Electronic Supplementary Material (ESI) for Biomaterials Science.

Controlled Degradation of Polycaprolactone-based Micropillar Arrays

Niamh Geoghegan,[1,2^] Mark O'Loughlin,[1^] Colm Delaney,[3] Keith D. Rochfort,[4] Meabh Kennedy,[5] Srikanth Kolagatla,[3,6] Lucia Podhorska,[1] Brian J. Rodriguez,[6] Larisa Florea,[3] and Susan M. Kelleher [1,2,5]

Supplementary Information

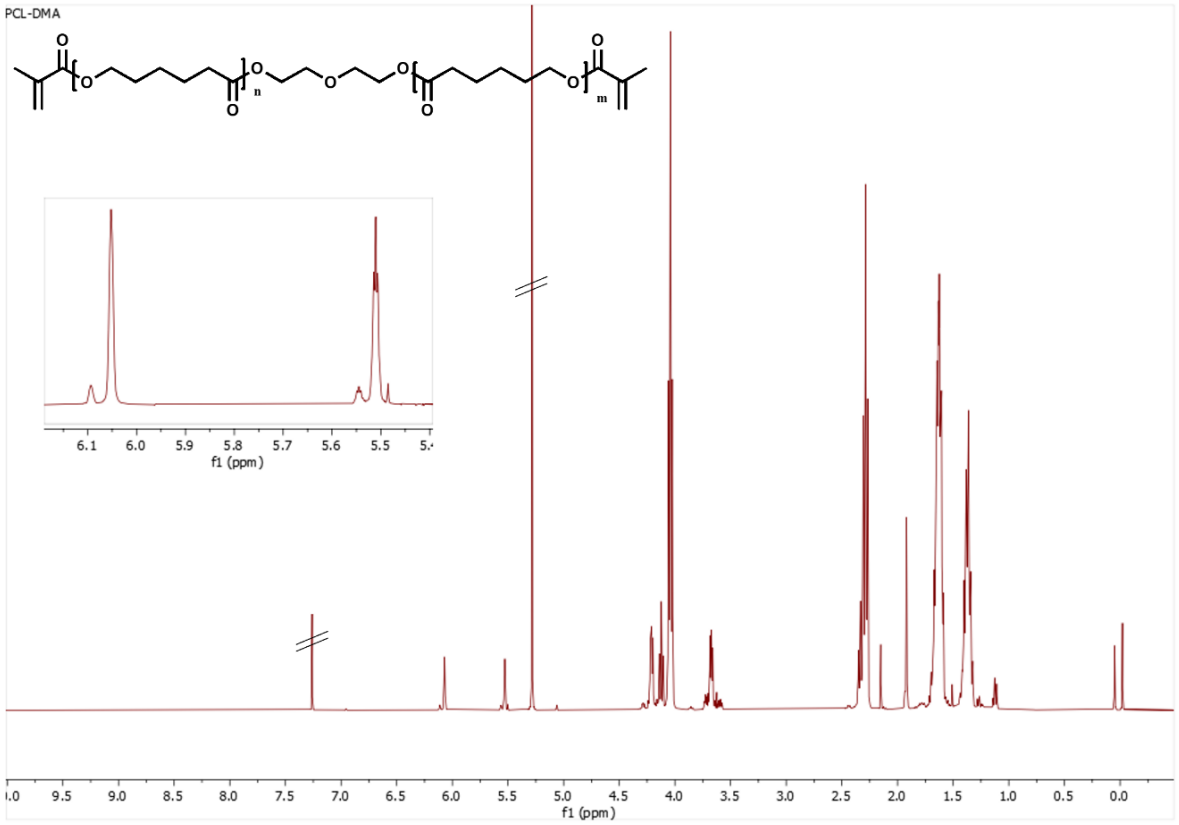

Figure S1: ^{1}H NMR spectra of PCLDMA

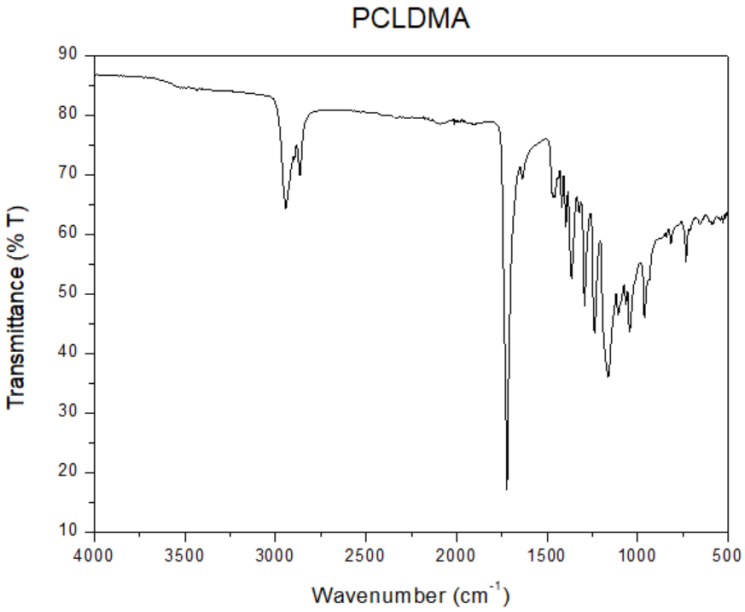

