

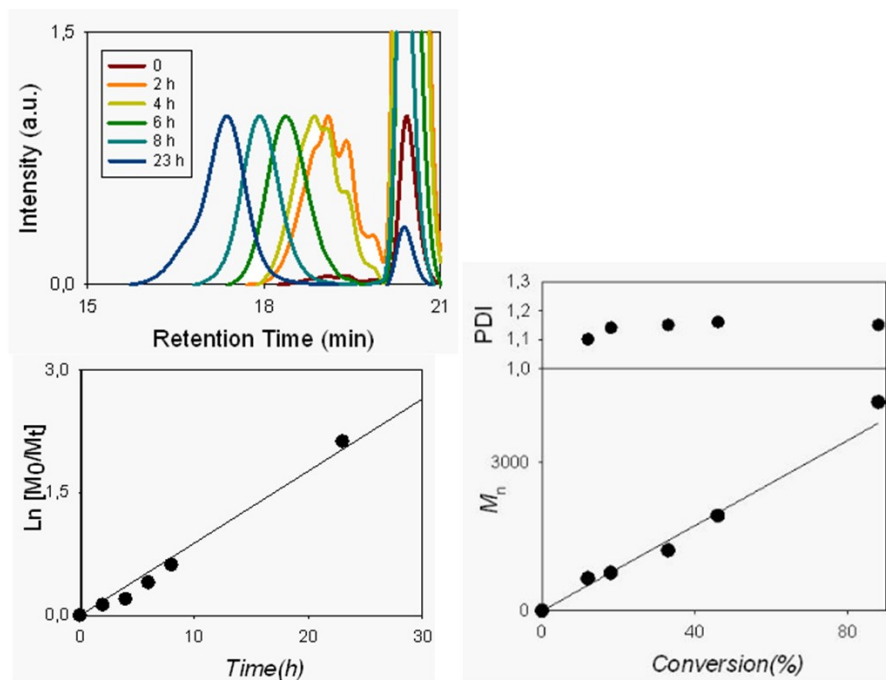
*Supporting Information for:*

# Biocompatible Graft Copolymers from Bacterial Poly( $\gamma$ -Glutamic Acid) and Poly(Lactic Acid)

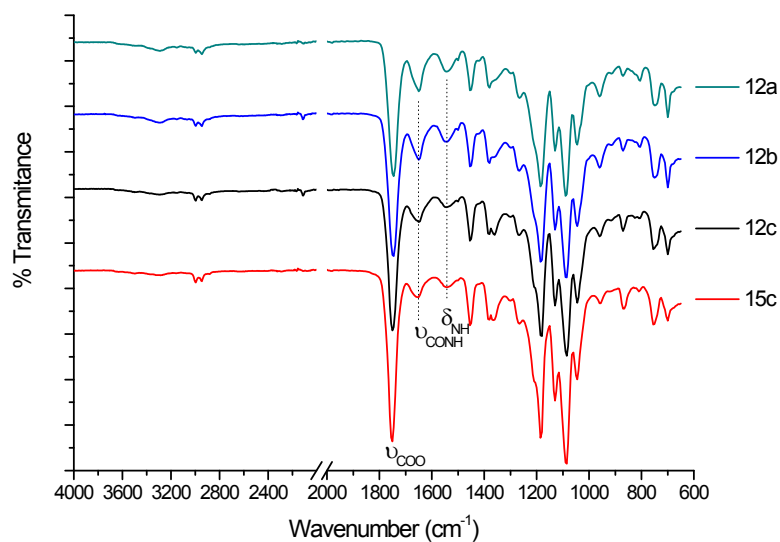
*Cristiana L. Zaccaria, Valeria Cedrati, Andrea Nitti, Enrica Chiesa, Antxon Martinez de Ilarduya, Monserrat Garcia-Alvarez, Massimiliano Meli, Giorgio Colombo, Dario Pasini*

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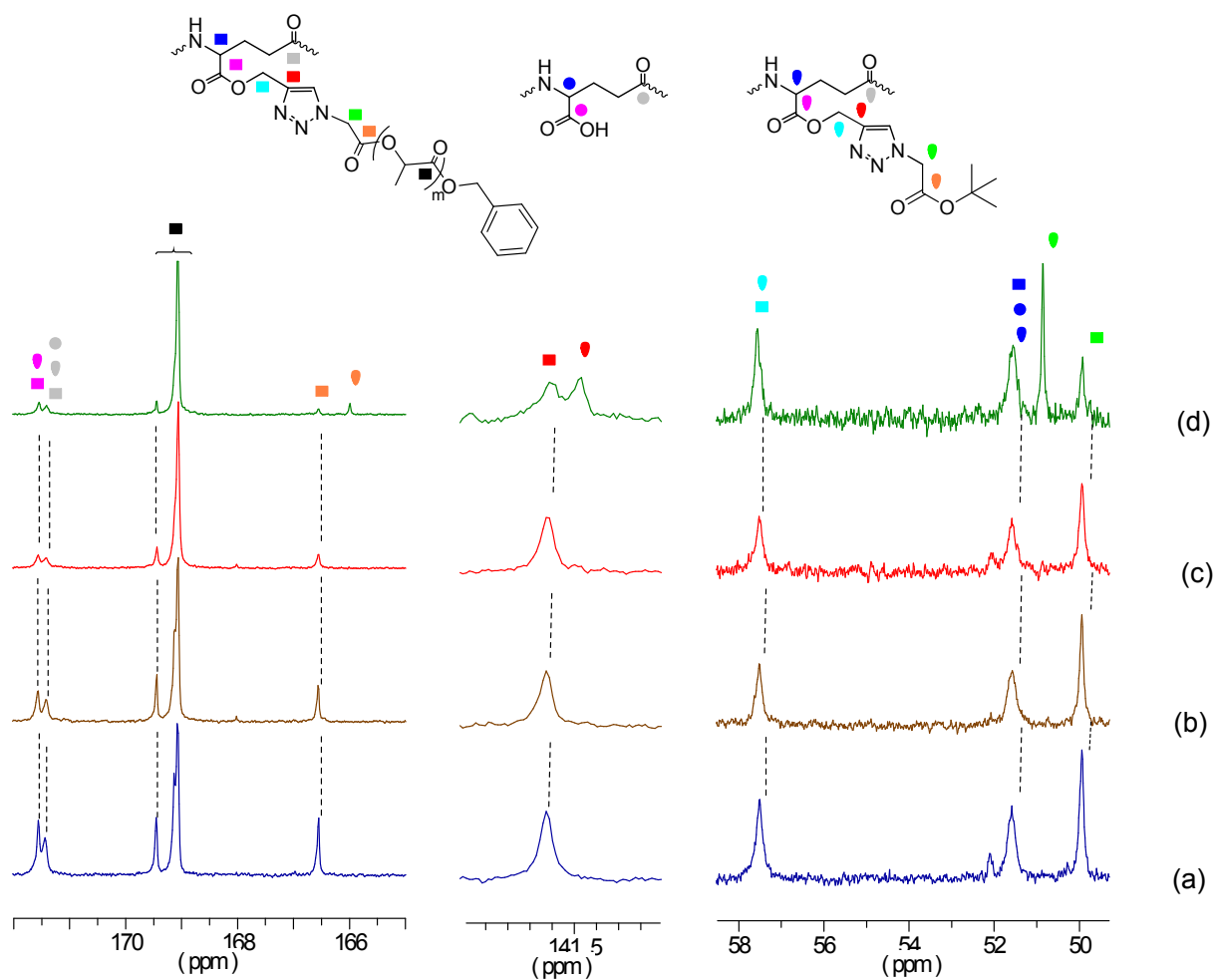
<i>1. Additional graphs and Figures</i>	<i>S2</i>
<i>2. Characterization of New Compounds</i>	<i>S9</i>



