}_6$ ) spectra of a)  $[\text{Zr}(\text{acac})_4]/\text{BA}/\text{TMC}$  (1/4/50) reaction mixture after 130 minutes of polymerization at 120 °C and b) purified PTMC obtained with  $[\text{Zr}(\text{acac})_4]/\text{BA}$  catalytic system