Figure S2: FTIR spectra of PCLDMA

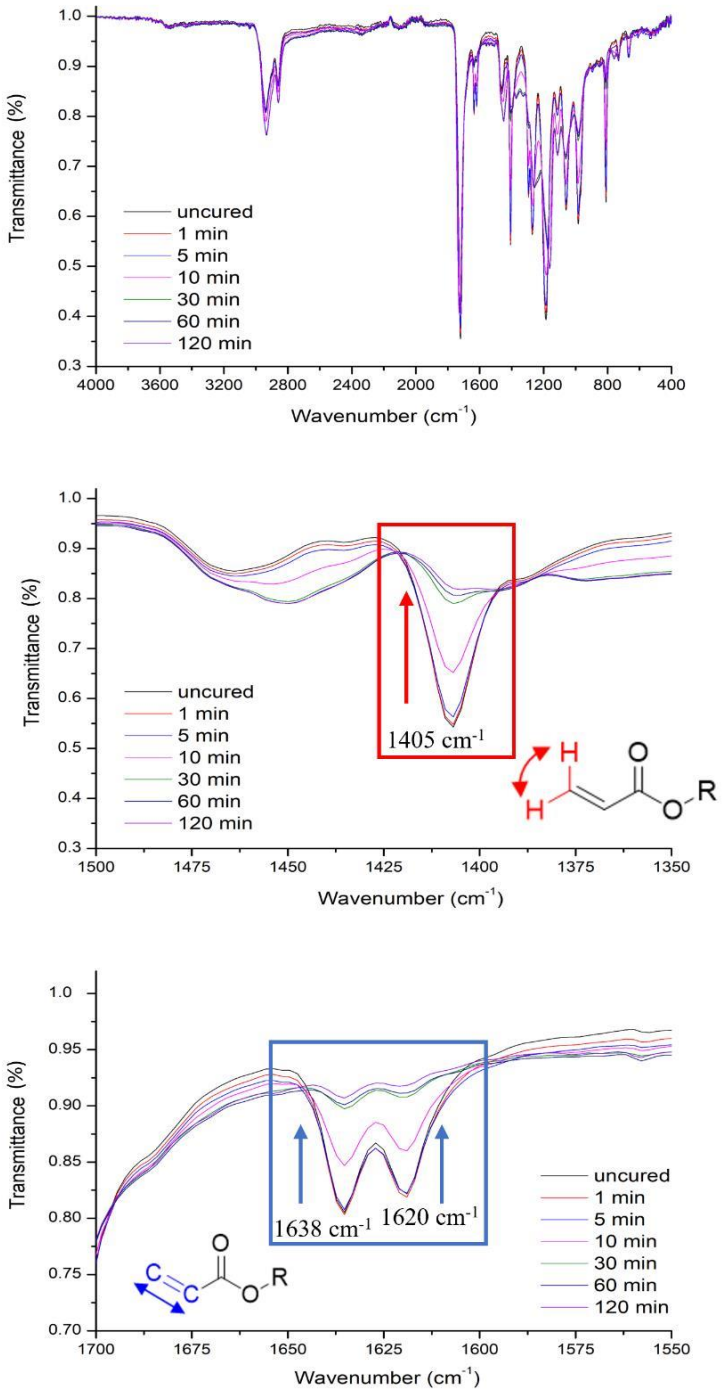

Figure S3: FTIR spectra of neat HDDA (1 % PBPO w/w) photopolymerised using the white light irradiation source at different time points from 0 - 120 mins. Top: The full spectra of the timepoints are shown. Middle: A close up of the peaks centred at 1410 cm $^{-1}$ related to the vibration of terminal allyl –CH groups. Bottom: 1620 cm $^{-1}$ and 1638 cm $^{-1}$ describe the stretching of the C=C bonds of acrylate groups.

