Poly(alditol sebacate)-PLA copolymers: enhanced degradability and tunable surface properties

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1. NMR analyses

2. Thermal analyses

3. EDX Analyses

1. NMR Analyses

1.1 Spectra of protected alditols

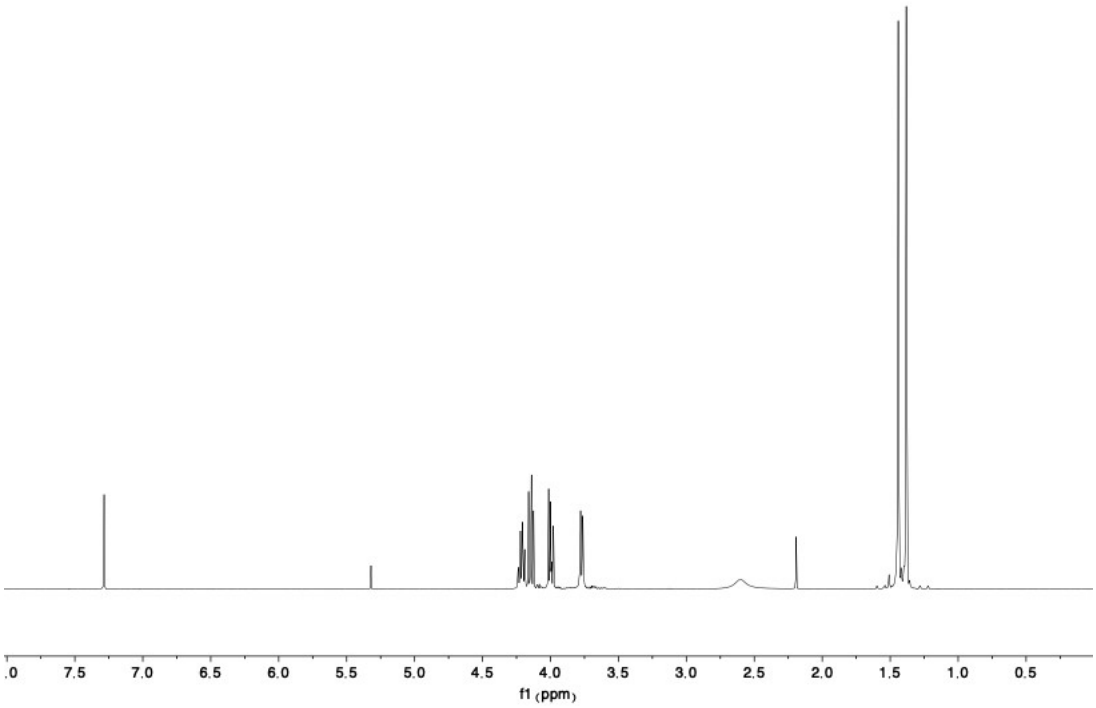

Figure S 1: ^{1}H NMR spectrum of i-PrMan.

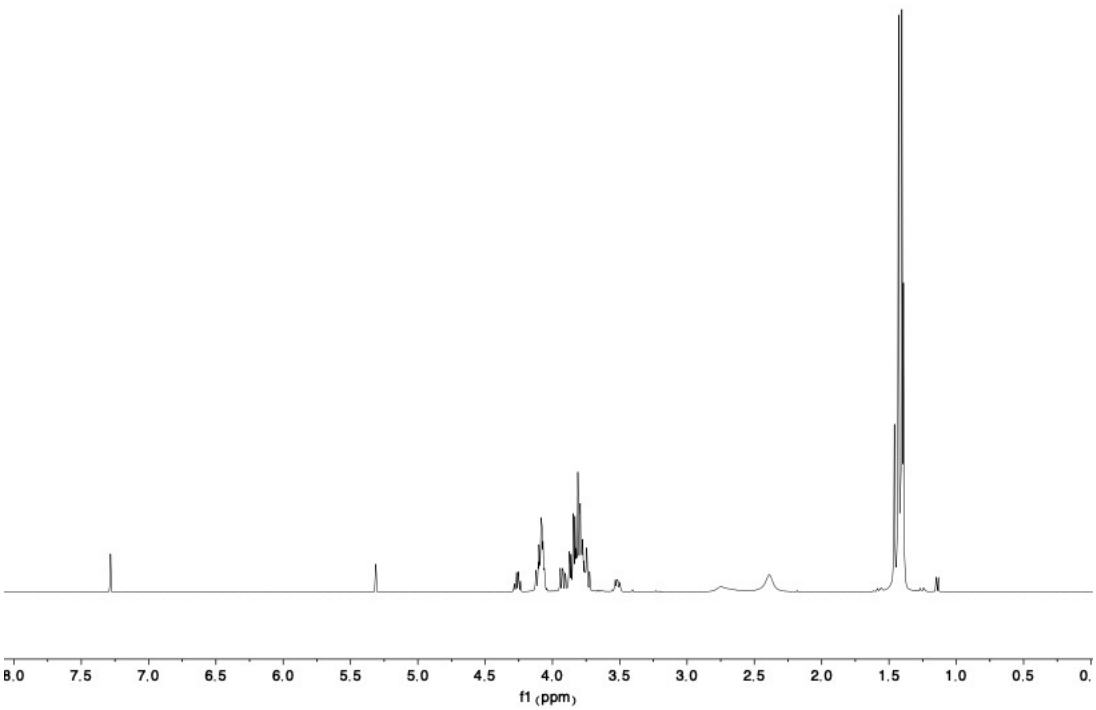

Figure S 2: ^{1}H NMR spectrum of i-PrDul as mixture of i-PrDul1 and i-PrDul2.

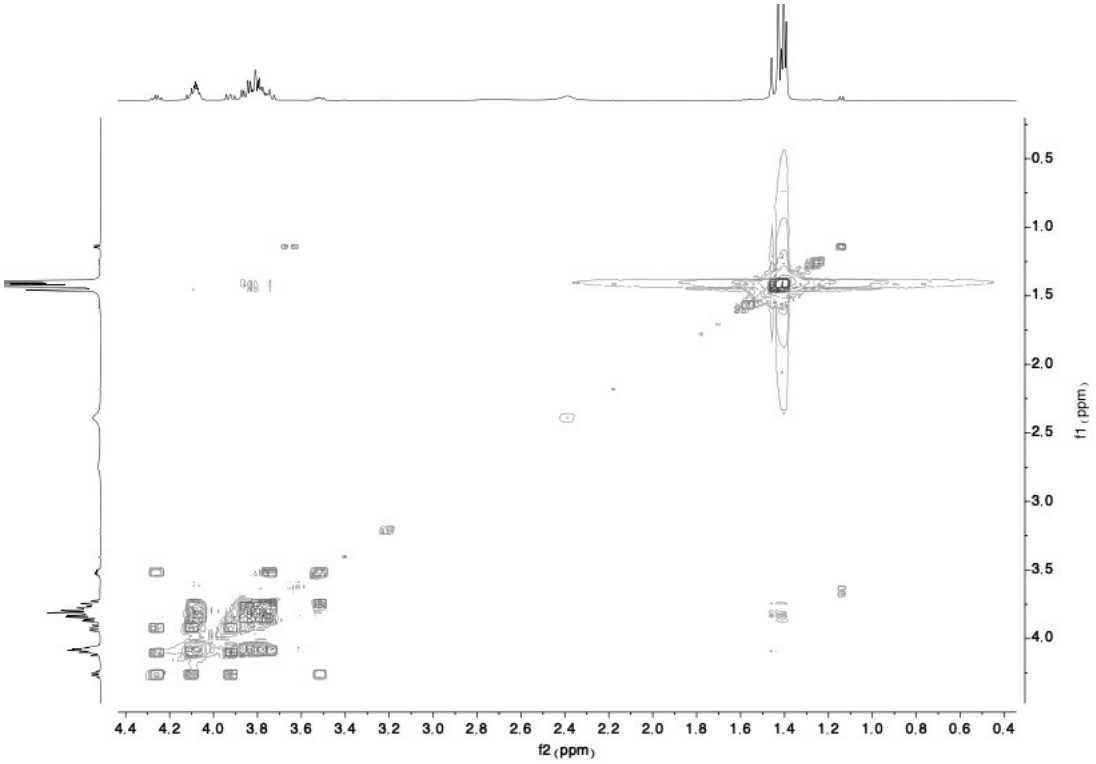

Figure S 3: COSY spectrum of i-PrDul as mixture of i-PrDul1 and i-PrDul2.

