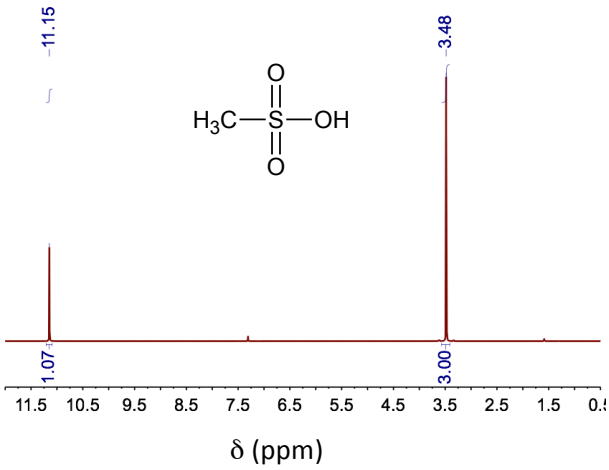
Supplementary Information of the Manuscript entitled

Eutectic Mixtures as Bifunctional Catalysts in the Low-Temperature-Synthesis of Polycaprolactone

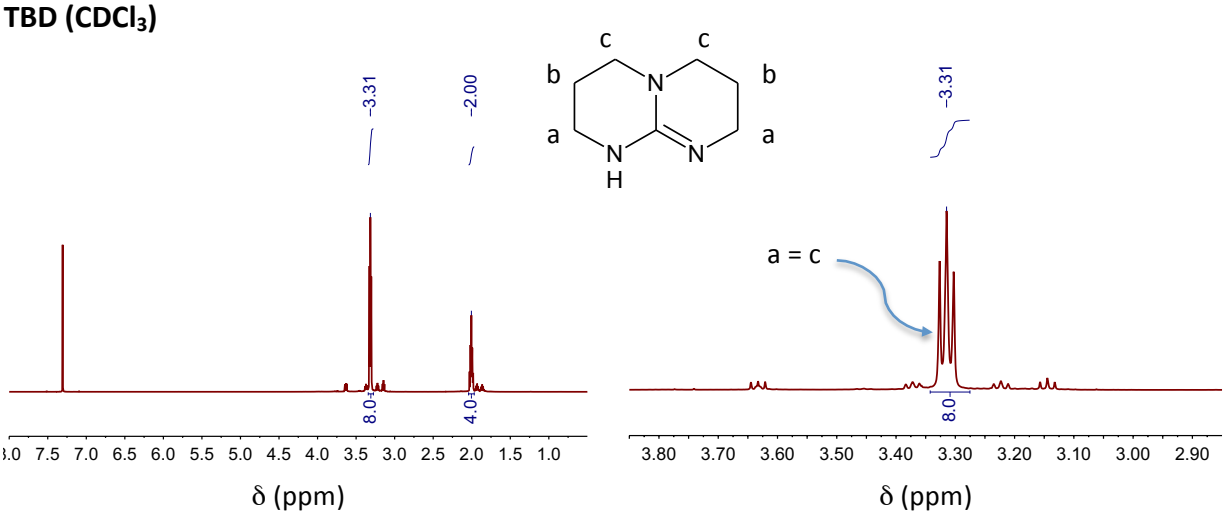
by Sara García-Argüelles et al.

Figure S1: ^{1}H NMR spectra of the components that form the DESs (e.g. TBD and $MeSO_3H$) and of the TBD:$MeSO_3H$ mixtures with 0.1:1.5 and 0.5:1.5 molar ratios.