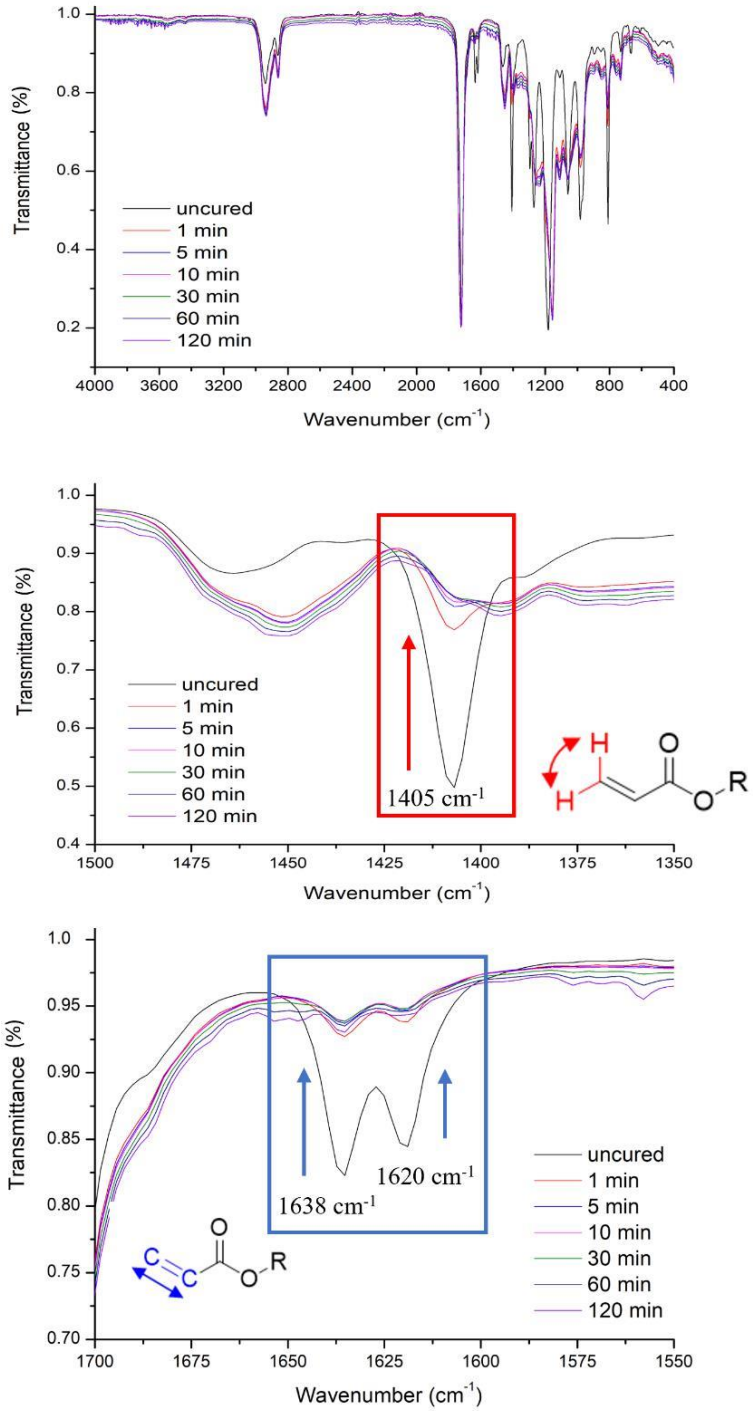

Figure S4: FTIR spectra of 1:9 PCLDMA:HDDA (1 % PBPO w/w) photopolymerised using the white light irradiation source at different time points from 0 - 120 mins. Top: The full spectra of the timepoints are shown. Middle: A close up of the peaks centred at 1410 cm^{-1} related to the vibration of terminal allyl –CH groups. Bottom: 1620 cm^{-1} and 1638 cm^{-1} describe the stretching of the C=C bonds of acrylate groups.