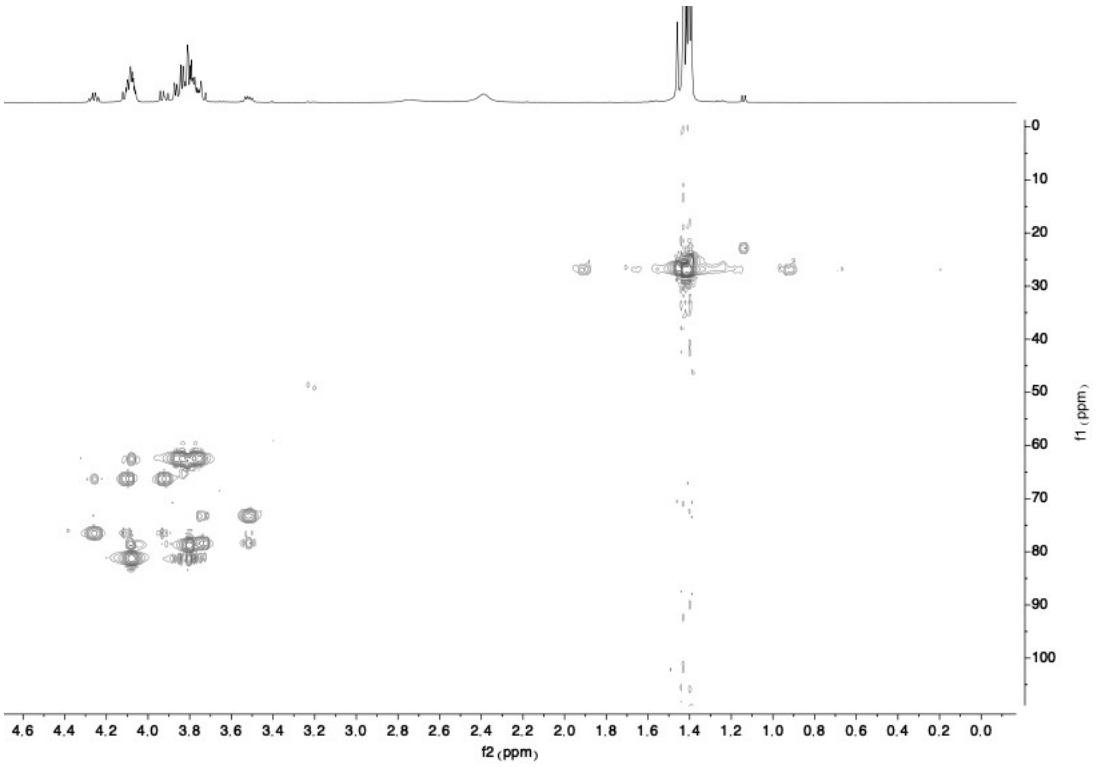

Figure S 4: HSQC spectrum of i-PrDul as mixture of i-PrDul1 and i-PrDul2.

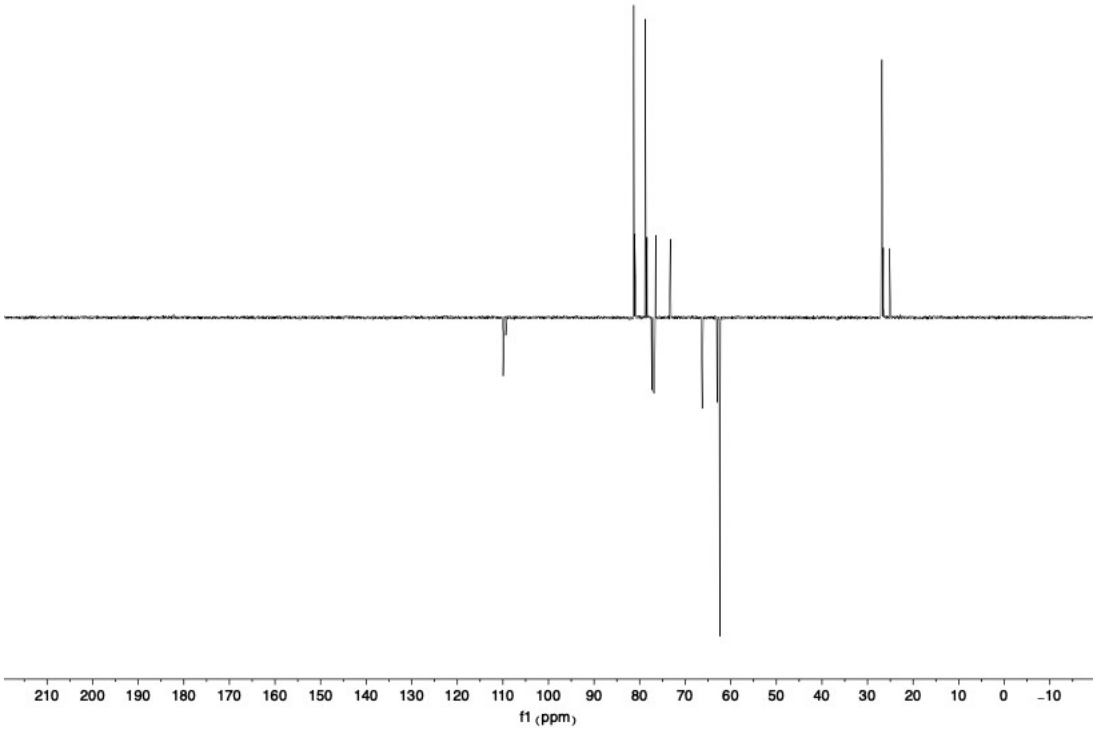

Figure S 5: ^{13}C NMR spectrum of i-PrDul as mixture of i-PrDul1 and i-PrDul2.

The protons of the carbohydrate backbone in i-PrDul1 give well separated signals as they are not related by any symmetry operation. Signals centered at 4.27, 3.94 and 3.52 ppm respectively can be spotted. The signals of free -OH groups can be identified as the broad peak centered at 2.75 ppm. On the other hand, i-PrDul2 is a meso structure resulting in a more crowded signal pattern. The protons of the carbohydrate backbone of i-PrDul2 give complex signal patterns centered at 4.08 and 3.81 ppm respectively, superimposed to the remaining signals of i-PrDul1. Signals relative to the OH groups of i-PrDul2 appear as a broad peak centered at 2.39 ppm, while the complex signal pattern centered at 1.41 ppm accounts for the methyl groups of both i-PrDul1 and i-PrDul2.

