Supplementary Information for

Cellulose-Based Polyacetal by Direct and Sensitized Photocationic Ring-Opening Polymerization of Levoglucosenyl Methyl Ether

Kerem Kaya[a], Tapas Debsharma[b], Helmut Schlaad*[b], Yusuf Yagci*[a,c]

[a]*Istanbul Technical University, Department of Chemistry, 34469, Maslak, Istanbul, Turkey*
[b]*University of Potsdam, Institute of Chemistry, 14476, Karl-Liebknecht-Straße 24–25, Potsdam, Germany*
[c]*Faculty of Science, Chemistry Department, King Abdulaziz University, 21589 Jeddah, Saudi Arabia*

Corresponding authors' e-mails: schlaad@uni-potsdam.de (H.S.), yusuf@itu.edu.tr (Y.Y.)

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Materials

Levoglucosenyl methyl ether was synthesized according to previous procedure (Debsharma et al. *Angew. Chem. Int. Ed.* 2019, *58*, 18492-18495.). Benzophenone (BP, 99%, Acros), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Ciba) and diphenyliodonium hexafluorophosphate (98%, Sigma-Aldrich) were used as purchased. Pyrene (98%, Sigma-Aldrich) was recrystallized from ethanol. *N,N*-Dimethylaniline (Sigma-Aldrich, 99.5%) and cyclohexene oxide (Sigma-Aldrich, 98%) were distilled over calcium hydride under nitrogen atmosphere. Dichloromethane, *n*-hexane, and tetrahydrofuran were purified using conventional drying and distillation procedures.

Analytical Instrumentation

NMR. Nuclear magnetic resonance (NMR) spectra were recorded on an Agilent VNMRS 500 spectrometer at 25 °C in deuterated chloroform ($CDCl_3$ with tetramethylsilane as an internal standard).

FT-IR. Fourier-transform infrared (FTIR) spectra were recorded on Perkin–Elmer Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and mercury cadmium telluride (MCT) detector. 32 scans were averaged.

GPC. Gel permeation chromatography (GPC) measurements were performed on a TOSOH EcoSEC GPC system equipped with an auto sampler system, temperature controlled pump, purge and degasser unit, column oven, refractive index (RI) detector. The stationary phase was a TSK gel superhZ2000 polystyrene gel column (6 mm ID × 15 cm), which is packed with rigid, porous, 3 μm polymer beads. Tetrahydrofuran was used as an eluent at flow rate of 1.0 mL/min at 40 °C. Polystyrene standards were used for calibration. Data were analyzed using Eco-SEC Analysis software.

DSC. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Diamond DSC with a heating rate of 10 K min^{-1} under nitrogen flow (20 mL min^{-1}).

TGA. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Diamond TA/TGA with a heating rate of 10 K min^{-1} under nitrogen flow (200 mL min^{-1}).

Powder X-Ray Scattering. Powder X-Ray scattering measurement was performed using Rigaku Miniflex 600 with Cu radiation and a wide area scintillation counter detection system.

Photopolymerization Procedure

For the photopolymerization procedure, 0.01 mmol of DPI was dissolved in 0.1 mL of dry dichloromethane inside a Schlenk tube which was previously degassed. Then 0.1 mL (~0.7 mmol) of LGME was added and the mixture was irradiated with 300 nm light for 2 h at room temperature. For reactions performed at -15 °C, ice-acetone mixture (50:50/v:v) was put into a thin glass vessel which was placed inside the photoreactor. The bottom of the Schlenk tube was immersed into the vessel until the reaction mixture level. Temperature of the mixture inside the vessel was checked every 15 min and ice was added if necessary to keep the ice-acetone temperature constant at -15 °C. The resulting brown colored mixture was precipitated in 10-fold dichloromethane. Equimolar amounts of the co-initiators (co-initiator: DPI) were used for the free-radical promoted and sensitized photo-polymerizations The precipitated polymer was dried for 1 day in vacuum at 40 °C. The monomer conversions were determined either by comparing peak integrals in proton spectrum or by gravimetry. Average molecular weights and dispersities were determined by size-exclusion chromatography (SEC) in THF eluent using polystyrene standards. For the NMR studies, 0.05 mmol of DPI and 0.5 mL of **1** were dissolved in 0.5 mL deuterated chloroform ($CDCl_3$) and proton spectra were checked in 60 min intervals.