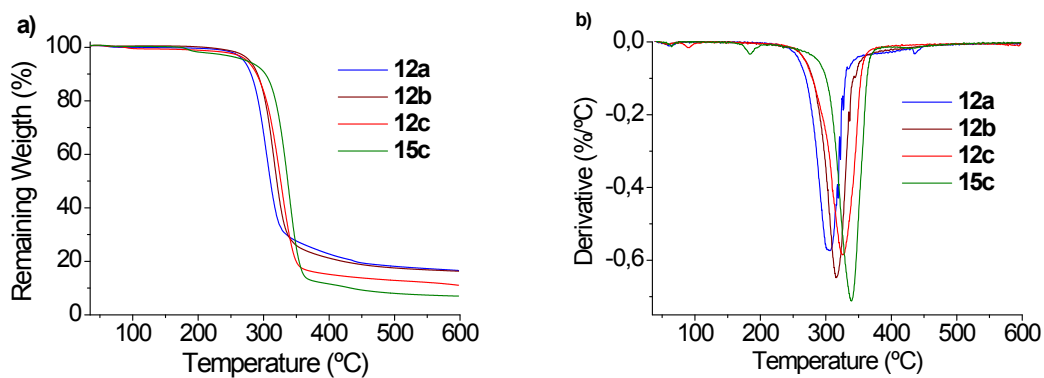
**Figure S1.** Monitoring the formation of polymer **4c**. Top: normalized GPC traces. The peak at retention time ca. 20 min corresponds to unreacted lactide monomer. Bottom: linear relationship between conversion and number average  $M_n$ , first order nature of the kinetics, and the narrow resulting dispersities.



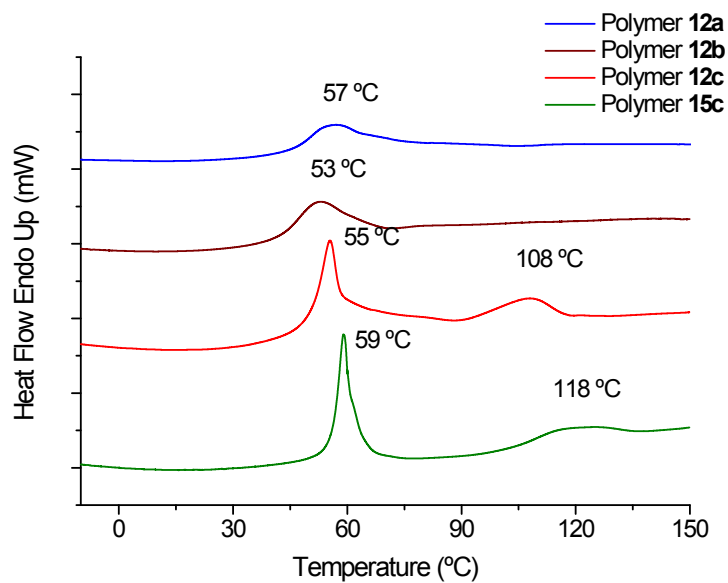
**Figure S2.** IR spectra of copolymers **12a-c**; **15c**.



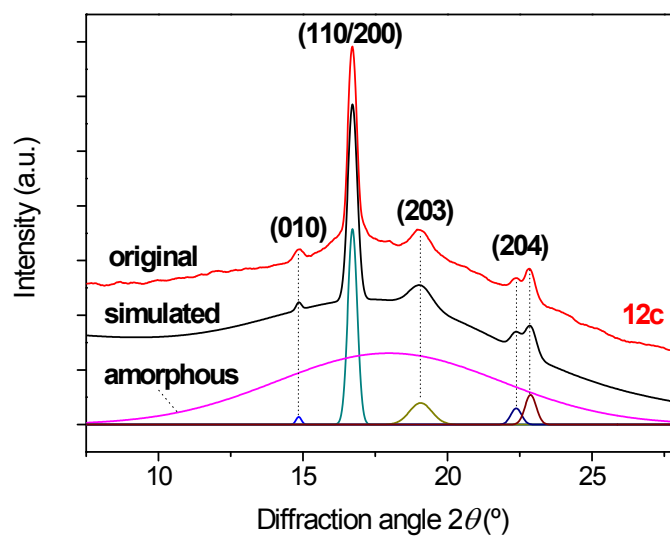
**Figure S3.** Expanded regions of the  $^{13}\text{C}$ -NMR spectra of (a) polymer **12a**, (b) polymer **12b**, (c) polymer **12c** with increasing length of PLA side chains and (d) polymer **15c**.