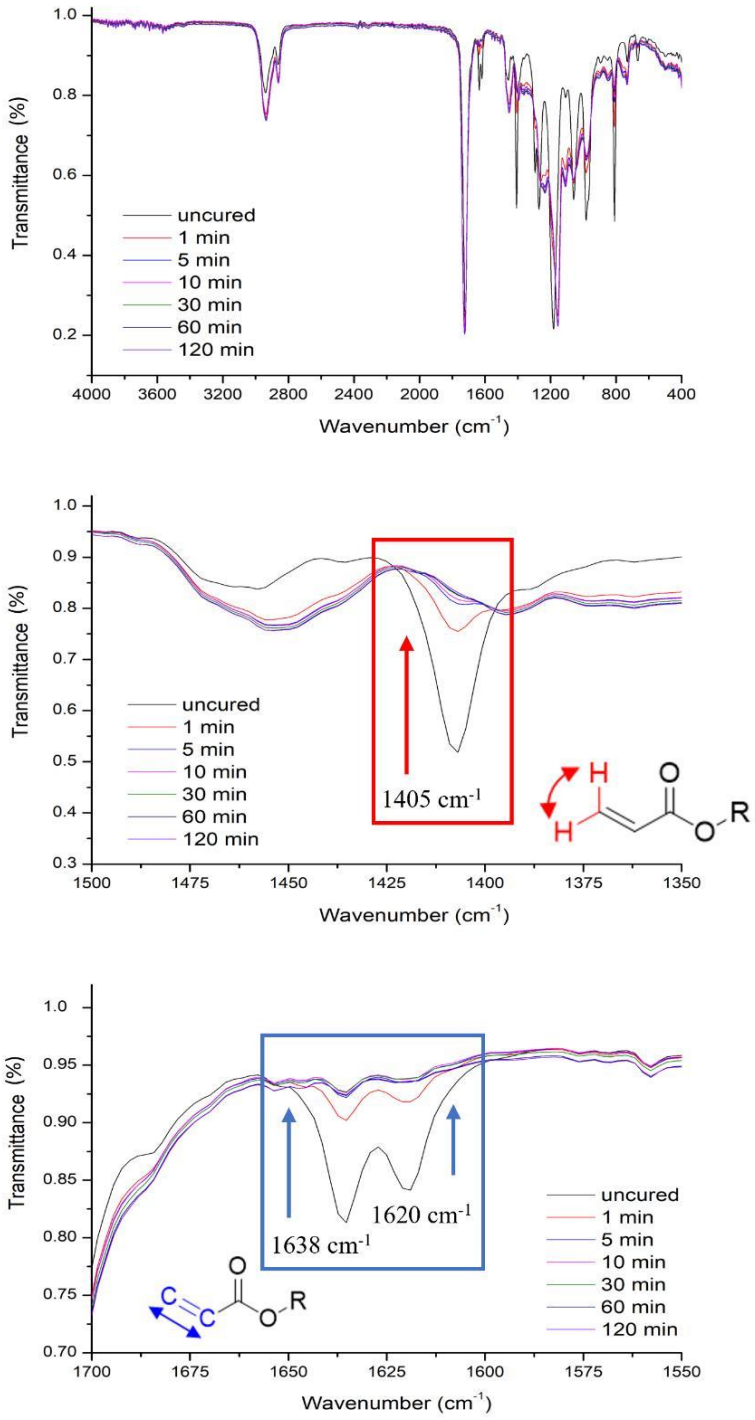

Figure S5: FTIR spectra of 1:4 PCLDMA:HDDA (1 % PBPO w/w) photopolymerised using the white light irradiation source at different time points from 0 - 120 mins. Top: The full spectra of the timepoints are shown. Middle: A close up of the peaks centred at 1410 cm^{-1} related to the vibration of terminal allyl –CH groups. Bottom: 1620 cm^{-1} and 1638 cm^{-1} describe the stretching of the C=C bonds of acrylate groups.