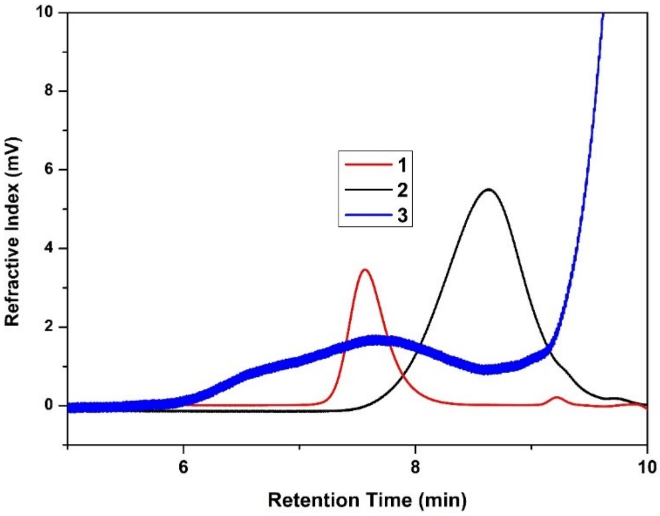

Figure S1. GPC traces of the PLGME samples 1 (red), 2 (black), and 3 (blue) (from Table 1).

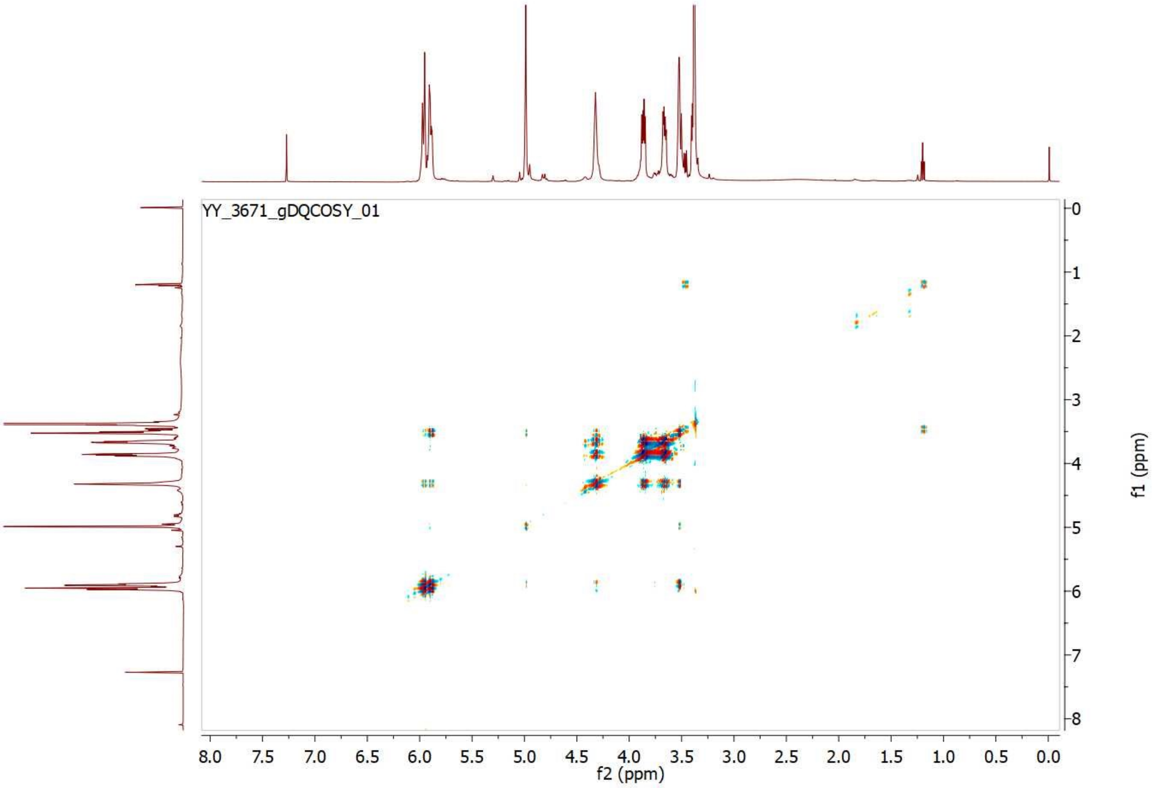