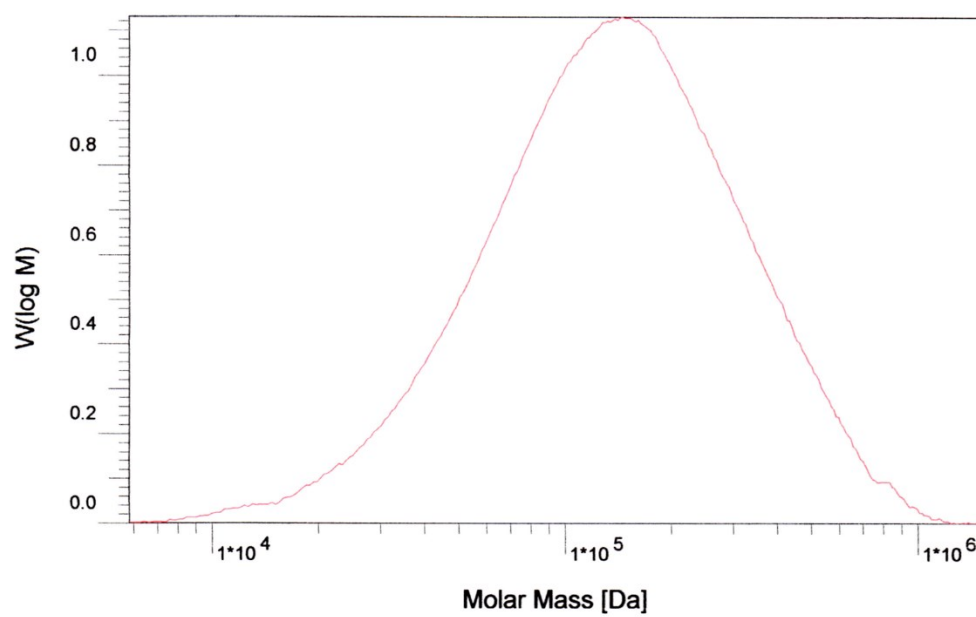
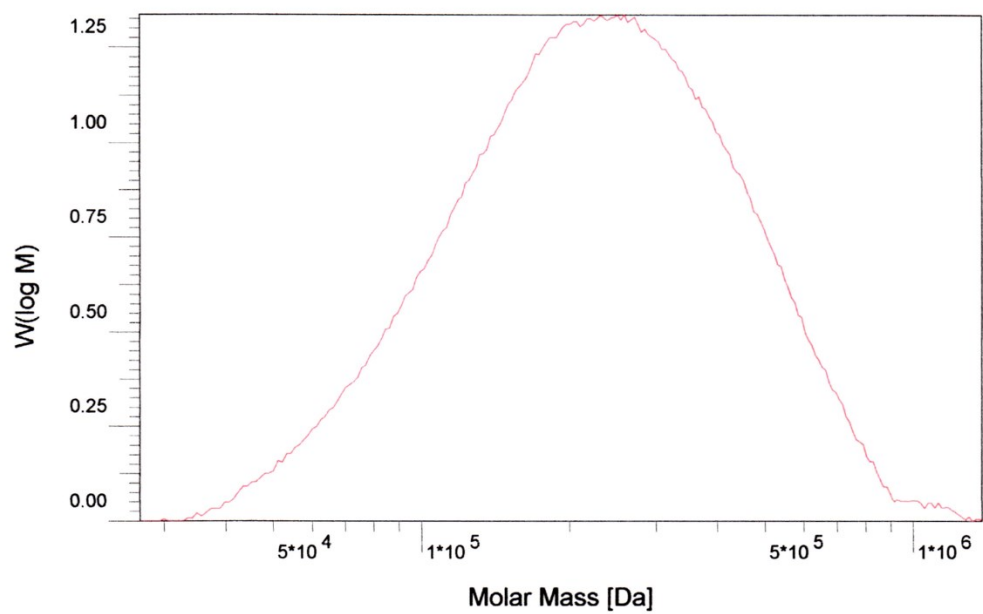
**Figure S4.** TGA traces (a) and derivative curves (b) of PLA grafted  $\gamma$ -PGA samples **12a-c** and **15c**.



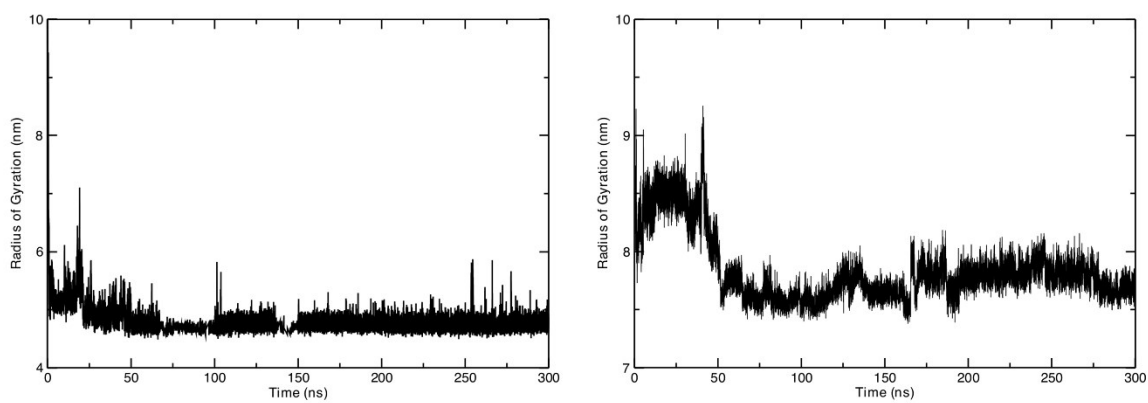
**Figure S5.** First scan DSC traces of PLA grafted  $\gamma$ -PGA samples **12a-c** and **15c** recorded at 10 °C/min.