1.2 ^{1}H NMR spectra of PMS and PDS

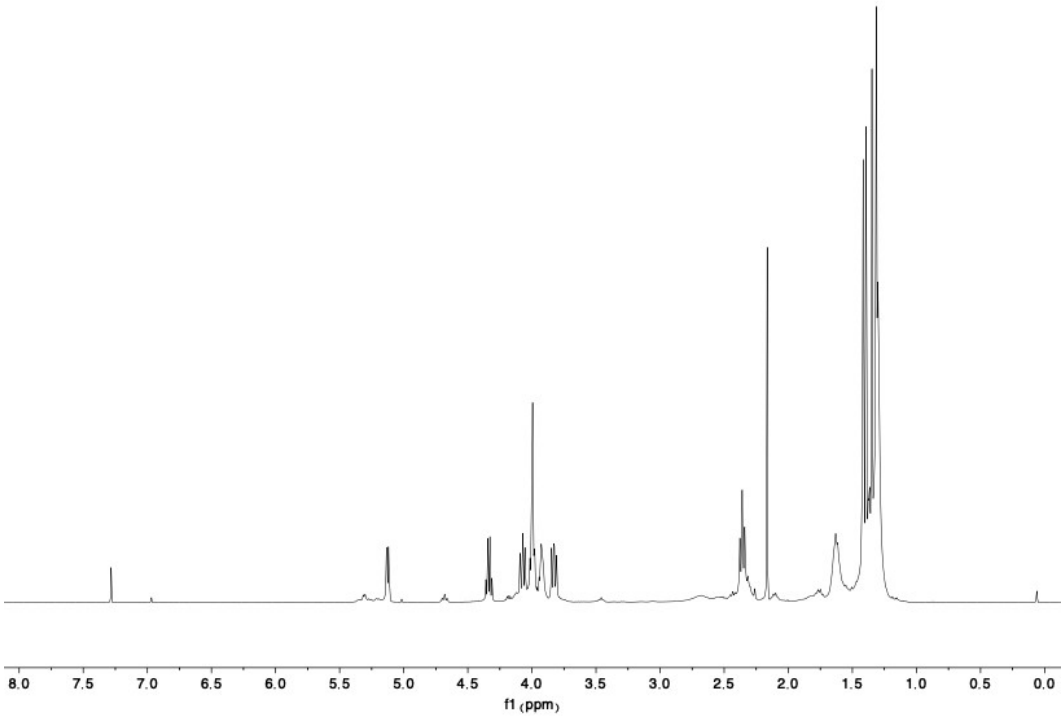

Figure S 6: ^{1}H NMR spectrum of PMS.

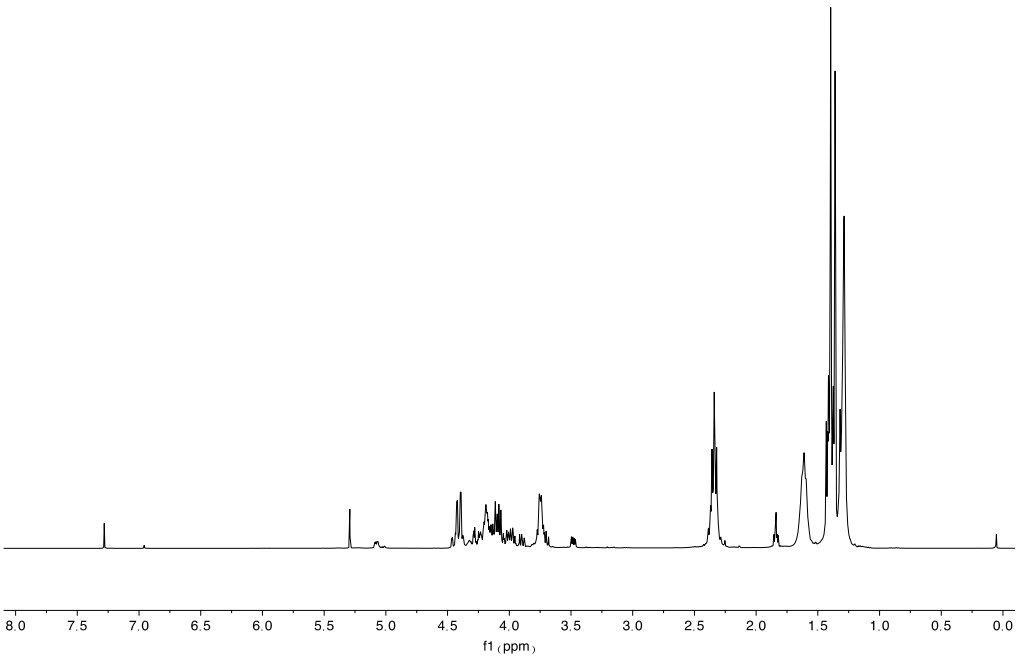

Figure S 7: ^{1}H NMR spectrum of PDS.

1.3 ^{1}H NMR spectra of PLA and PLA-PMS and PLA-PDS copolymers

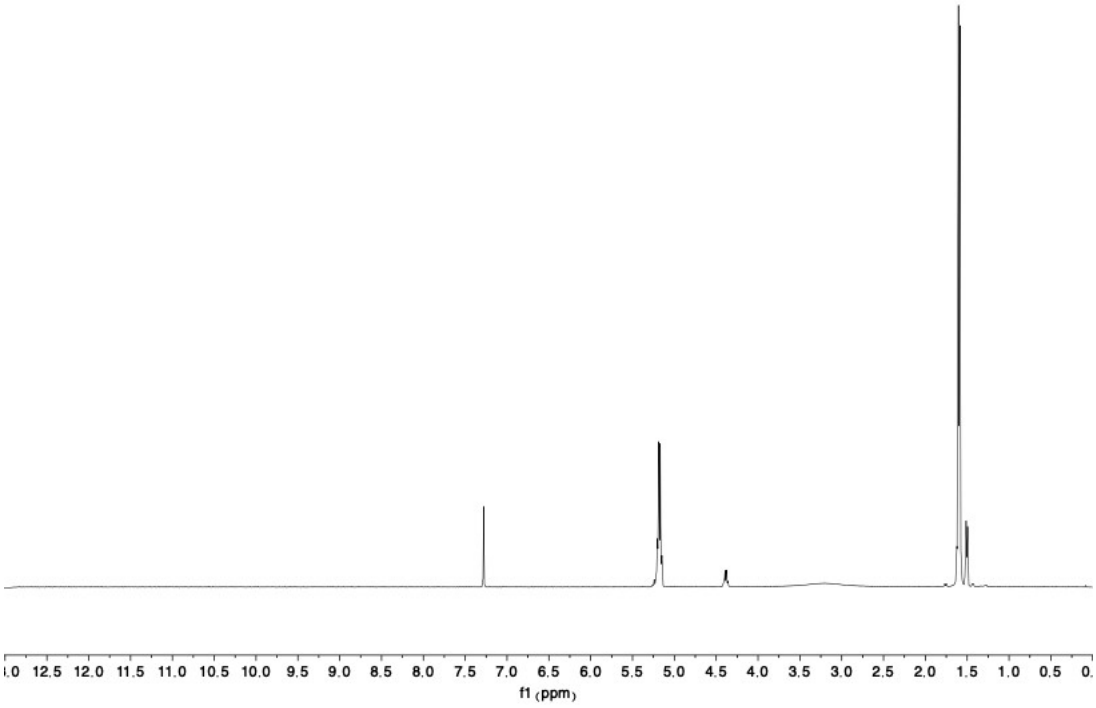

Figure S 8: ^{1}H NMR spectrum of PLA.