Figure S2. COSY NMR (500 MHz) spectrum of PLGME sample 2 in $CDCl_3$.

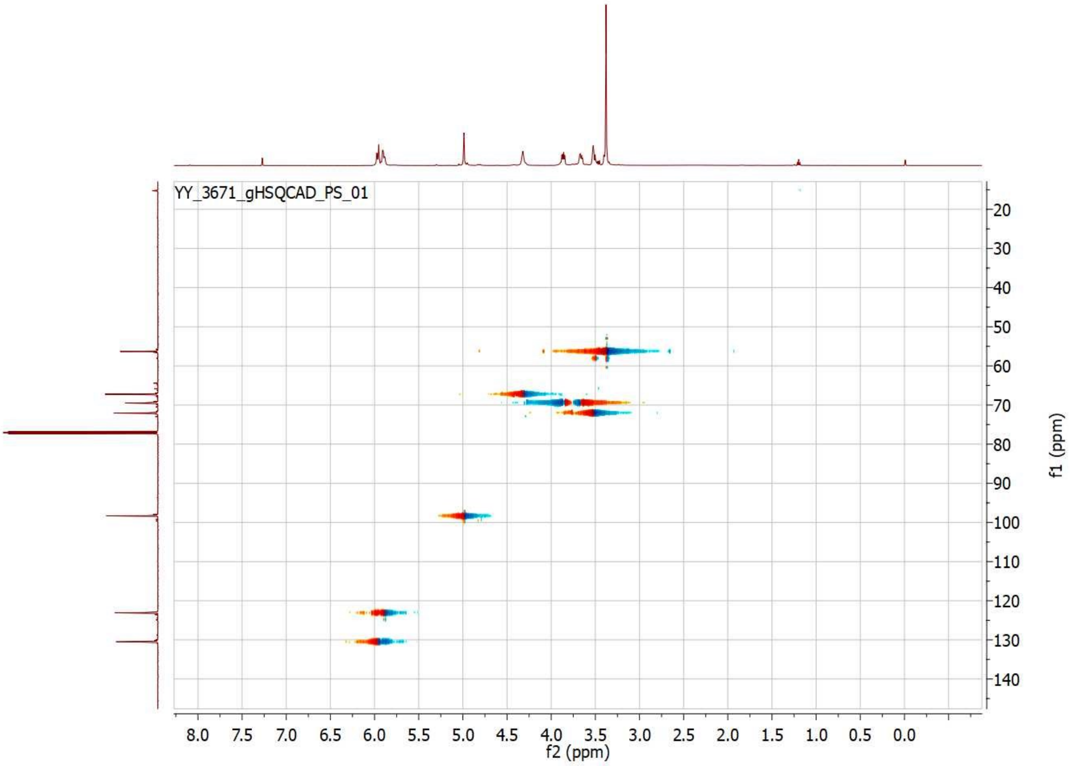

Figure S3. HSQC NMR (125 MHz) spectrum of PLGME sample 2 in $CDCl_3$.