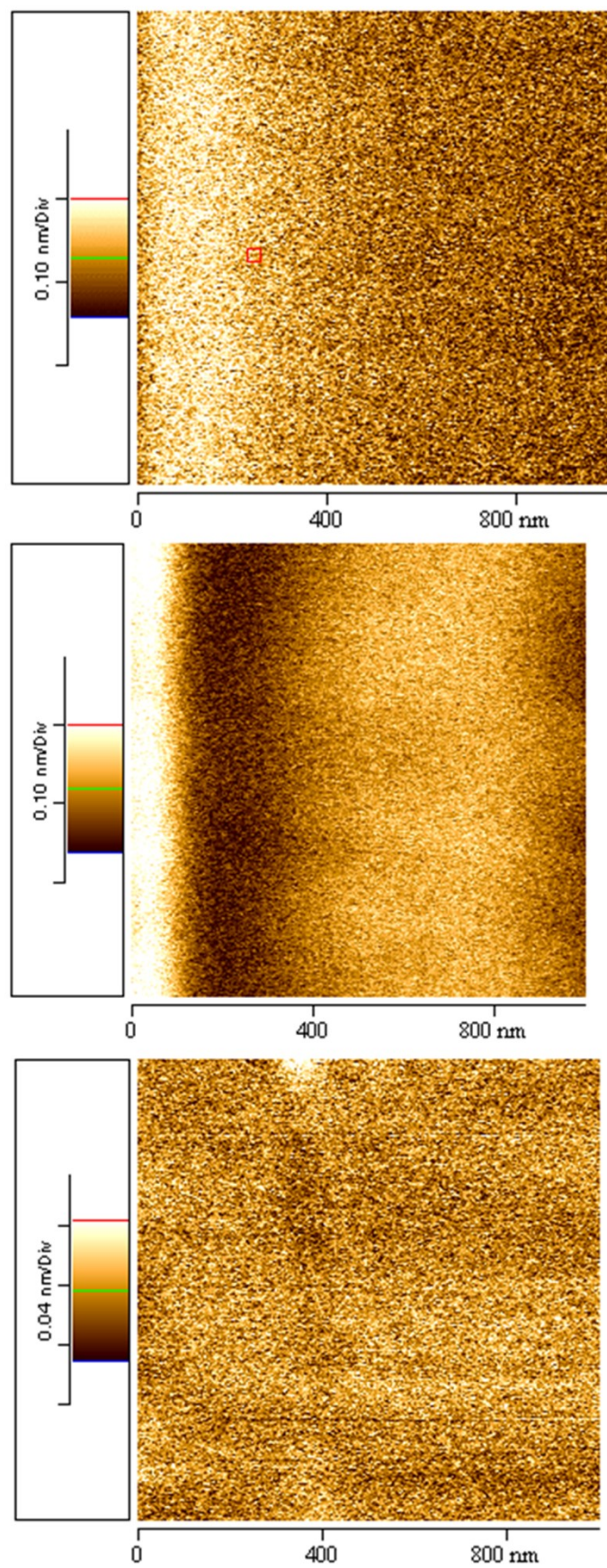
**Figure S6.** Peaks deconvolution of WAXS diffractogram using PeakFit 4.6 software.



**Figure S7.** GPC traces of polymer **12b** (top) and **15c** (bottom)



**Figure S8.** The time evolution of the radius of gyration from MD simulations for the PLA-PGA copolymers. Left:  $n=1$ ,  $m=5$ ; Right:  $n=5$ ,  $m=5$  (see Figure 5 in the main text for reference)



**Figure S9.** AFM images of copolymers (from top to bottom): **12b**; **12c**; **12a**.

**Table S1.** Thermal parameters of Polymers **12a-c** and **15c**.

Sample	TGA <sup>a</sup>			DSC		
	$^{\circ}T_d$ (°C)	$^{\max}T_d$ (°C)	W (%)	$T$ (°C) and $\Delta H$ (J·g <sup>-1</sup> )		
				$T_g^b / \Delta H^b$	$T_m^b / \Delta H^b$	$T_g^c$
Polymer <b>12a</b>	270	305	16	56 / 13.1	-	45
Polymer <b>12b</b>	280	316	16	51 / 11.0	-	41
Polymer <b>12c</b>	275	325	11	55 / 9.7	108 / 4.7	46
Polymer <b>15c</b>	270	336	7	59 / 16.4	118 / 8.1	47

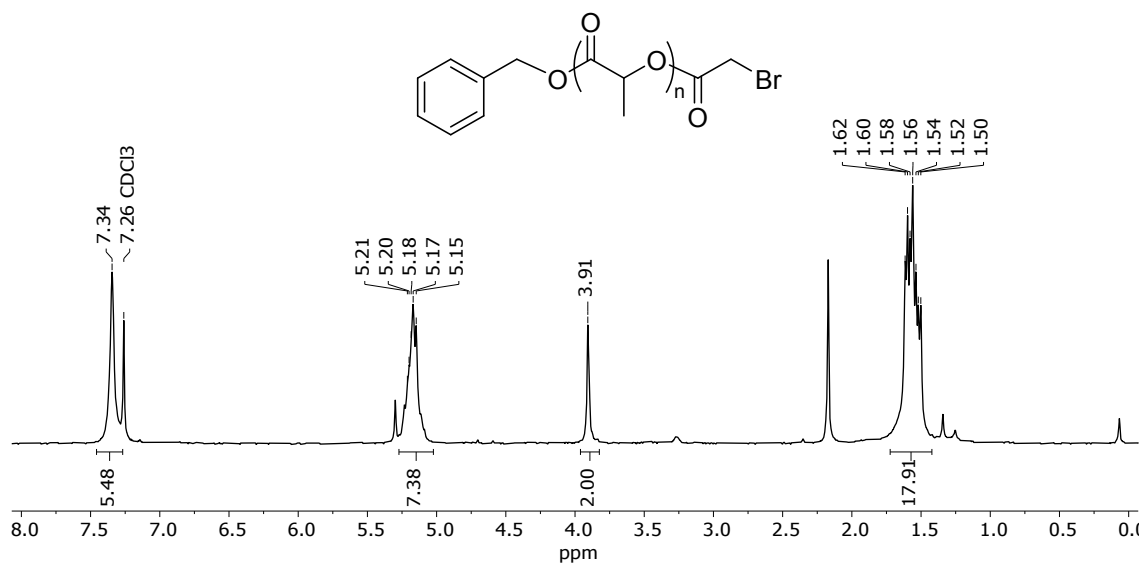
<sup>a</sup> Thermal stability of under nitrogen atmosphere.  $^{\circ}T_d$  the onset decomposition temperature for 5 % weight loss.  $^{\max}T_d$  the maximum rate decomposition temperature and W the remaining weight at 600 °C. <sup>b</sup> First heating scan recorded at 10 °C·min<sup>-1</sup>. <sup>c</sup> 2<sup>nd</sup> heating scan recorded at 20 °C·min<sup>-1</sup>.