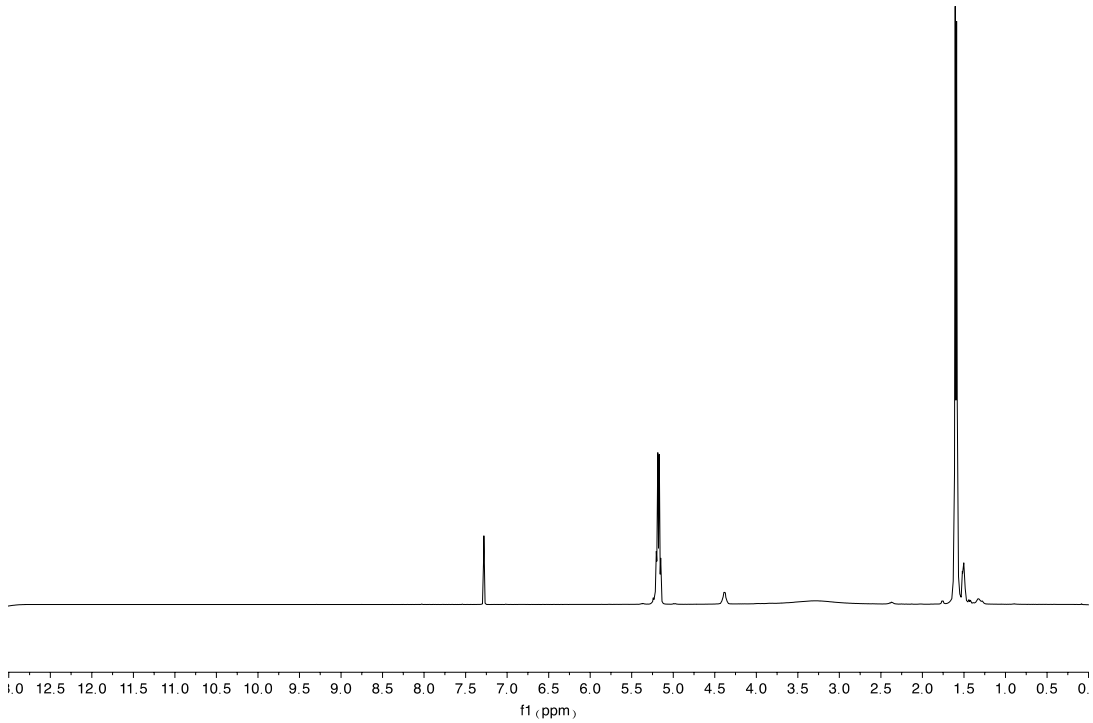

Figure S 9: ^{1}H NMR spectrum of PLA-PMS5.

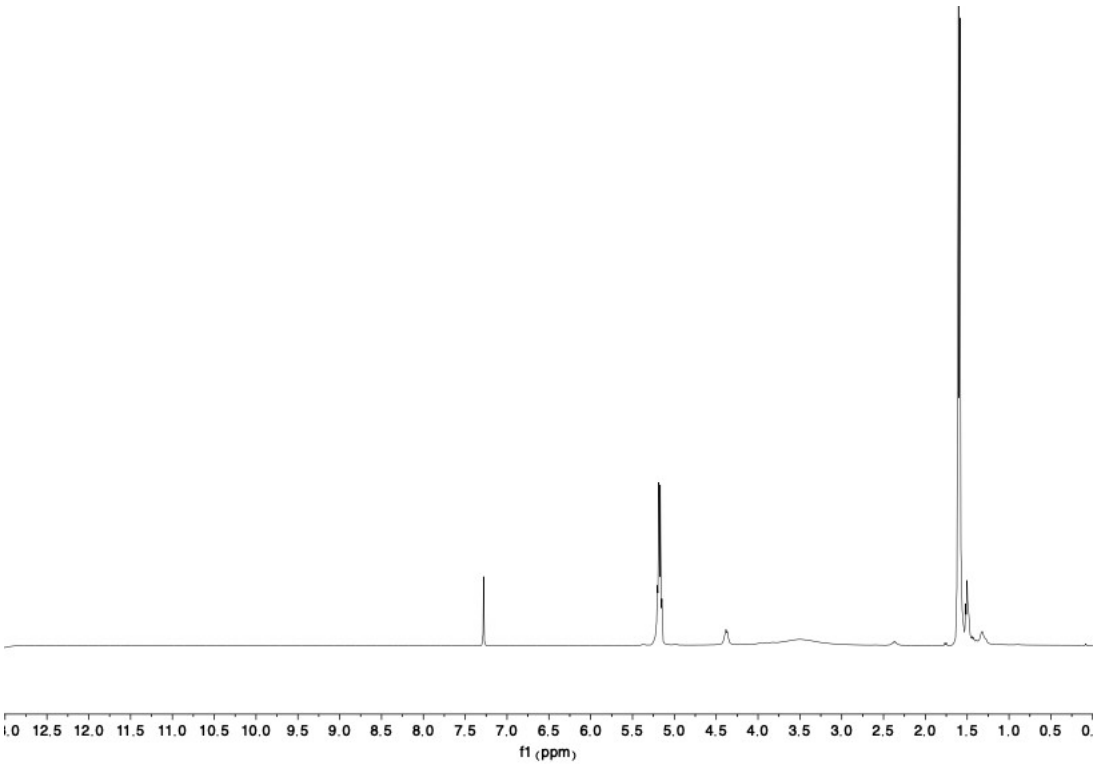

Figure S 10: ^{1}H NMR spectrum of PLA-PMS10.

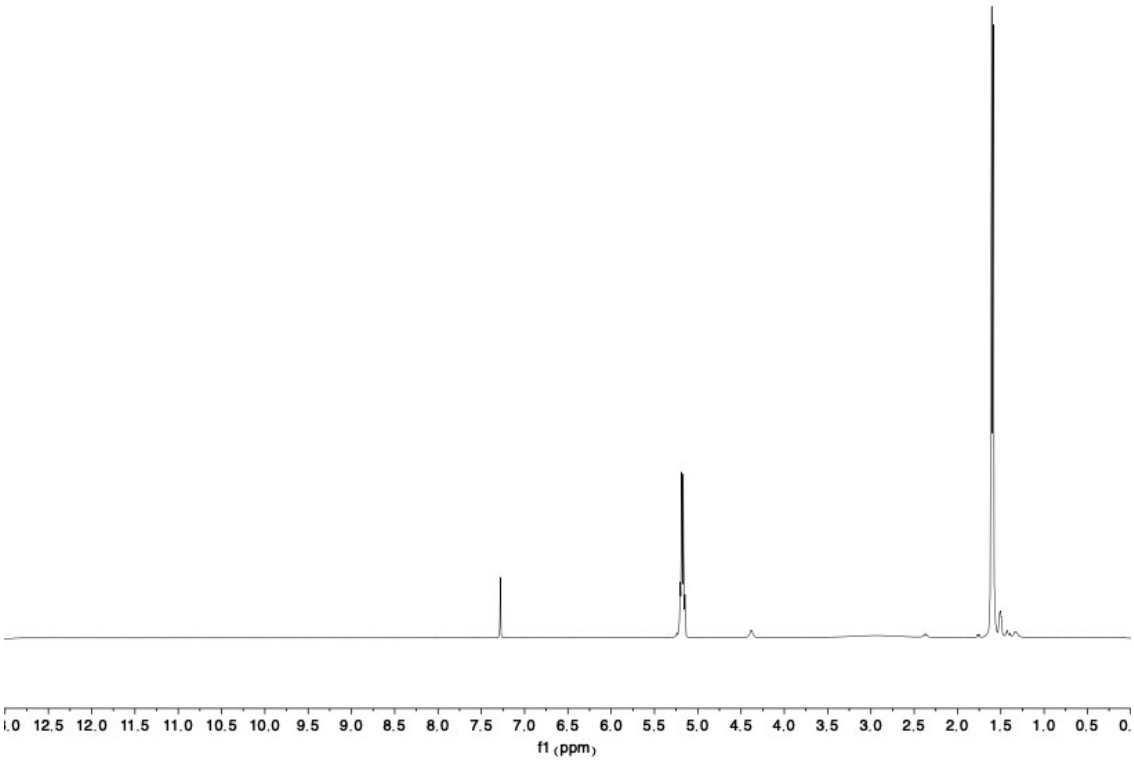

Figure S 11: ^{1}H NMR spectrum of PLA-PDS5.