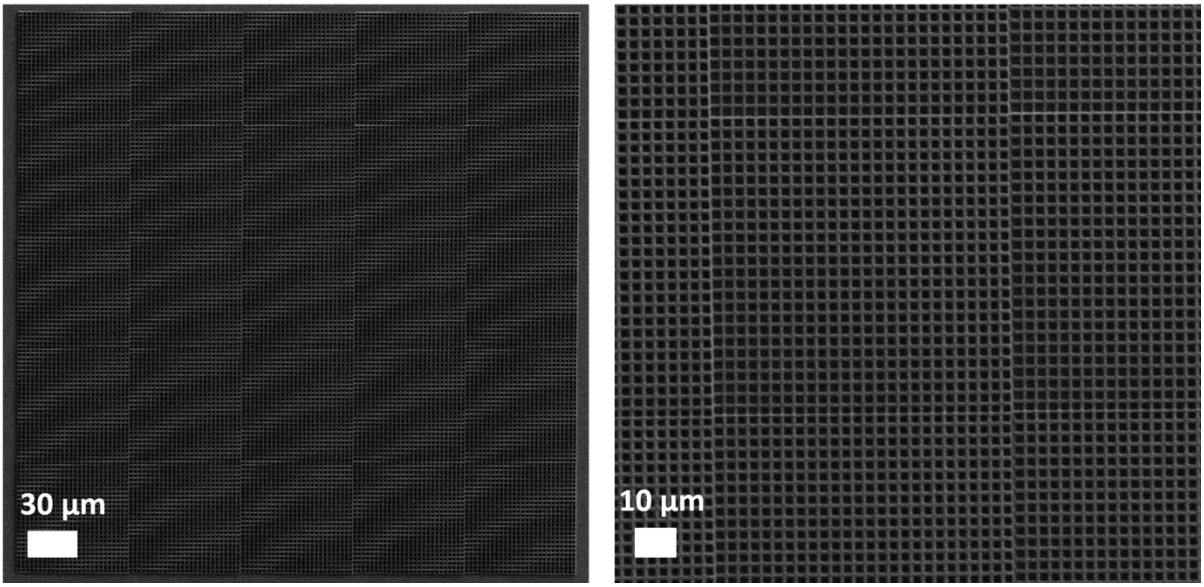

Figure S6: SEM images of multiple two-photon polymerised templates 'stitched' together to form a large 390 × 390 µm template.

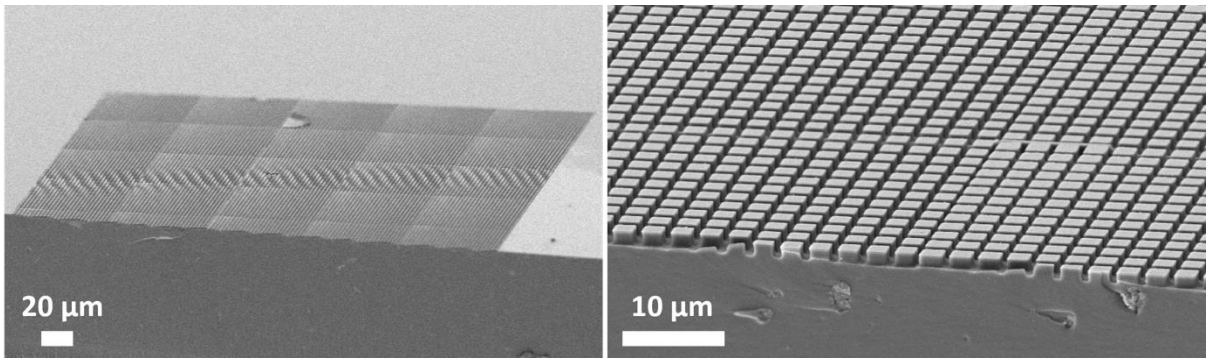

Figure S7: SEM images of large arrays of pillars replicated using **10%PH** from the large 390 × 390 µm template *via* NIL.