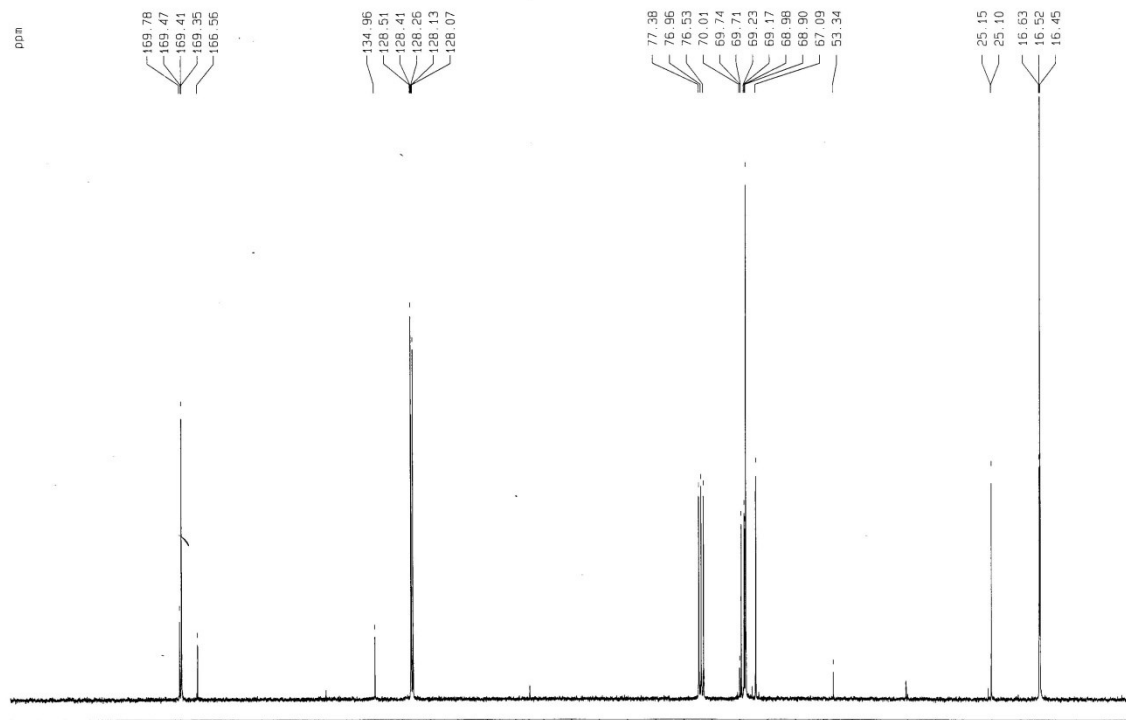
# Copies of NMR Spectra for Polymers.

## Polymer 6a.

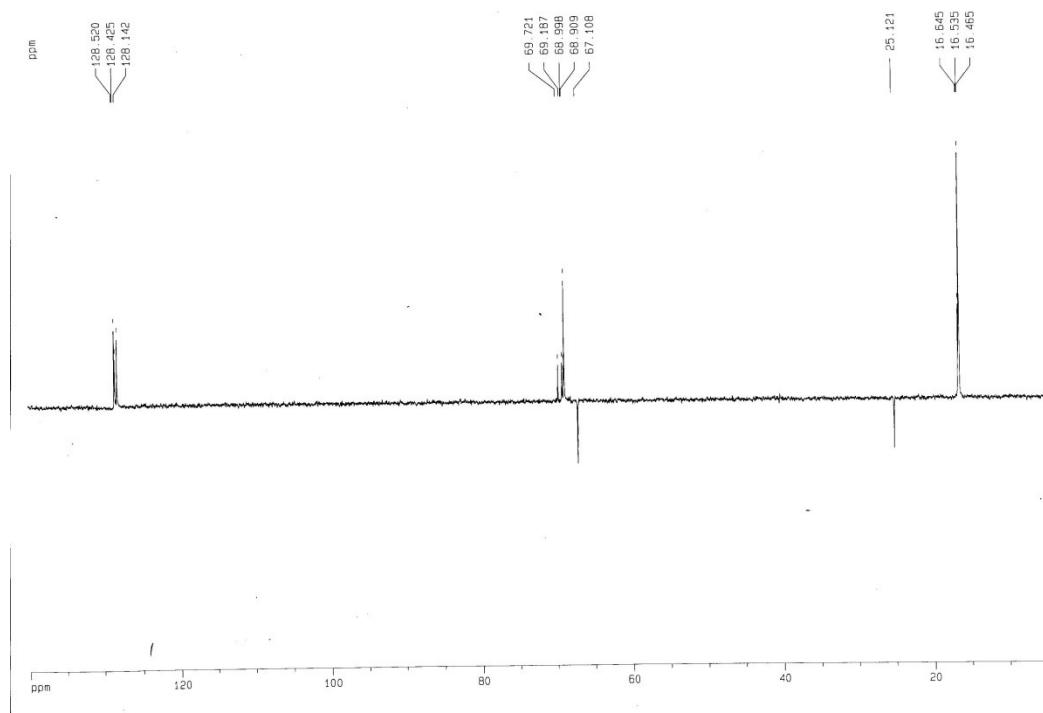
<sup>1</sup>HNMR.14.fid  
CZ6 dopo lavaggio CDCl<sub>3</sub>



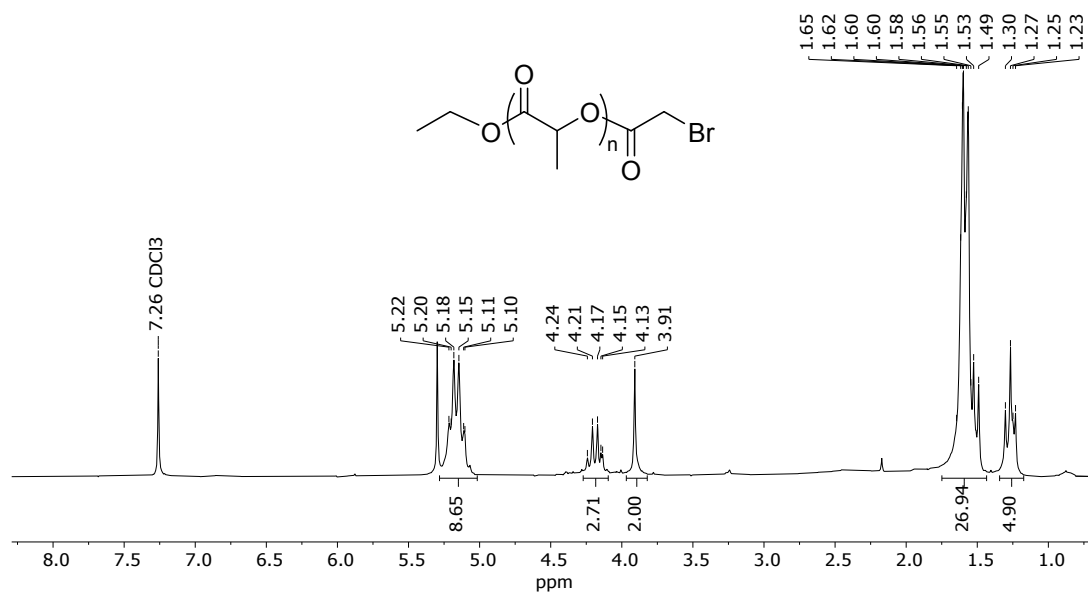
## <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