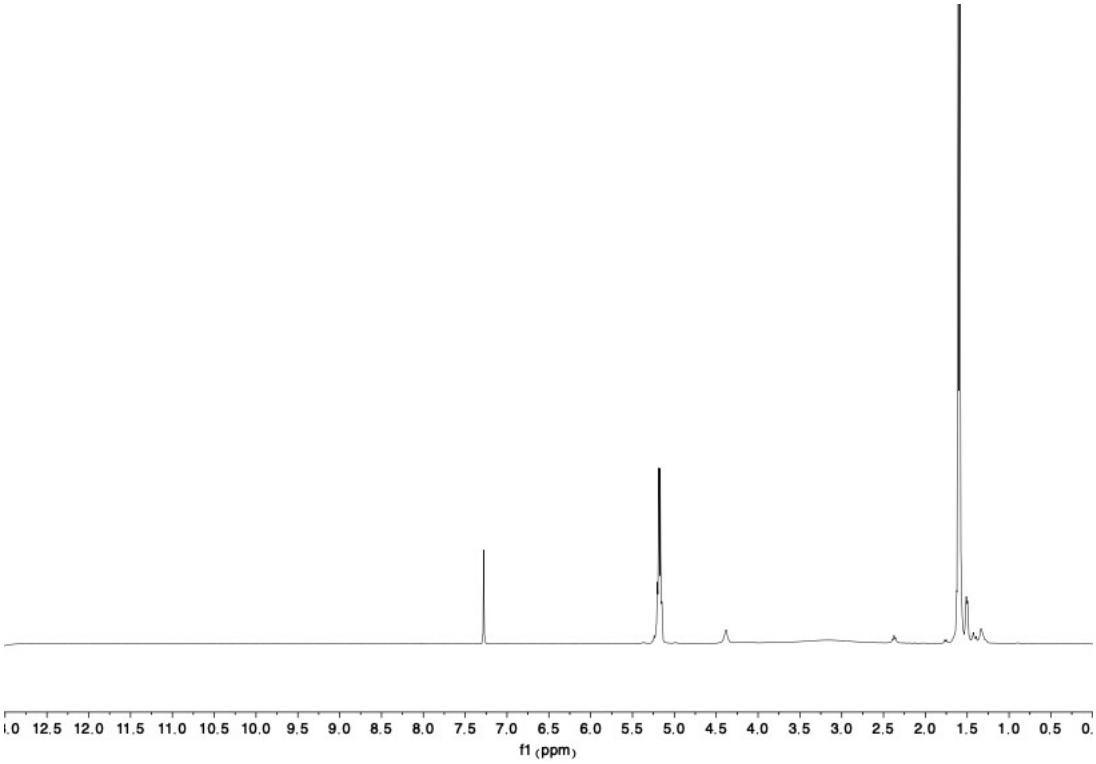

Figure S 12: ^{1}H NMR spectrum of PLA-PDS10.

1.4 DOSY spectra with diffusion coefficients

PLA-PDS5 DOSY spectrum is reported in Figure S13. Diffusion coefficients have been calculated for both the main species highlighted by green dots (D = 1.82 x 10^{-10} m^2/s) and the secondary species highlighted by red boxes (D = 1.00 x 10^{-9} m^2/s).

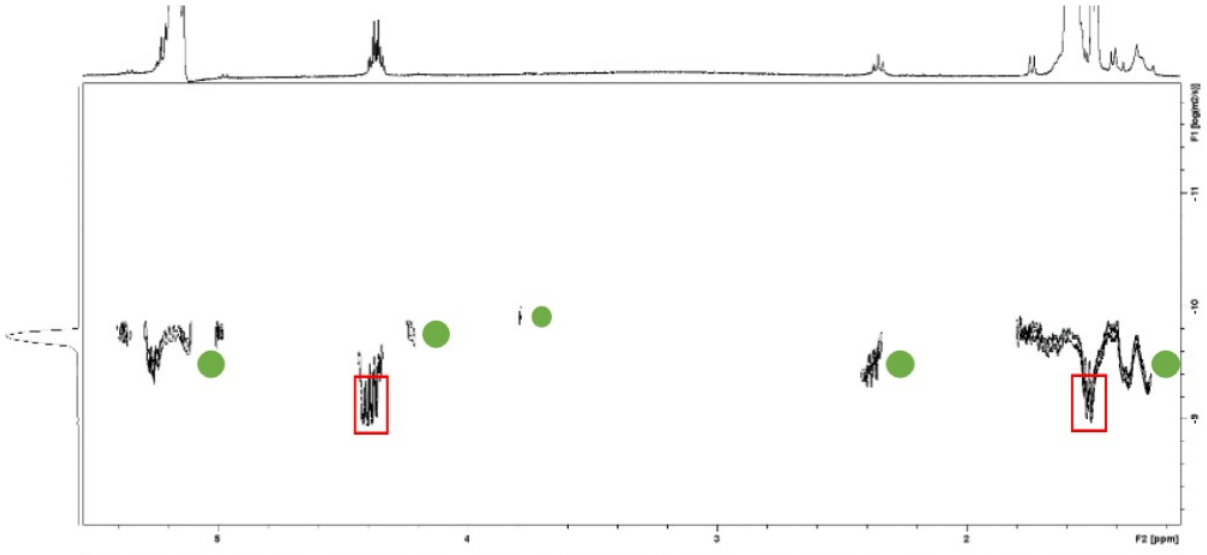

Figure S 13: DOSY spectrum of PLA-PDS5.

PLA-PDS10 DOSY spectrum is reported in Figure S14. Diffusion coefficients have been calculated for both the main species highlighted by green dots (D = 2.29 x 10^{-10} m^2/s) and the secondary species highlighted by red boxes (D = 1.10 x 10^{-9} m^2/s).