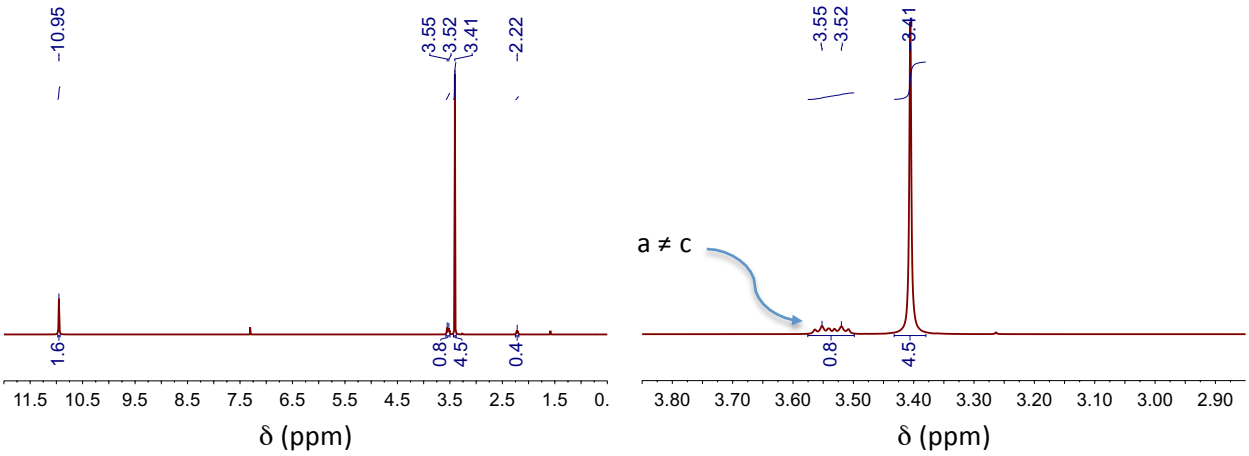
$MeSO_3H$ ($CDCl_3$)



TBD ($CDCl_3$)



DES 0.1:1.5



DES 0.5:1.5

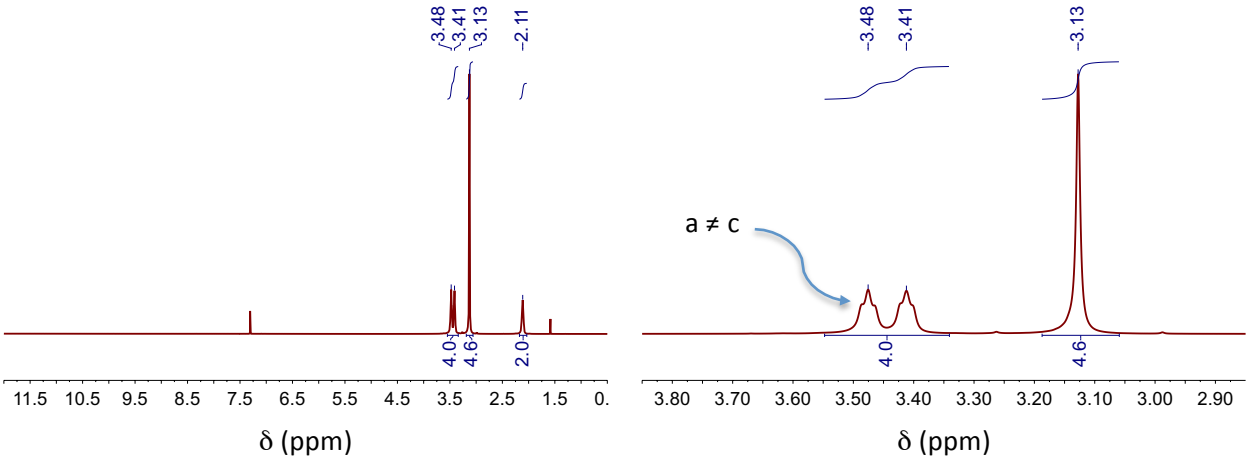


Figure S2: DSC scan of the eutectic TBD:$MeSO_3H$ mixture with a molar ratio of 0.05:1.5.