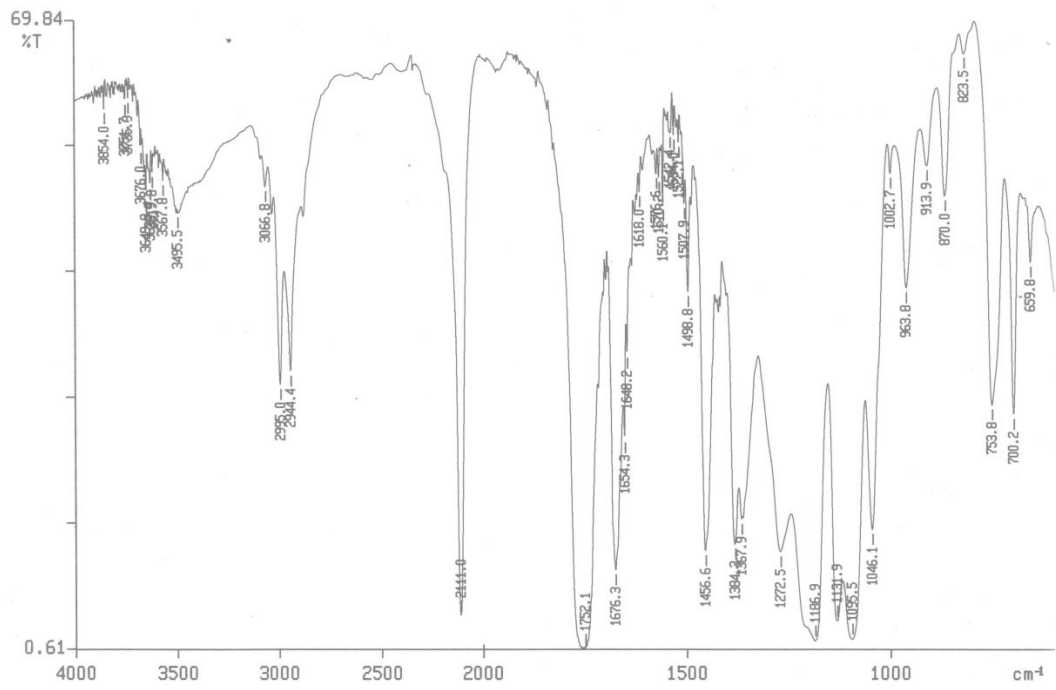
$^{13}\text{C}$  NMR DEPT ( $\text{CDCl}_3$ , 75 MHz)