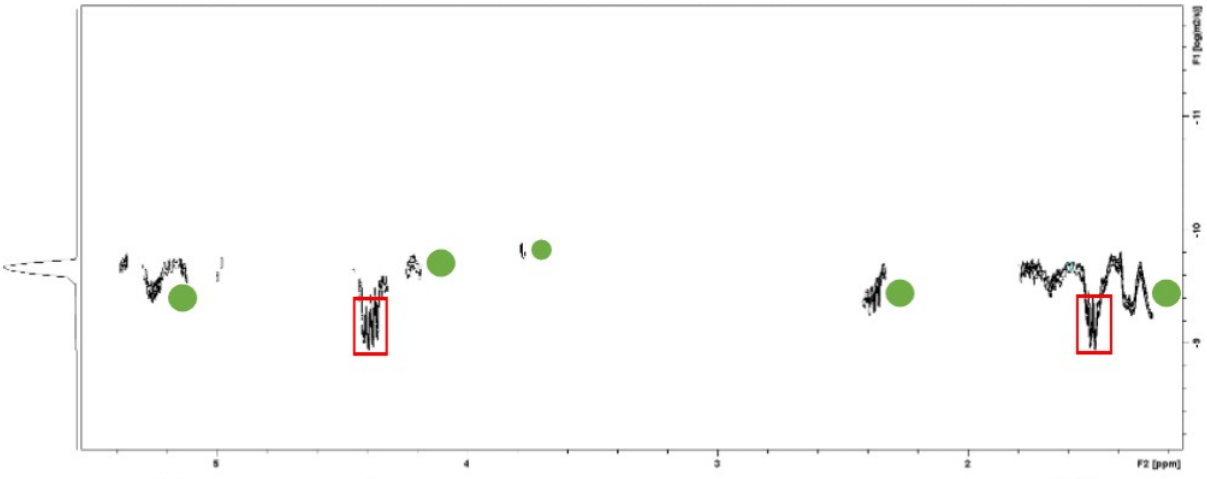

Figure S 14: DOSY spectrum of PLA-PDS10.

PLA-PMS5 DOSY spectrum is reported in Figure S15. Diffusion coefficients have been calculated for both the main species highlighted by green dots (D = 2.19 x 10^{-10} m^2/s) and the secondary species highlighted by red boxes (D = 1.05 x 10^{-9} m^2/s).

Figure S 15: DOSY spectrum of PLA-PMS5.

PLA-PMS10 DOSY spectrum is reported in Figure S16. Diffusion coefficients have been calculated for both the main species highlighted by green dots (D = 2.40 x 10^{-10} m^2/s) and the secondary species highlighted by red boxes (D = 1.21 x 10^{-9} m^2/s).

Figure S 16: DOSY spectrum of PLA-PMS10.

DOSY spectra were recorded in CDCl3 using a Brüker Avance III 400 MHz, with the Bruker 2D pulsed-gradient stimulated echo (LED-PFGSTE) sequence, using a bipolar gradient (ledbpgp2s pulse program: 2D sequence

for diffusion measurement using echo and led with bipolar gradient pulse: D. Wu, A. Chen & C.S. Johnson Jr., J. Magn. Reson. A 115, 260-264 (1995).

The diffusion coefficient, D, was determined from Equation:

$$f(g) = I_0 \, e^{-\gamma^2 \cdot g^2 \cdot \delta^2 \cdot (\Delta - \delta/3) \cdot D}$$

where f(g) is the intensity as function of g, g the magnetic field gradient strength, I0 the initial intensity, γ the gyromagnetic ratio 4.258 10^3 Hz/G, δ and Δ the delays, in particular δ the little delta value (3000 μs) and Δ the big delta value (250 ms), D the diffusion coefficient.

1.5 Deprotection Reaction

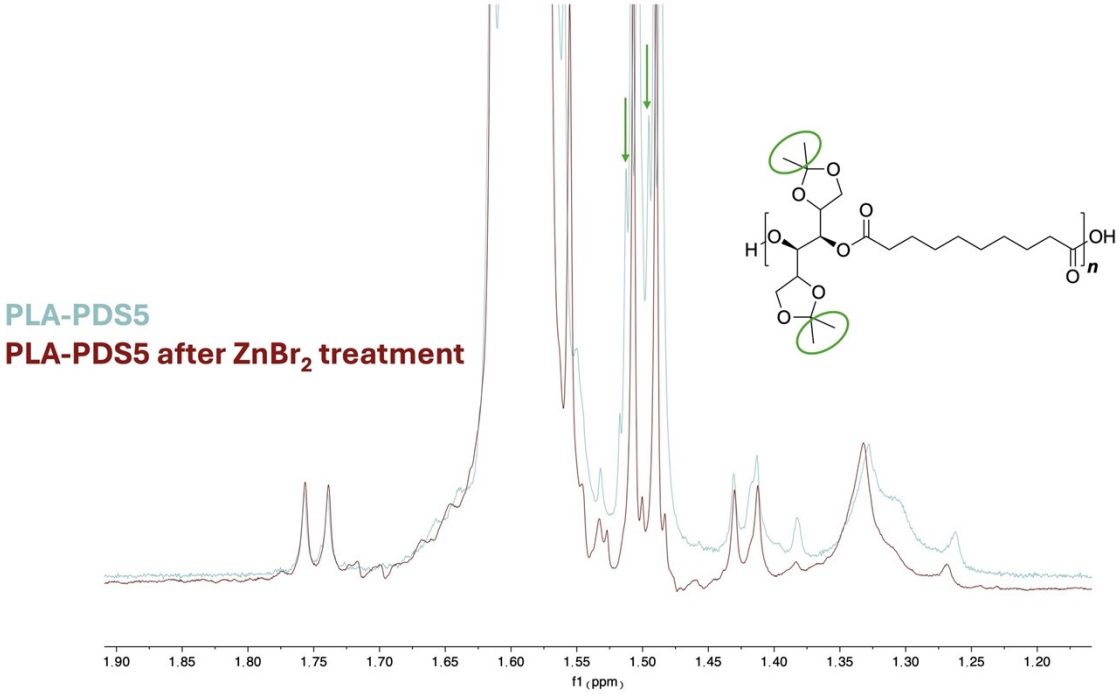

Figure S 17: Comparison of the ^{1}H NMR spectra of PLA-PDS5 before and after the treatment with $ZnBr_2$ highlighting the disappearance of the acetal methyl signals.

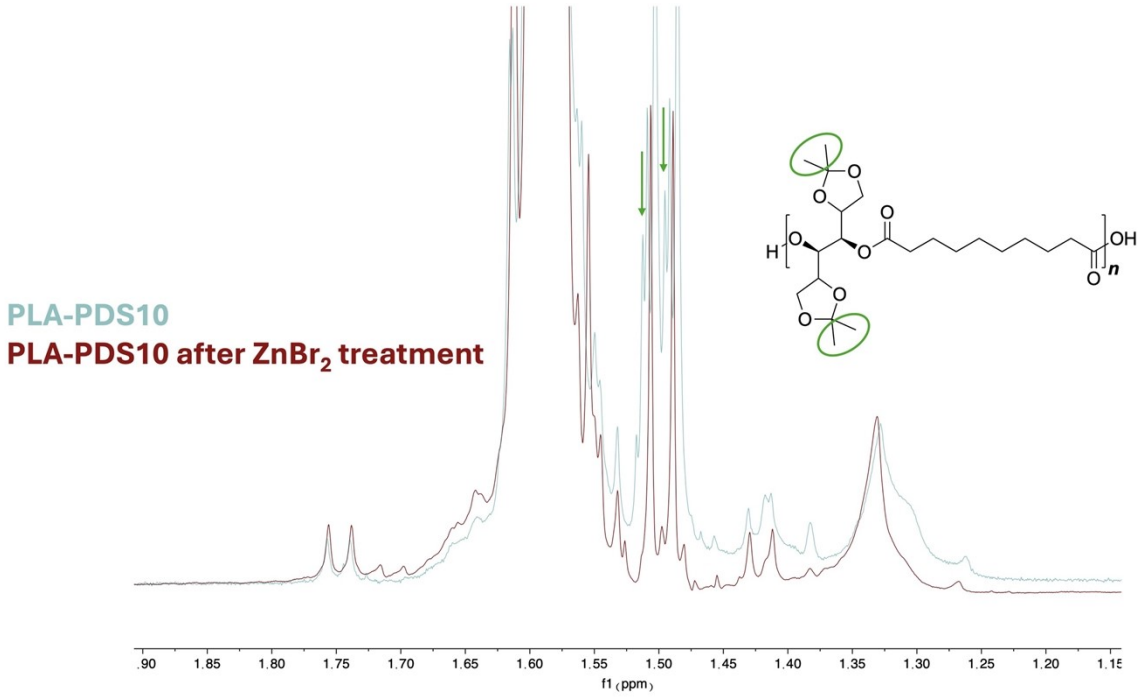

Figure S 18: Comparison of the ^{1}H NMR spectra of PLA-PDS10 before and after the treatment with $ZnBr_2$ highlighting the disappearance of the acetal methyl signals.

