

†Electronic Supplementary Information (ESI)

Synthesis and cellular compatibility of multi-block biodegradable poly(ϵ -caprolactone)-based polyurethanes

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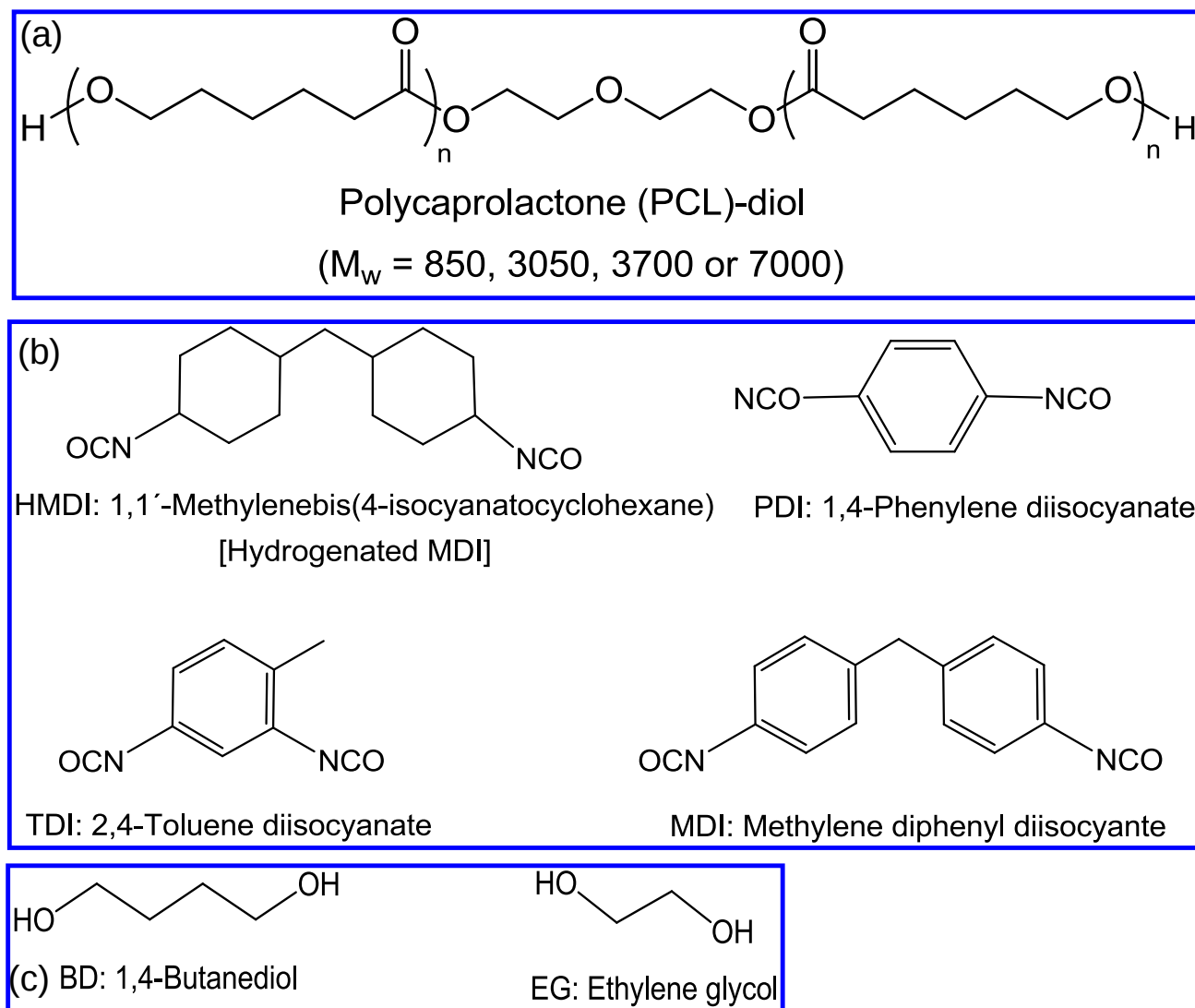


Figure S1. Chemical structure of poly(ϵ -caprolactone)(PCL)-diol (a), diisocyanates (b) and chain extenders (c) used for the synthesis of PUs.

FTIR Analysis

The structural characterisation of all copolymers (PUs) was performed by FTIR analysis. FTIR spectra of the polyurethane (PU) copolymers showed broad characteristic absorption peak at $3300 - 3450\text{ cm}^{-1}$ corresponding to —NH vibration, and the exact peak position varied, for example peak was at 3342 cm^{-1} for PU3 and 3325 cm^{-1} for PU10 (Figure S2). The variation of the peak position of —NH vibration is attributed to the strength of the H-bonding formation as reported by Zhu et al (*Acta Biomaterialia* 2009, 5, 3346) and Lee et al (*Macromolecules* 1987, 21, 270). The absorption bands at 2943 cm^{-1} and 2864 cm^{-1} attributed to the assymetric and symmetric $\text{—CH}_2\text{—}$ groups. While showing very strong absorption bands in the range of between $1600 - 1800\text{ cm}^{-1}$ with a peak maximum at about 1722 cm^{-1} and 1683 cm^{-1} (for all PUs) which were assigned to —C=O groups. The bands at 1600 cm^{-1} and 1106 cm^{-1} were responsible for aromatic and —C—O—C— groups, respectively.