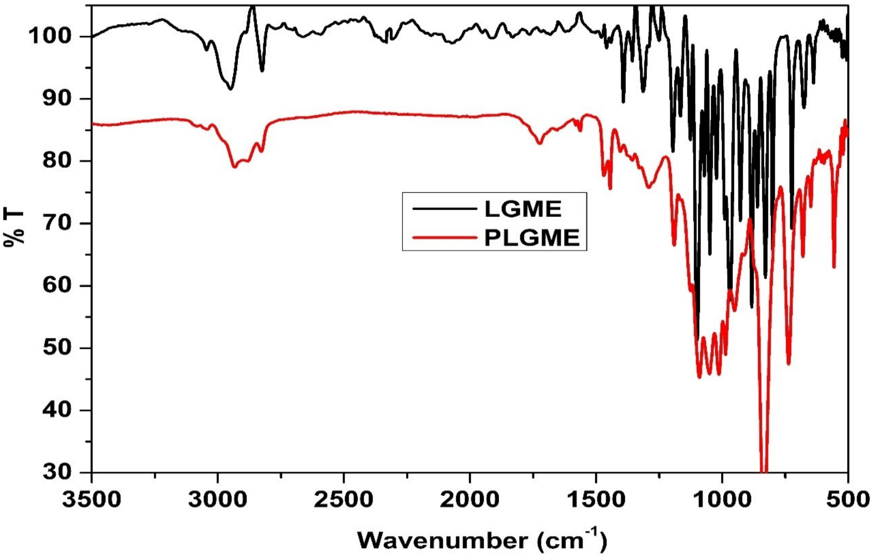

Figure S4. Infrared spectra of LGME (black) and PLGME sample 2 (red).

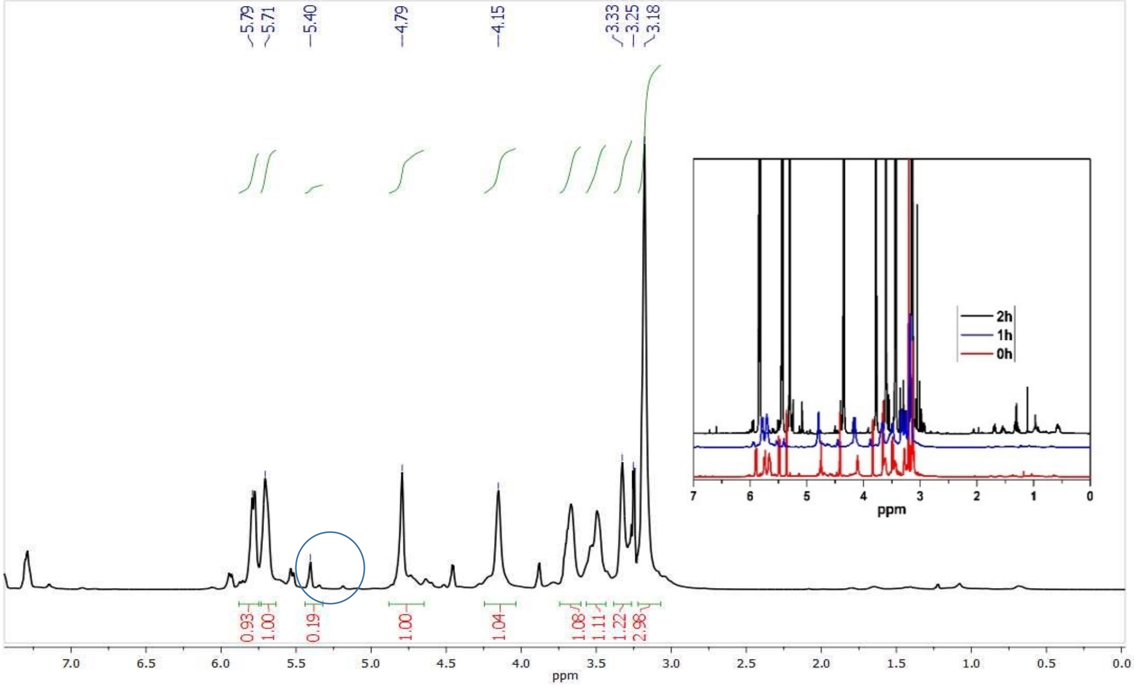

Figure S5. Determination of LGME conversion by ^{1}H-NMR spectroscopy.