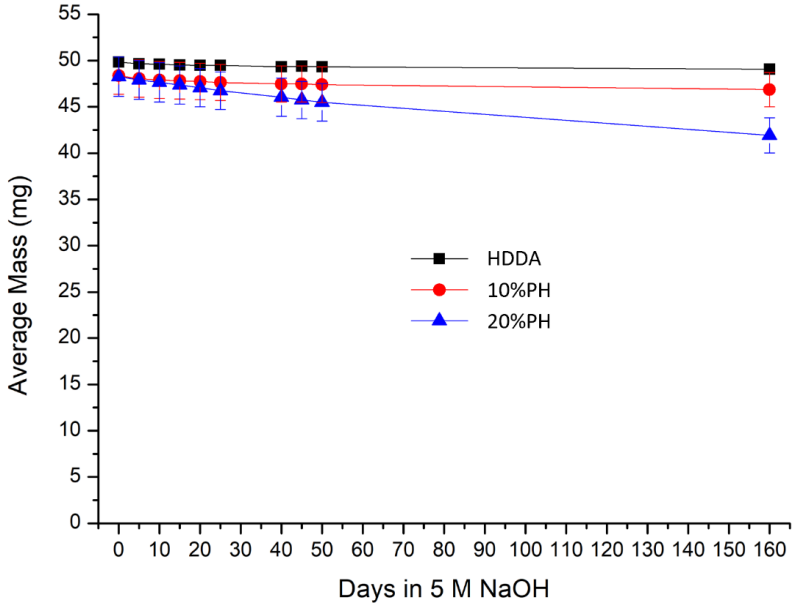

Figure S8: Average mass vs days in 5 M NaOH of bulk samples of HDDA control (black), **10%PH** (red), and **20%PH** (blue).

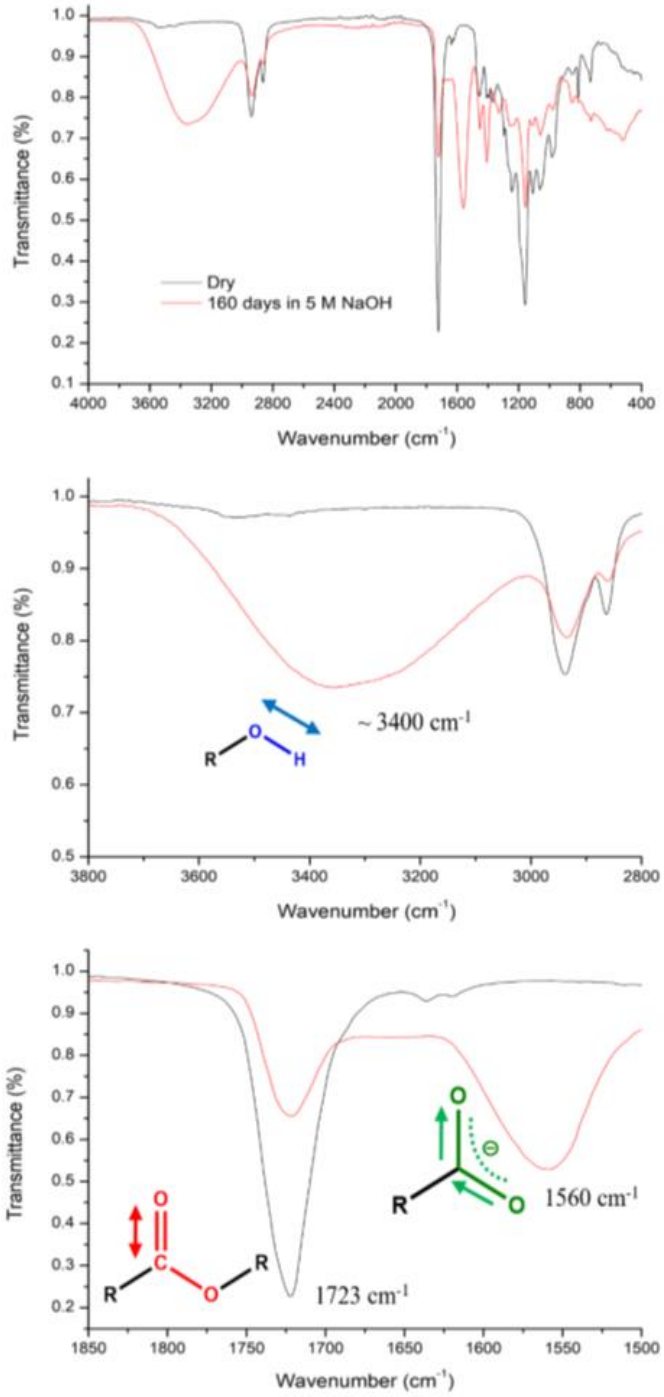

Figure S9: FTIR spectra of **20%PH** containing 1 % w/w PBPO before degradation in 5 M NaOH (dry) and after degradation for 160 days in 5 M NaOH. The full spectra are shown (top) as well as a close up of the regions peaks centred at 3400 cm^{-1} which described the stretching of the OH bonds (middle) and 1723 cm^{-1} and 1560 cm^{-1} related to the stretching of C=O bonds and carboxylate anions, respectively (bottom).