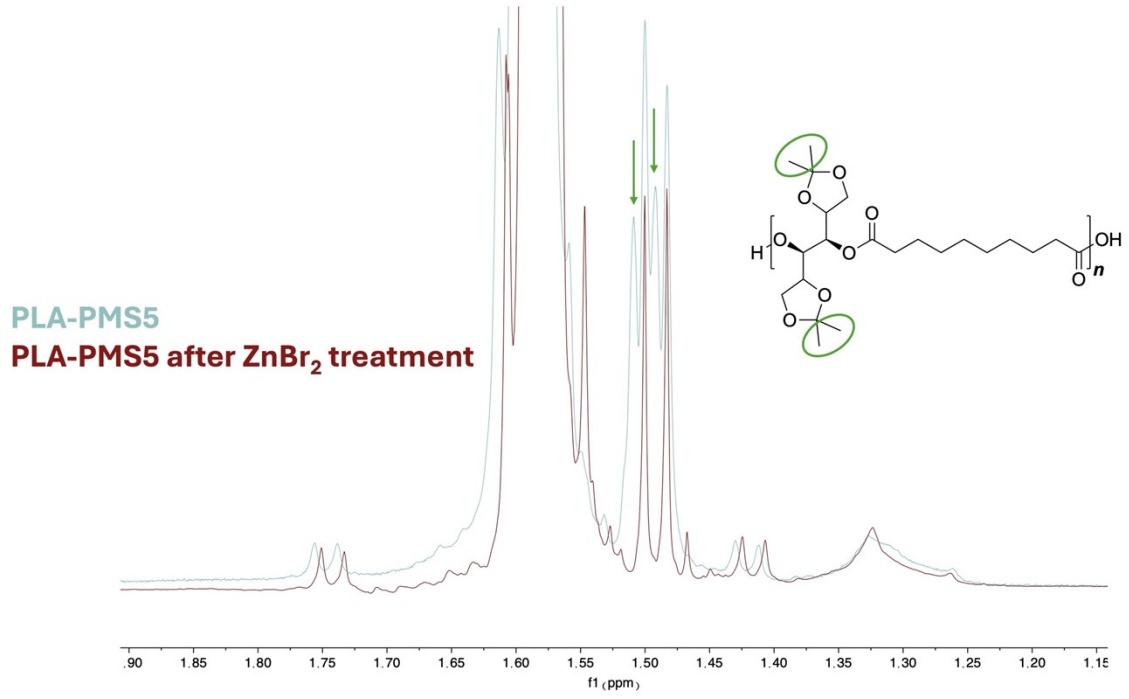

Figure S 19: Comparison of the ^{1}H NMR spectra of PLA-PMS5 before and after the treatment with $ZnBr_2$ highlighting the disappearance of the acetal methyl signals.

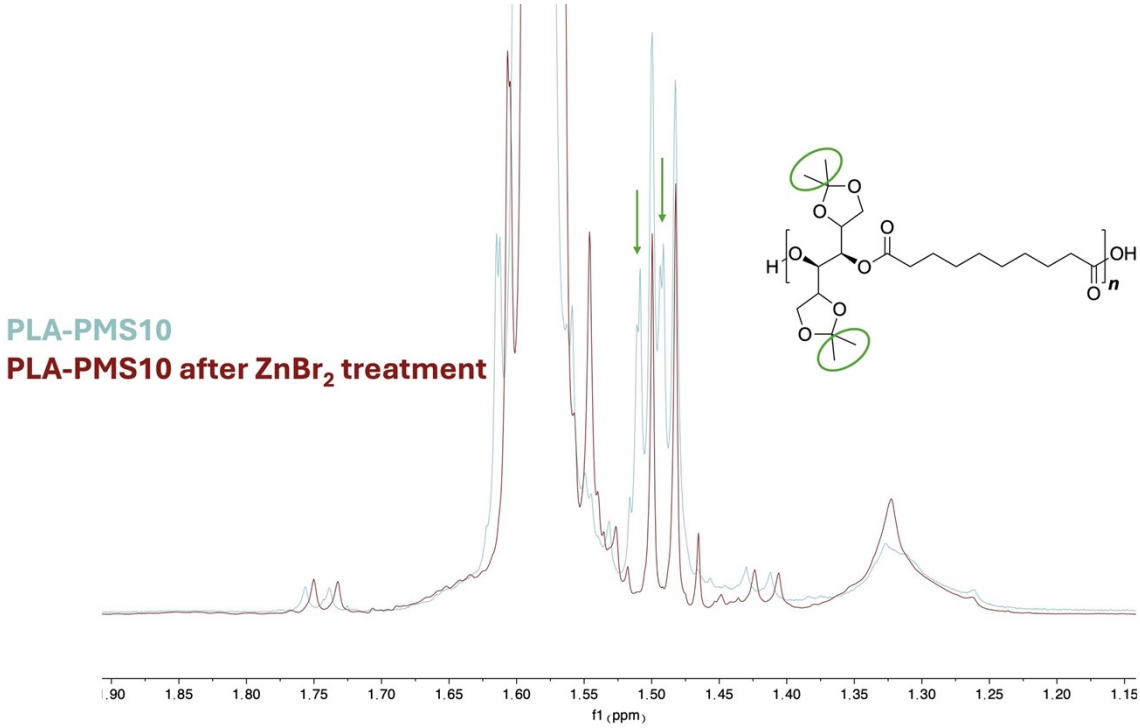

Figure S 20: Comparison of the ^{1}H NMR spectra of PLA-PMS10 before and after the treatment with $ZnBr_2$ highlighting the disappearance of the acetal methyl signals.

2 Thermal Analyses

2.1 TGA curves

TGA analyses were carried out on PLA and the copolymers, in order to determine whether the addition of the macrodiol units could have any effect on the thermal stability of the final materials. **Table S1** reports $T_{5\%}$, $T_{50\%}$ and $T_{95\%}$ i.e. the temperatures at which the material loses the 5, 50 and 95% of the weight, respectively. **Figure S13** reports the thermal degradation curves of the samples.

Table S1: thermal degradation data for PLA and PDS and PMS-loaded copolymers.