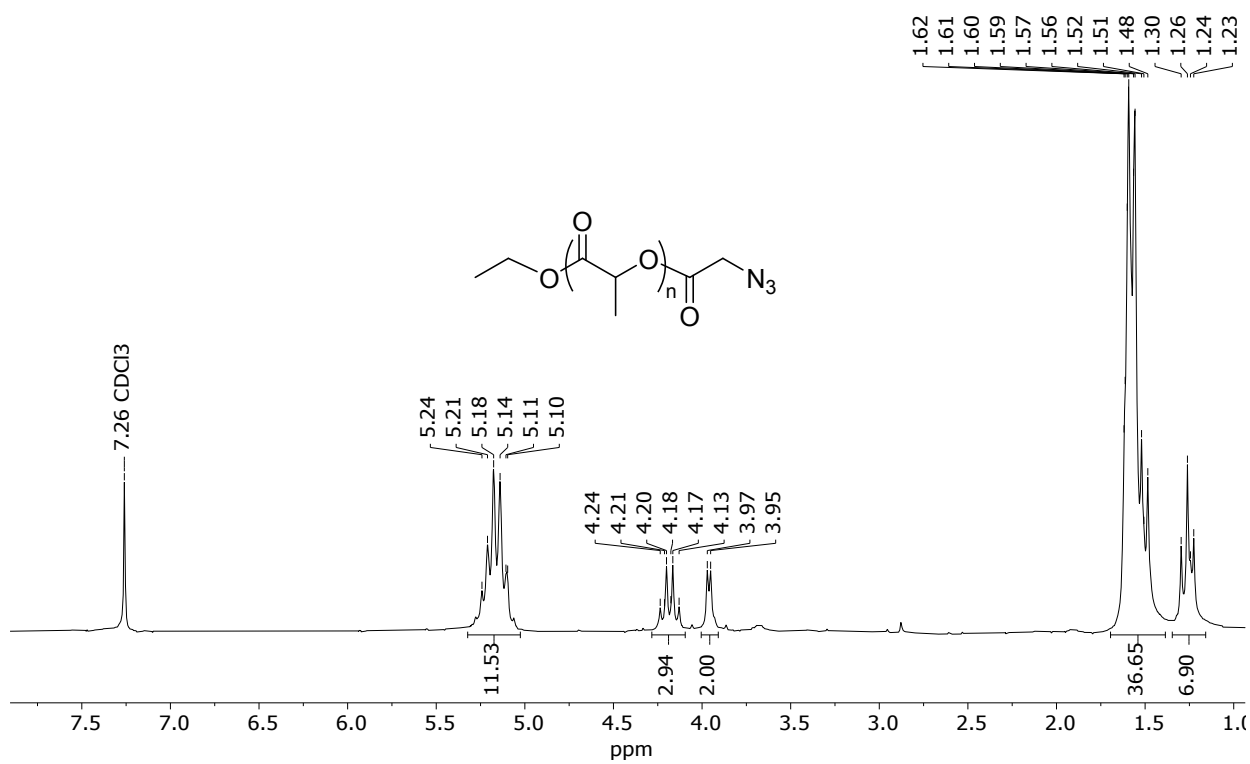
# Polymer 7a



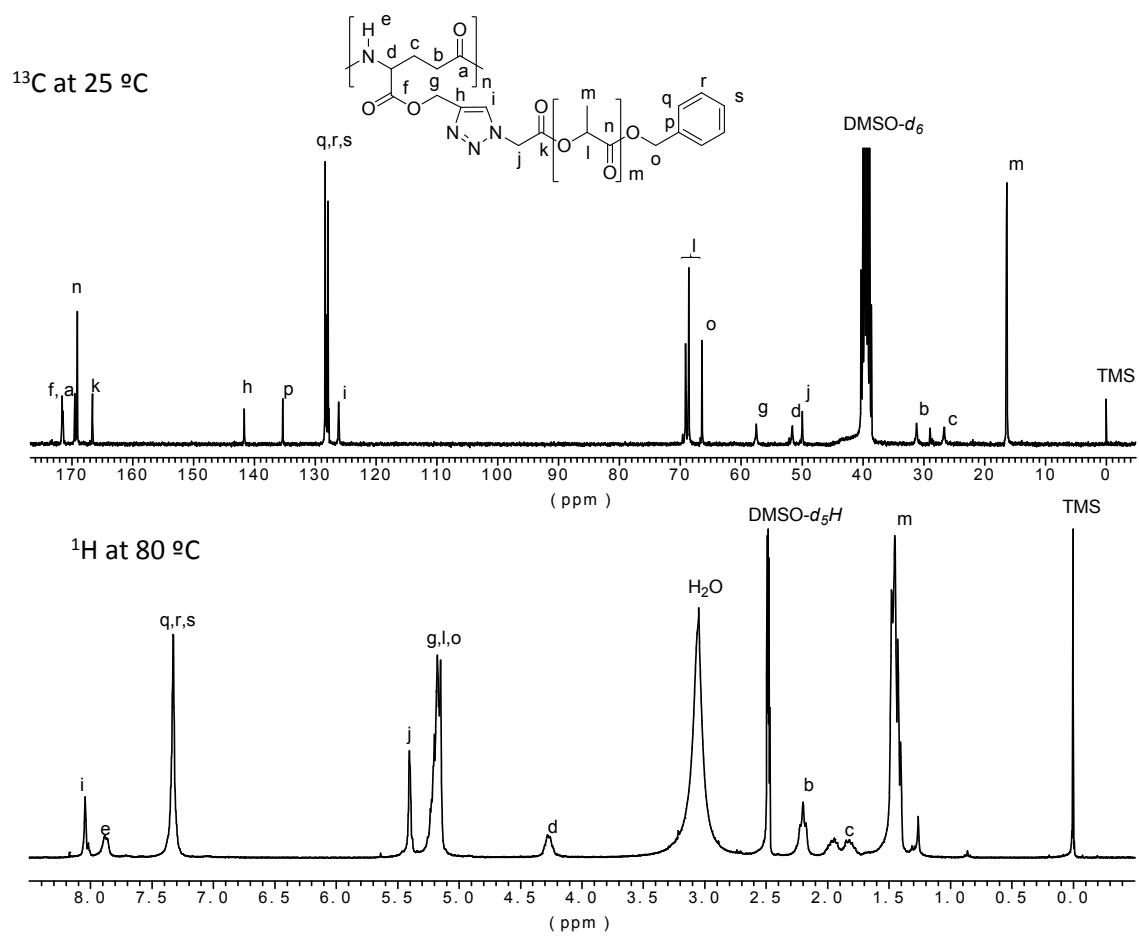




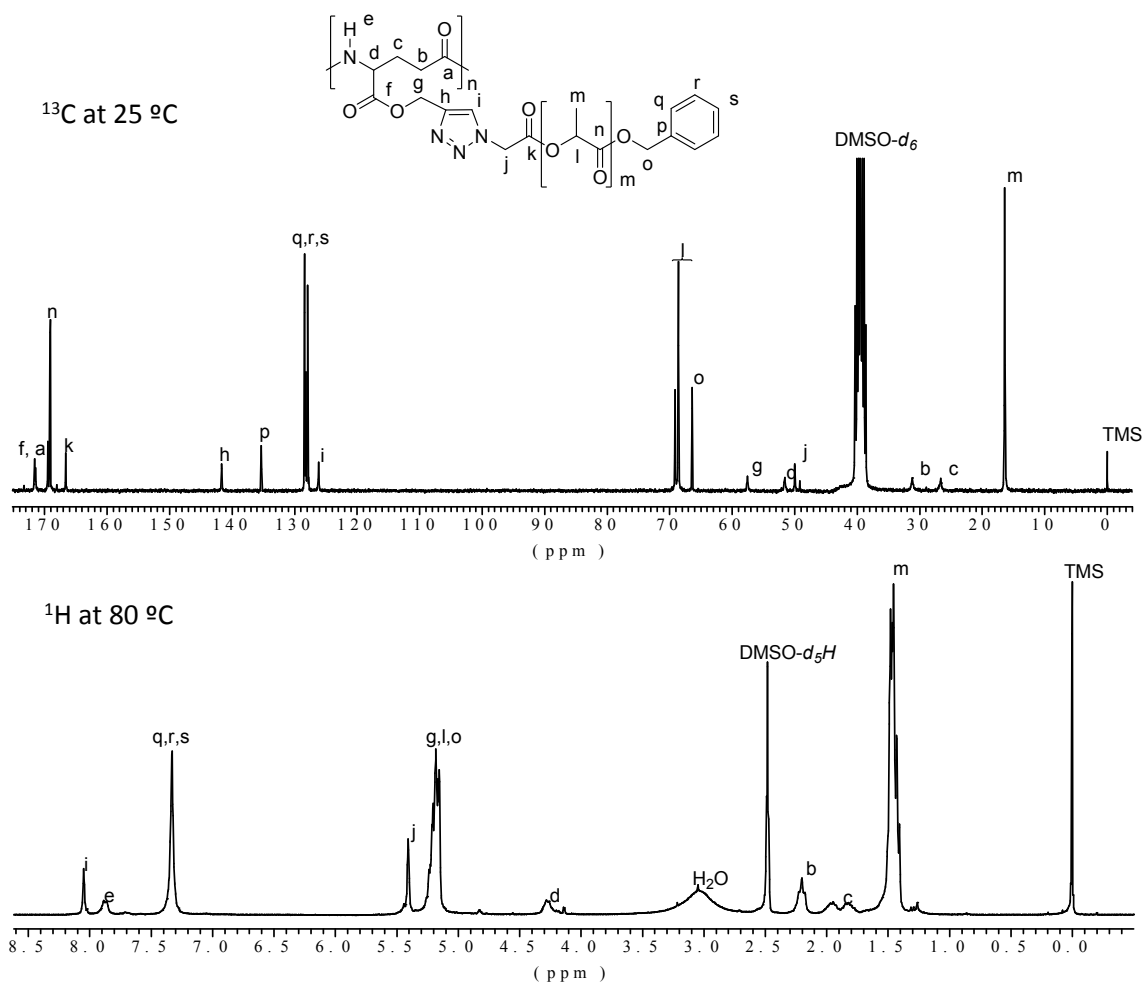
# Polymer 9a



$^1\text{H}$  and  $^{13}\text{C}$  NMR of **12a** sample in  $\text{DMSO-}d_6$

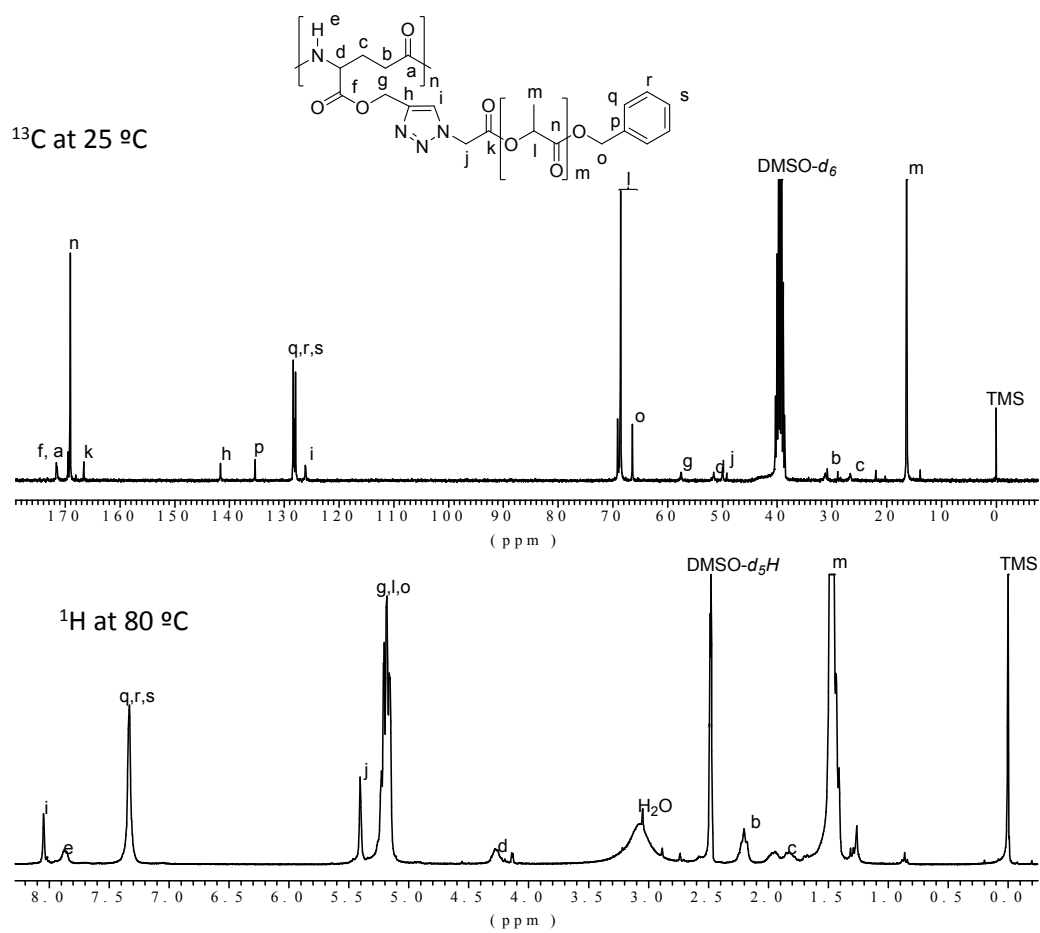


$^1\text{H}$  and  $^{13}\text{C}$  NMR of **12b** sample in  $\text{DMSO-}d_6$