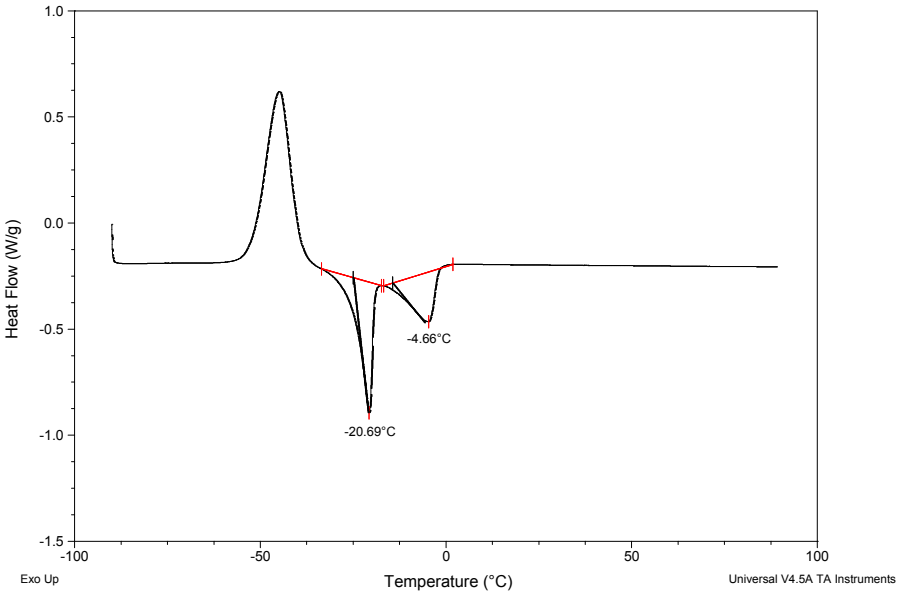


Figure S3: GPC separation of the PCLs obtained in this work with initiator (a) and without initiator (b).

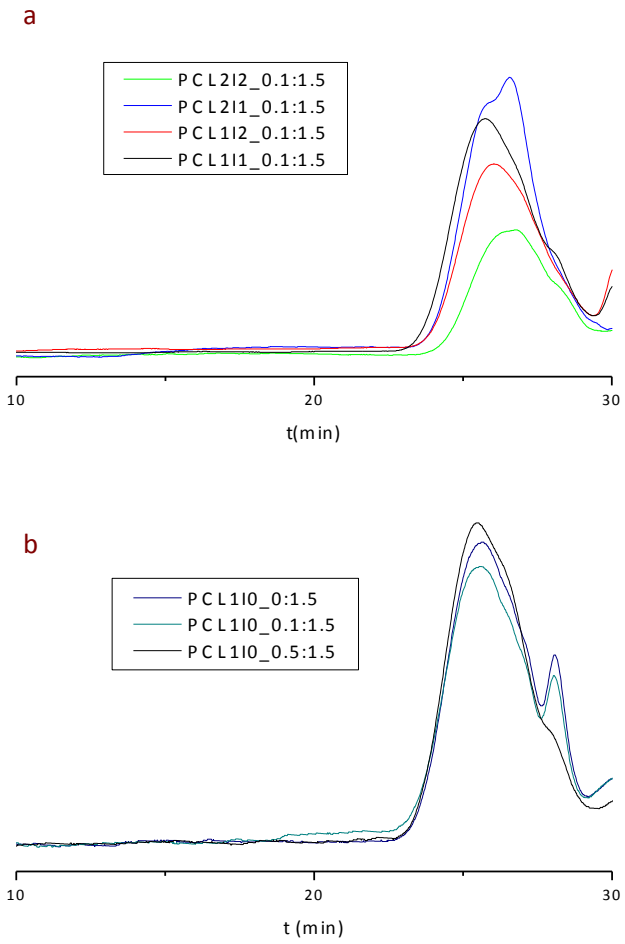


Table S1: ^{1}H NMR chemical shifts (δ, in ppm) of different PCLs obtained with initiator.

Set 1	e-caprolactone	Polycaprolactone						Initiator	
	-CO-O-CH_2-	-CO-O-CH_2- (f)	H-O-CH_2- (q)	Ph-CH_2-O-CO-CH_2- (b)	-O-CO-CH_2- (h)	-CH_2-CH_2-CH_2-O- (d,e)	-O-CO-CH_2-CH_2- (I)	Ph-CH_2-O-CO-	Ph-CH_2-O-CO-
PCL1I1_0.1:1.5	4.25	4.09	3.68	2.39	2.34	1.68	1.42	7.38	5.15
PCL1I2_0.1:1.5	4.26	4.10	3.69	2.40	2.34	1.69	1.42	7.39	5.15
PCL2I1_0.1:1.5	4.24	4.09	3.68	2.39	2.34	1.69	1.42	7.38	5.15
PCL2I2_0.1:1.5	4.26	4.10	3.69	2.40	2.34	1.69	1.42	7.39	5.15