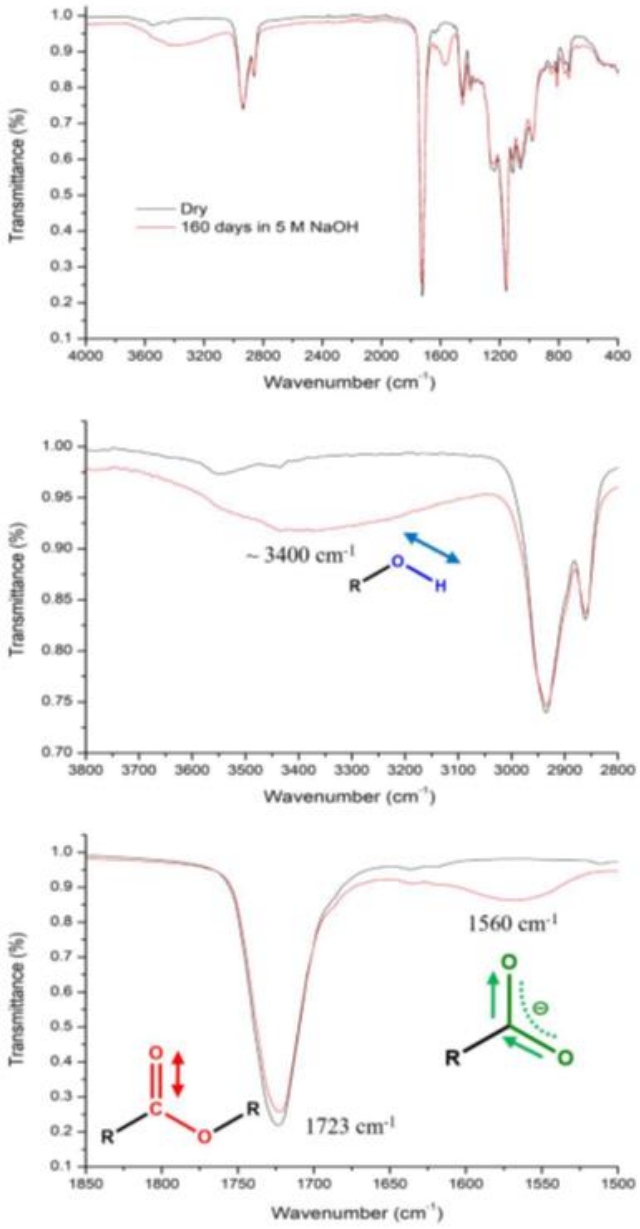

Figure S10: FTIR spectra of **10%PH** containing 1 % w/w PBPO before degradation in 5 M NaOH (dry) and after degradation for 160 days in 5 M NaOH. The full spectrum is shown (top) as well as a close up of the regions peaks centred at 3400 cm^{-1} which described the stretching of the OH bonds (middle) and 1723 cm^{-1} and 1560 cm^{-1} related to the stretching of C=O bonds and carboxylate anions, respectively (bottom).