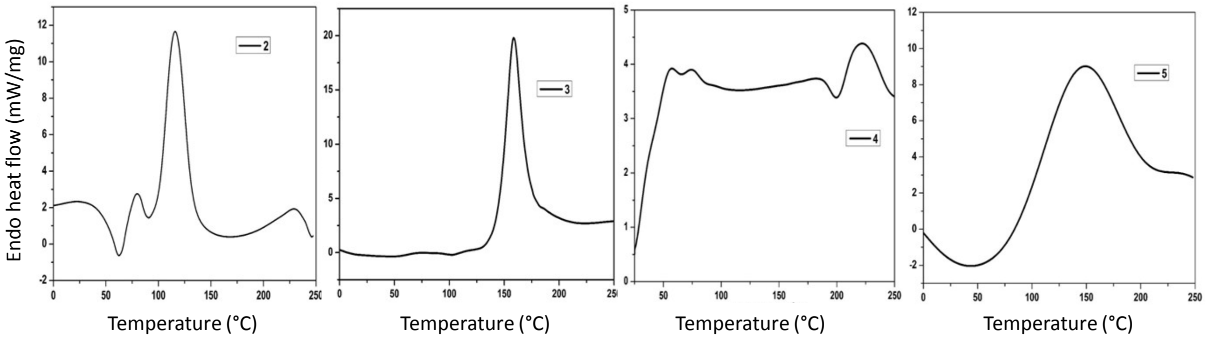

Figure S6. DSC thermograms (1st heating) of PLGME samples 2, 3, 4, and 5.

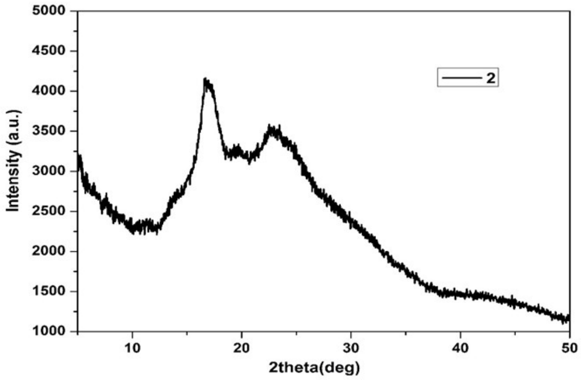

Figure S7. Powder X-Ray diffractogram of PLGME sample 2.