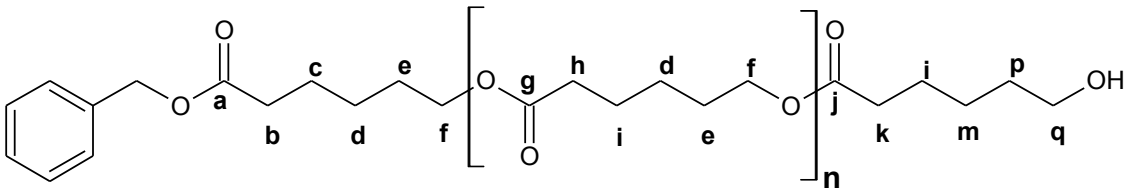


Table S2: ^{1}H NMR chemical shifts (δ, in ppm) of different PCLs obtained without initiator.

Set 2	e-caprolactone	Polycaprolactone					
	-CO-O-CH_2-	-CO-O-CH_2- (f)	H-O-CH_2- (q)	H-O-CO-CH_2- (b)	-O-CO-CH_2- (h)	-CH_2-CH_2-CH_2-O- (d,e)	-O-CO-CH_2-CH_2- (I)
PCL1I0_0.1:1.5	4.26	4.10	3.69	2.40	2.36	1.69	1.42
PCL1I0_0.5:1.5	4.24	4.10	3.69	2.40	2.34	1.69	1.42
PCL1I0_0:1.5	4.26	4.10	3.69	2.40	2.34	1.69	1.42

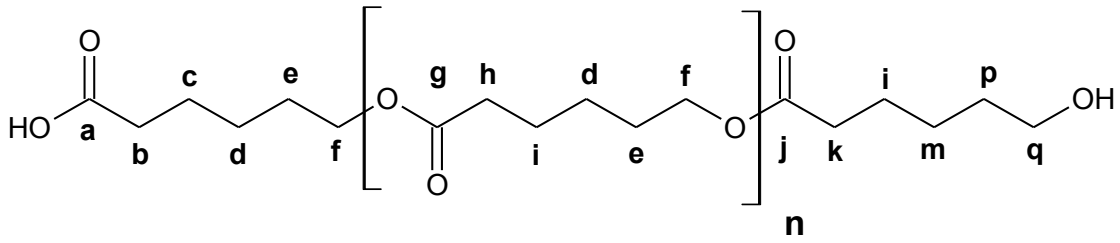
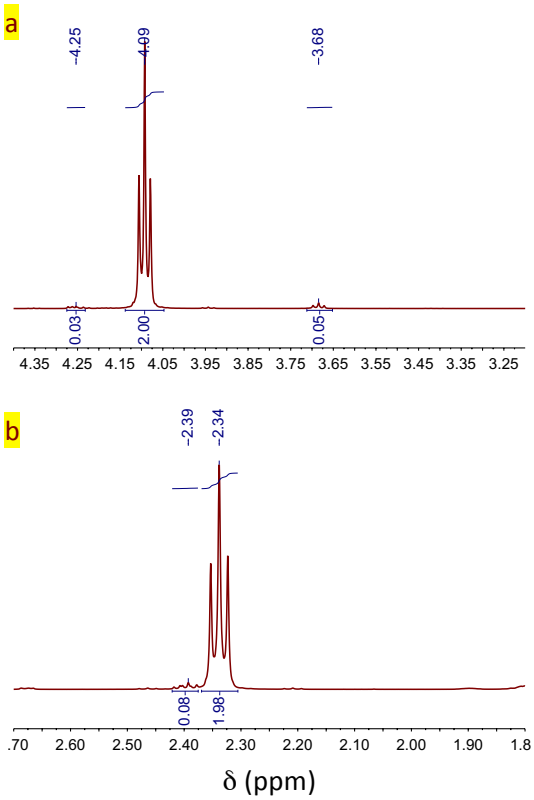
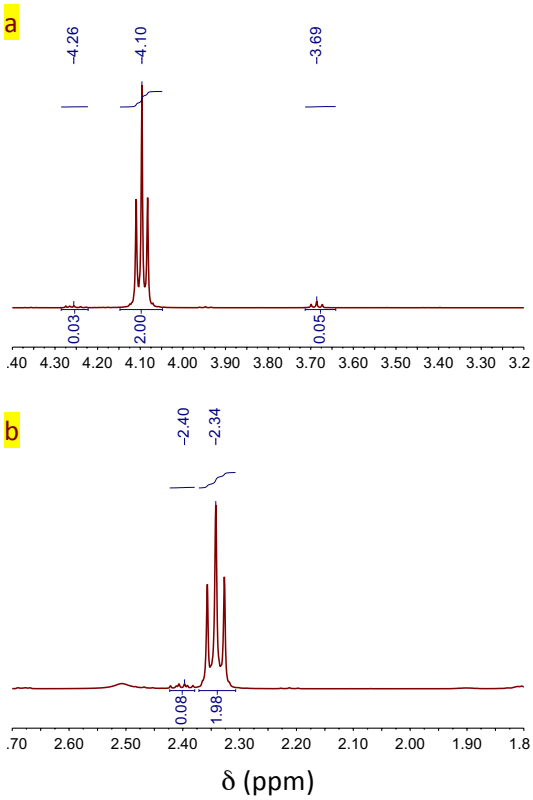