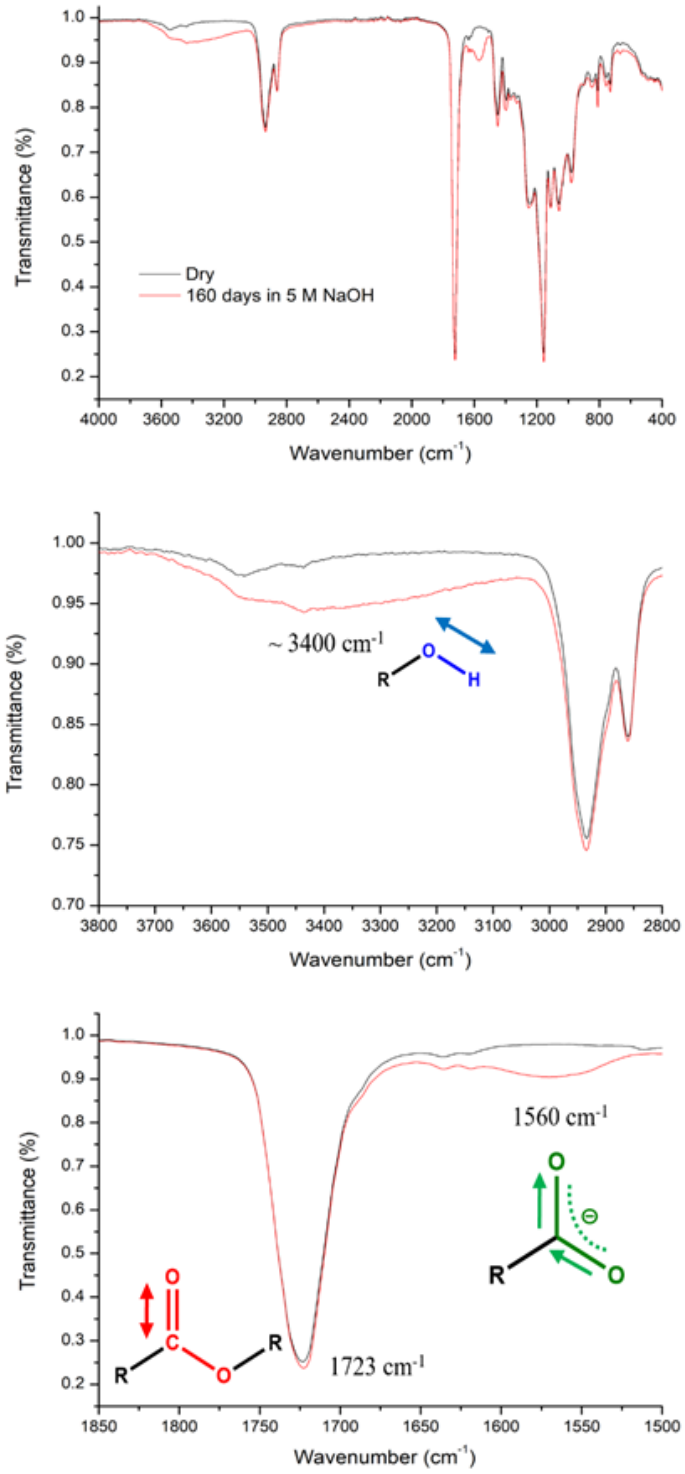

Figure S11: FTIR spectra of neat HDDA containing 1 % w/w PBPO before degradation in 5 M NaOH (dry) and after degradation for 160 days in 5 M NaOH. The full spectrum is shown (top) as well as a close up of the regions peaks centred at 3400 cm^{-1} which described the stretching of the OH bonds (middle) and 1723 cm^{-1} and 1560 cm^{-1} related to the stretching of C=O bonds and carboxylate anions, respectively (bottom).

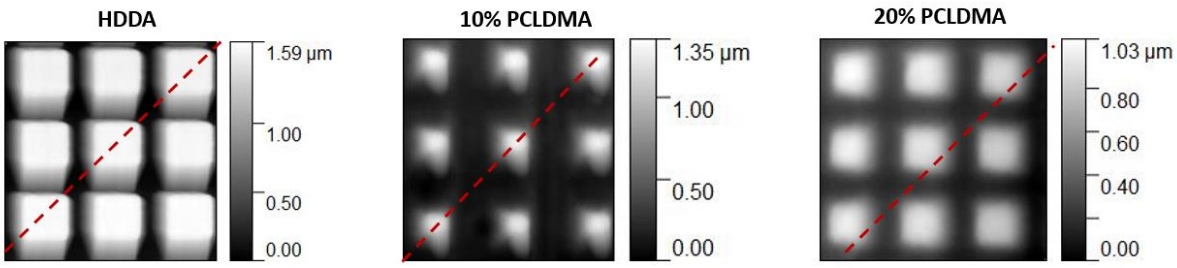

Figure S12: Atomic force height images of 2x2x2 µm samples, shows traces used to give height profiles in **Figure 5**. From left to right: HDDA, **10%PH** and **20%PH**, all after 5 days NaOH exposure.