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	$T_{95\%}$ (°C)
PLA	227	297	339
PLA-PDS5	247	287	309
PLA-PDS10	224	282	403
PLA-PMS5	178	281	375
PLA-PMS10	153	279	350

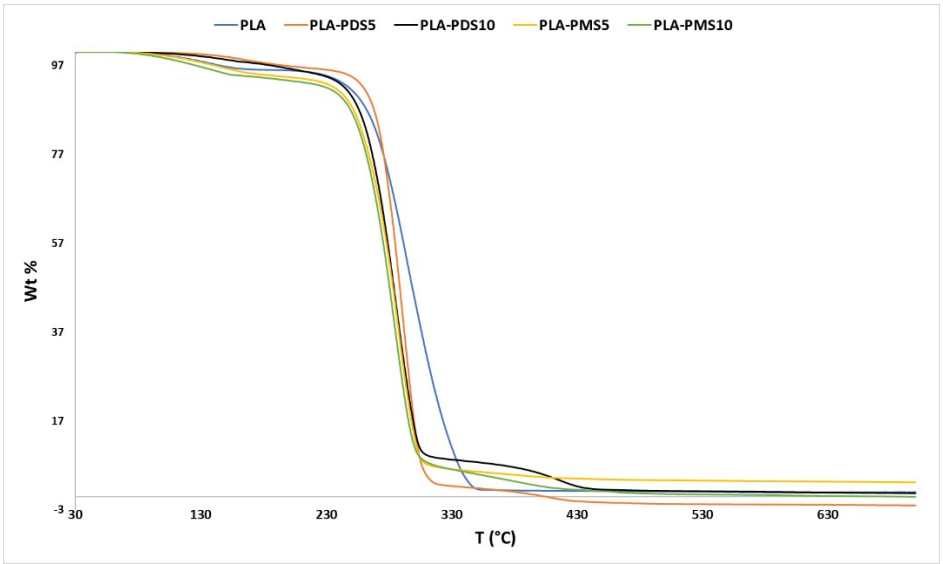

Figure S21: thermal degradation curves of PLA and PDS and PMS-loaded copolymers.

On a general level, PDS-loaded copolymer showed a slight increase in thermal stability. PLA-PDS5 shows a $T_{5\%}$ 20°C higher with respect to PLA, while $T_{5\%}$ appears to be only 3°C lower with respect to PLA despite the great difference in the molecular weight of the two samples. On the other hand, PMS-loaded copolymers show a lower thermal stability, with a $T_{5\%}$ for PLA-PMS5 and PLA-PMS10 of 178 and 153°C respectively. After the beginning of the degradation all copolymers show a drastic weight loss and they all present a lower $T_{50\%}$ when compared to standard PLA. Finally, besides PLA-PDS5, all copolymers show higher $T_{95\%}$ with respect to standard PLA, possibly indicating the formation of carbonaceous residues promoted by the presence of carbohydrates derivatives within the chains.

2.2 DSC Cooling scans

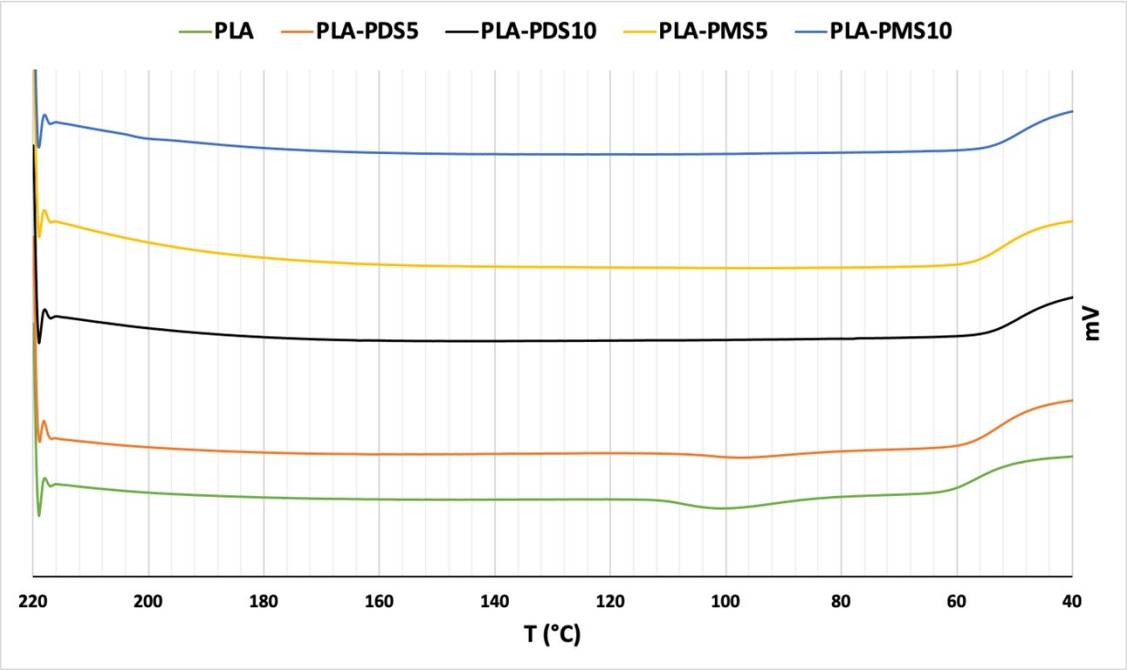

Figure S 22: DSC cooling scans of thermograms for PLA and PLA-PMS and PLA-PMS copolymers.

3 EDX analyses

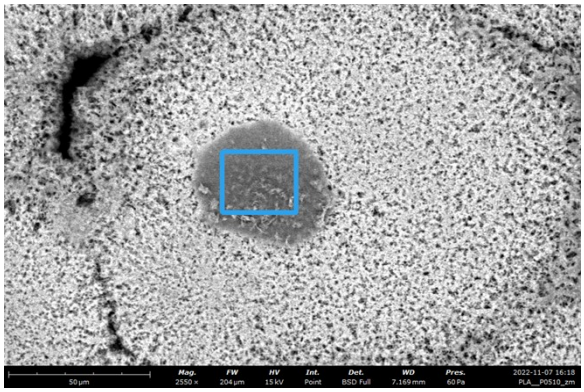

Figure S 23: EDX area analysis of the dark region at the center of spherulites in PLA-PDS10 sample after the treatment with $ZnBr_2$.

FW: 204 µm, Mode: 15 kV - Point, Detector: BSD Full, Time: 11/7/22 4:18 PM

Table S 2: Elemental composition of the analyzed area. Reported in **Figure S23**.

Element Number	Element Symbol	Element Name	Atomic Conc.
6	C	Carbon	74.932
8	O	Oxygen	25.068

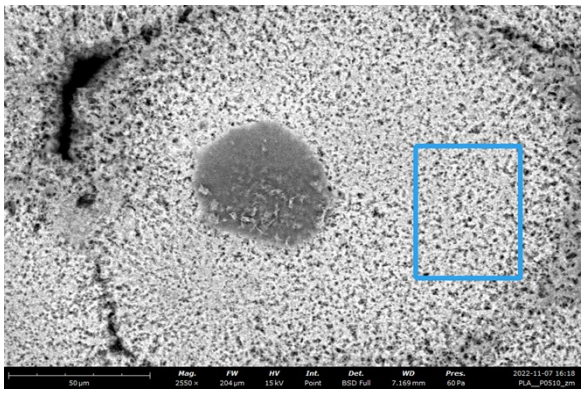

Figure S 24: EDX area analysis of the dark region at the center of spherulites in PLA-PDS10 sample after the treatment with $ZnBr_2$.

FW: 204 µm, Mode: 15 kV - Point, Detector: BSD Full, Time: 11/7/22 4:18 PM

Table S 3: Elemental composition of the analyzed area. Reported in **Figure S24**.

Element Number	Element Symbol	Element Name	Atomic Conc.
6	C	Carbon	67.458
8	O	Oxygen	32.542