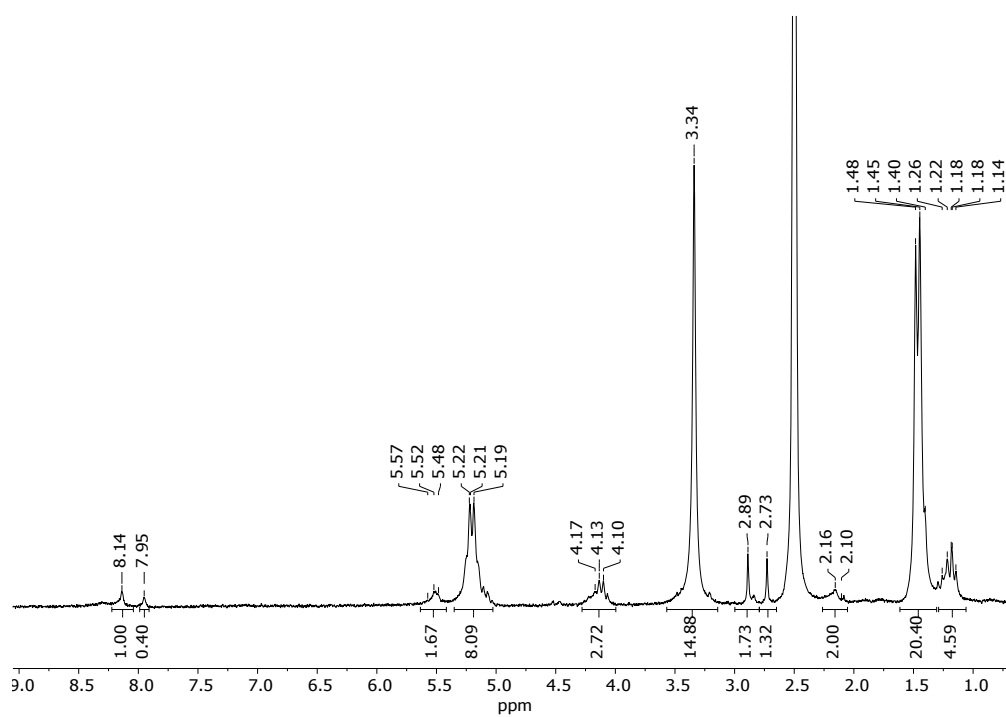




$^1\text{H}$  and  $^{13}\text{C}$  NMR of **12c** sample in  $\text{DMSO-}d_6$



$^1\text{H}$  and  $^{13}\text{C}$  NMR of **13a** sample in  $\text{DMSO-}d_6$



$^1\text{H}$  and  $^{13}\text{C}$  NMR of **15c** sample in  $\text{DMSO-}d_6$