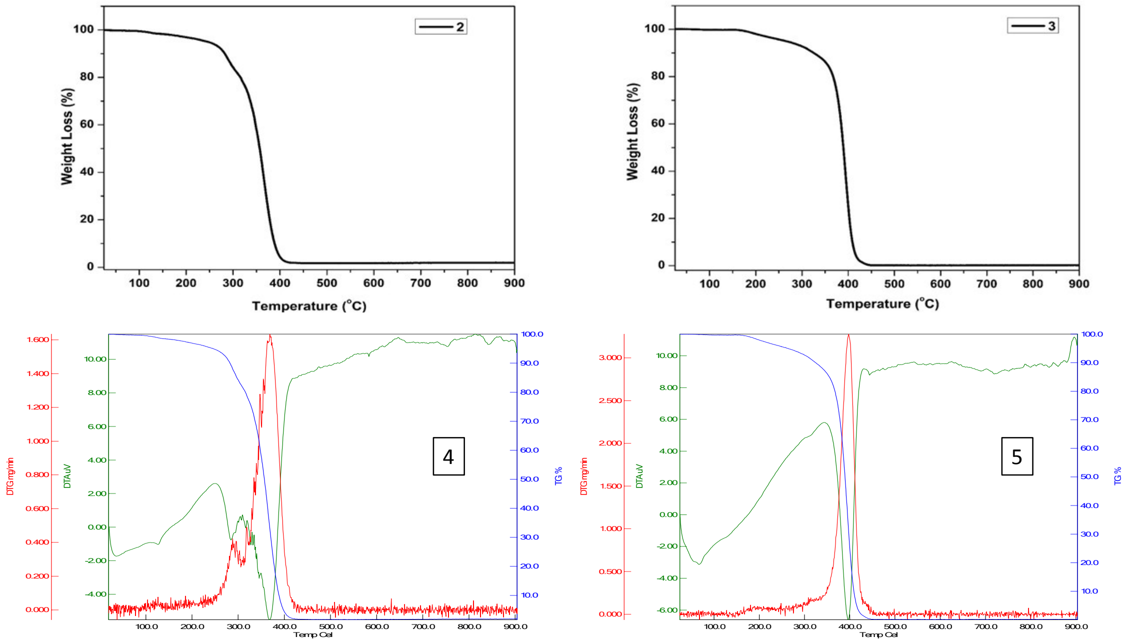

Figure S8. TGA thermograms of samples 2, 3, 4, and 5.

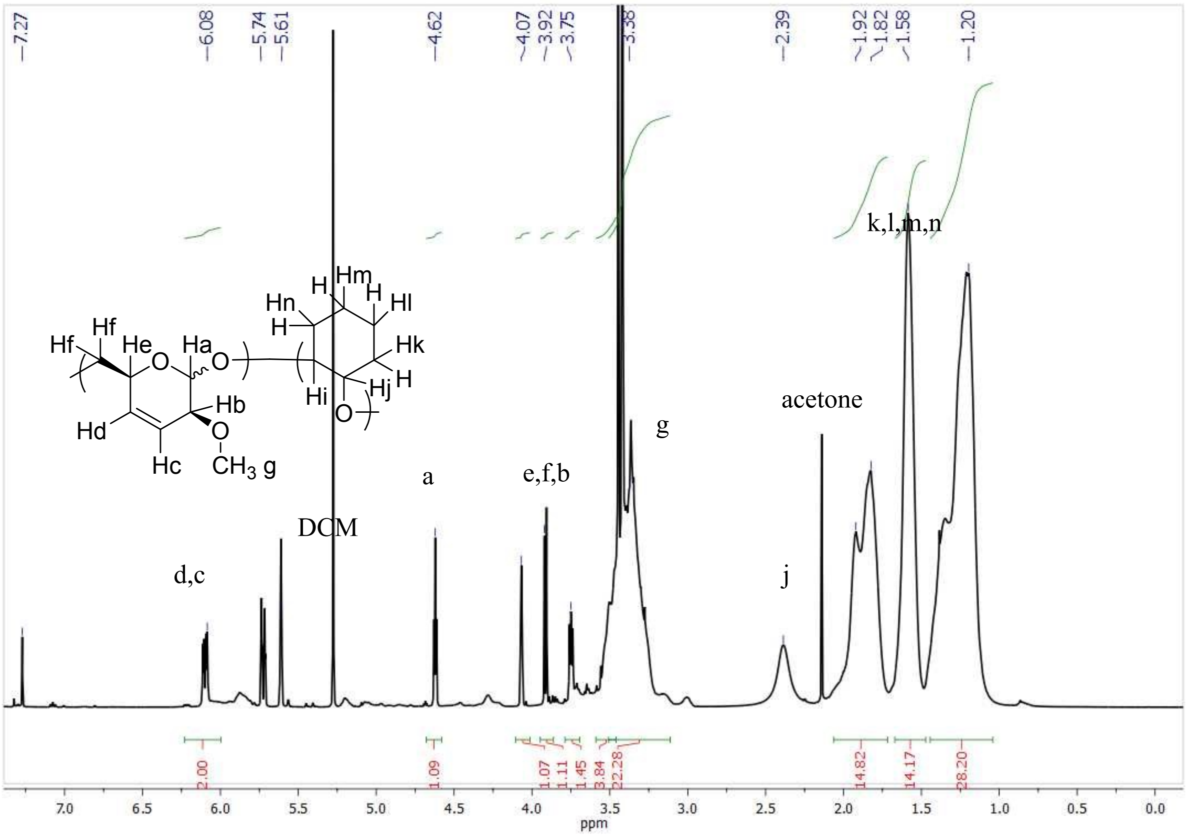

Figure S9. ^{1}H-NMR (500 MHz) spectrum of PLGME-*b*-PCHO in CDCl$_3$.