Figure S4: Details of the ^{1}H NMR spectra of different PCLs obtained with initiator depicted in Figure S2 for better visualization of peaks ascribed to terminal methylene groups; (a) at ca. 3.7 ppm for those bonded to hydroxyl groups and (b) at ca. 2.4 ppm for those bonded to carboxylic groups.

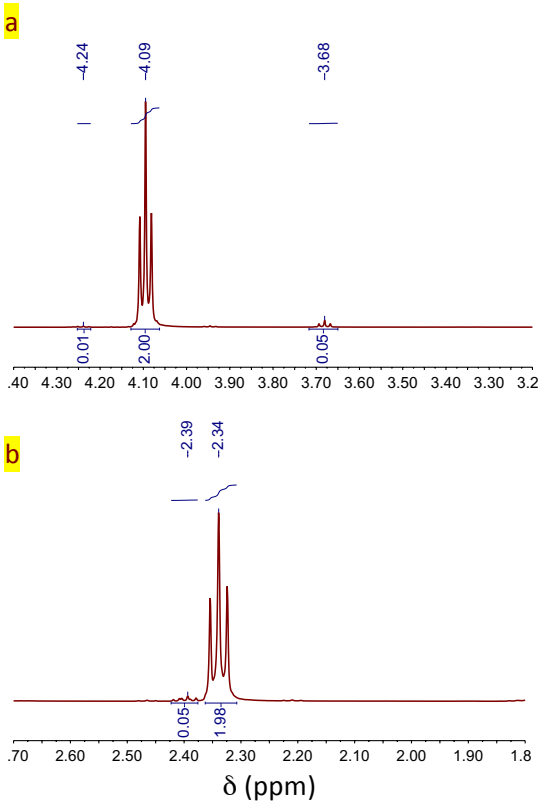
PCL1I1_0.1:1.5