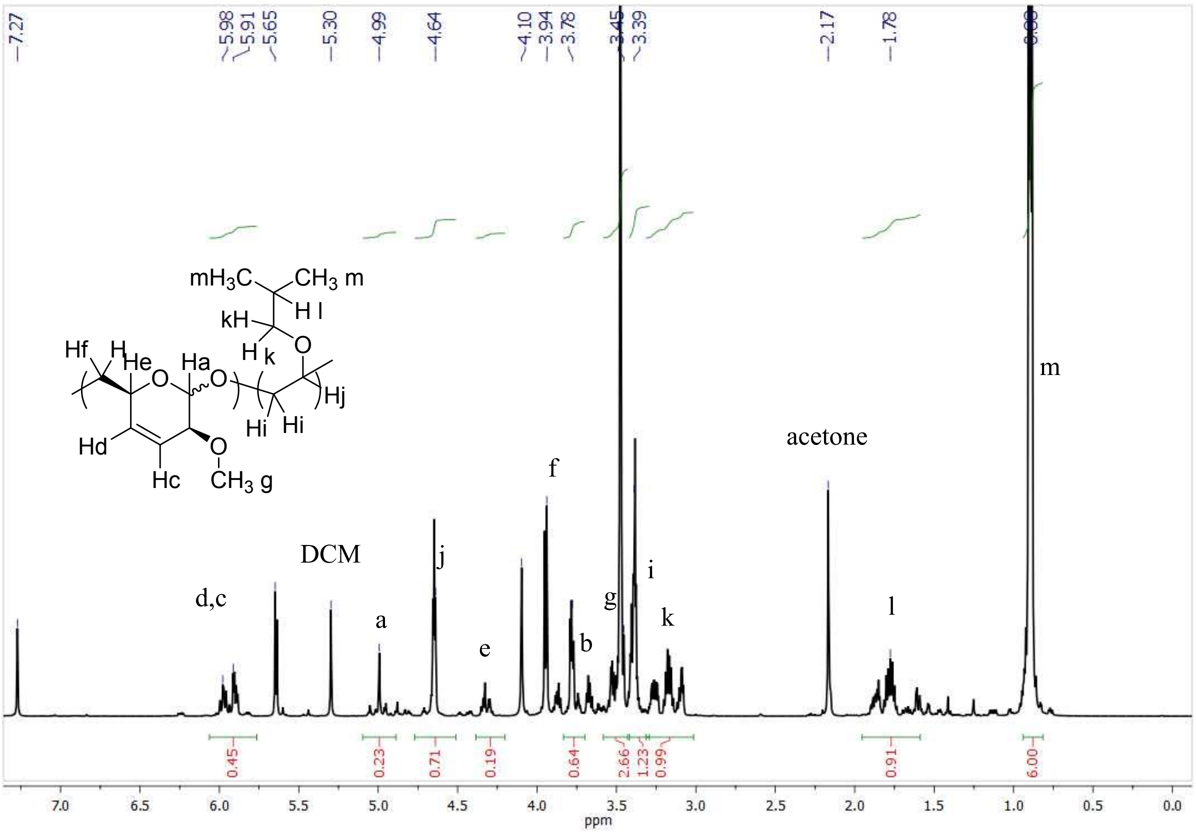

Figure S10. ^{1}H-NMR (500 MHz) spectrum of PLGME-*b*-PIBVE in CDCl$_3$.