PCL1I2_0.1:1.5



PCL2I1_0.1:1.5



PCL2I2_0.1:1.5

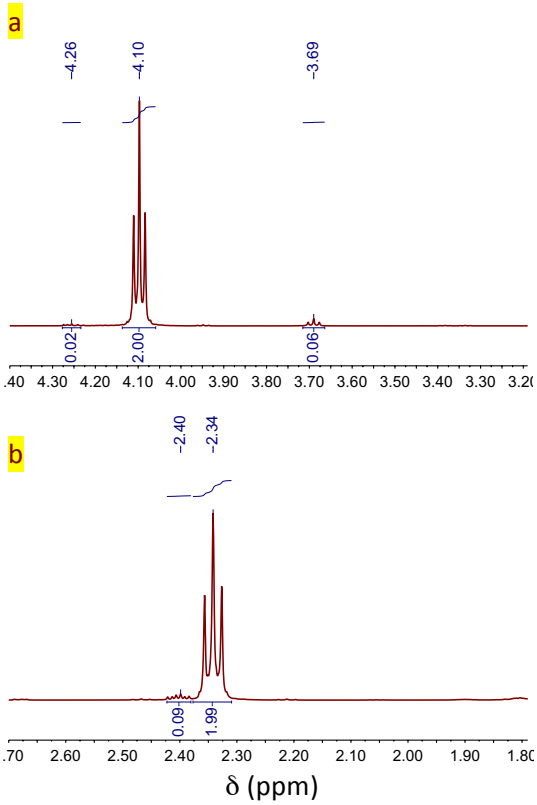
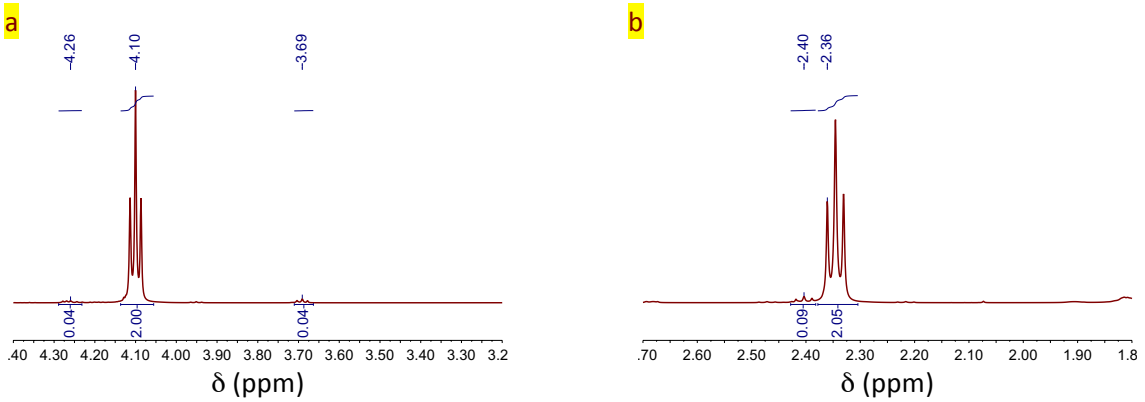
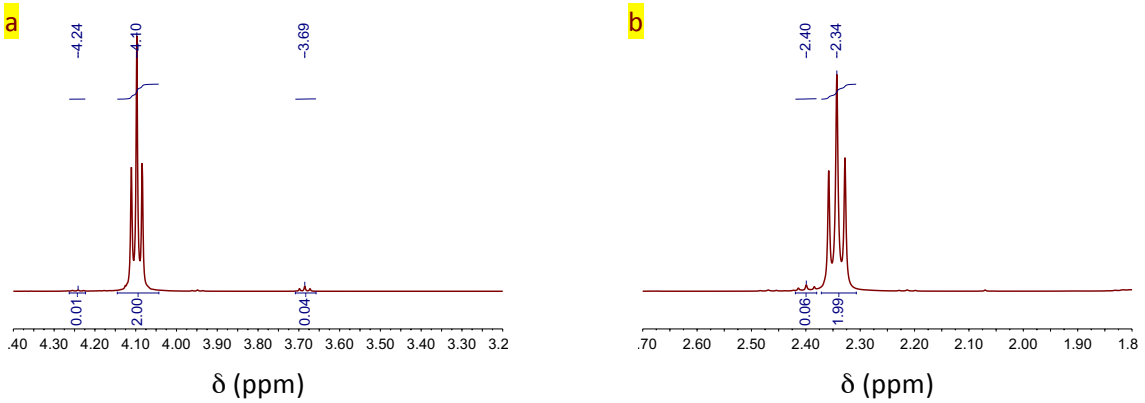


Figure S5: Details of the ^{1}H NMR spectra of different PCLs obtained with initiator depicted in Figure S2 for chemical shifts ranging from (a) 3.20 to 4.40 ppm and (b) from 2.0 to 2.75 ppm.

PCL1I0_0.1:1.5



PCL1I0_0.5:1.5



PCL1I0_0:1.5

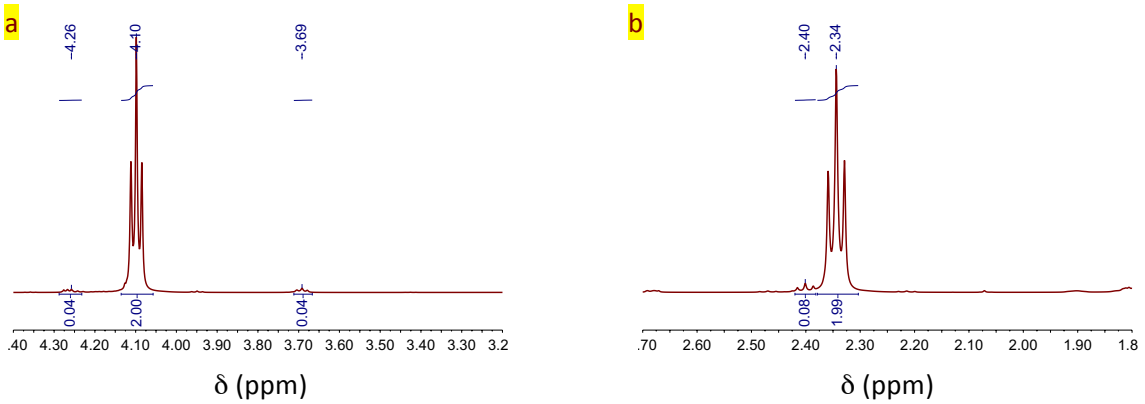


Figure S6: DSC scans – 1st and 2nd runs – of PCLs synthesized as described in Table 1.

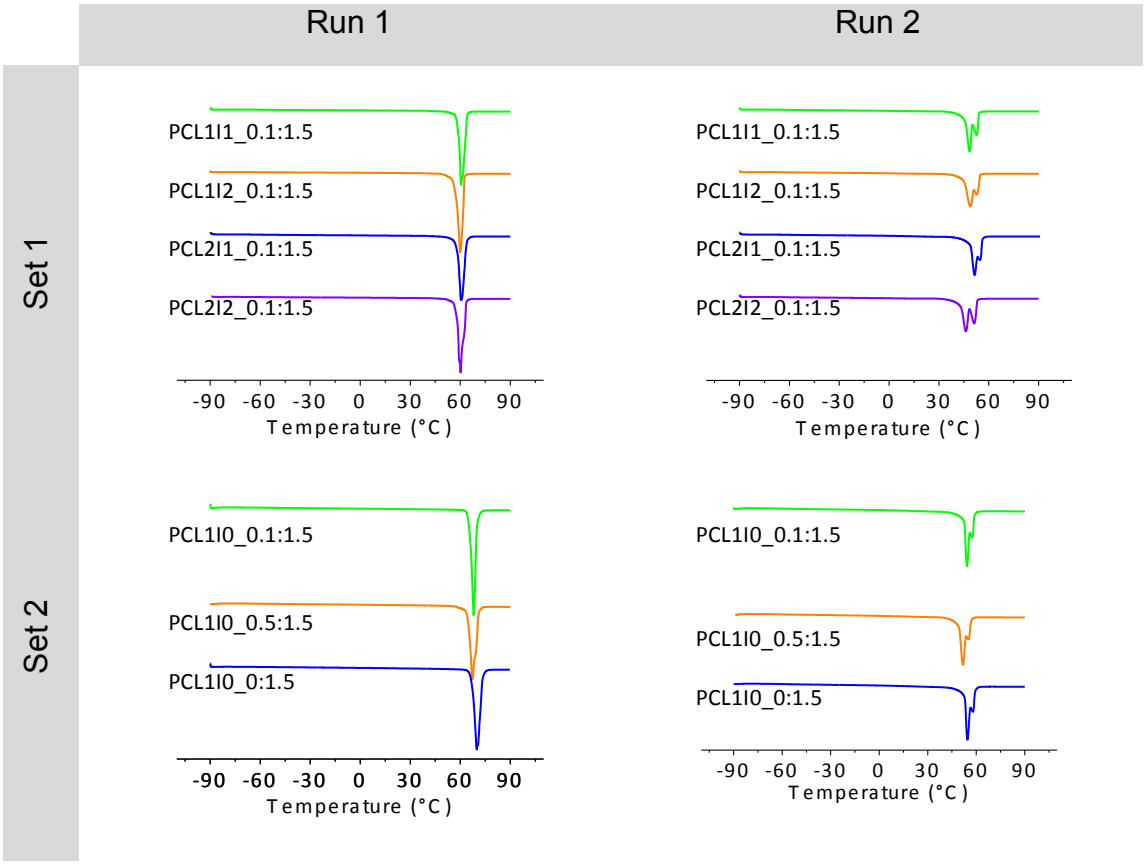


Figure S7: XRD of PCLs synthesized as described in Table 1.