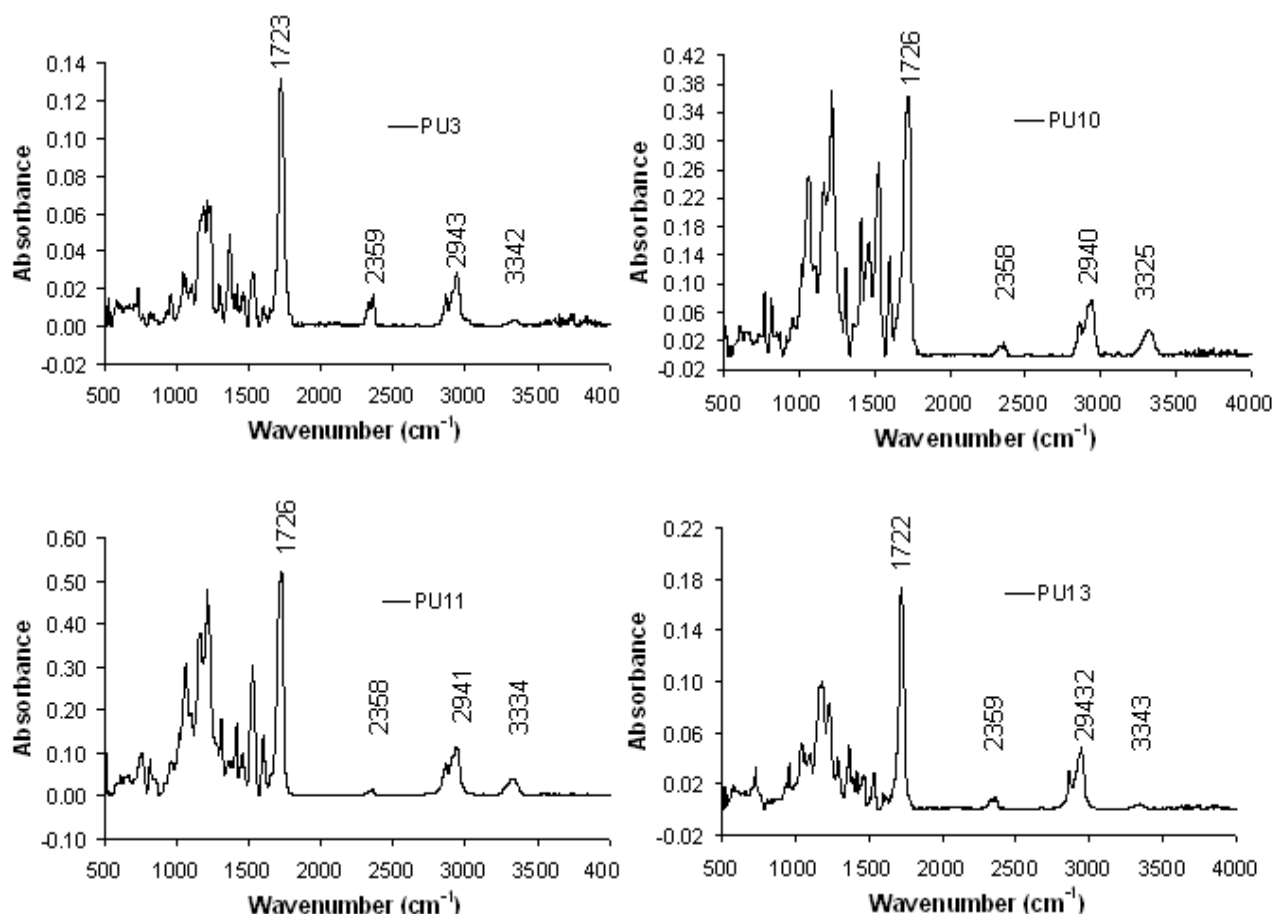


Figure S2. Representative examples of FTIR spectra of four copolymers are showing the absorption bands.

Table S1. Details analysis of all PUs shows the glass transitions, melting transitions, heat capacity, heat of fusion and their qualitative assessment.

PU	Composition	Glass Transition				Width/°C	Melting Transitions				Width/°C	Other Transitions	Colour	Mechanical Strength	PCL-diol		Diisocyanate			Chain Extender		
		Onset/°C	Midpoint/°C	Offset/°C	$\Delta C_p/Jg^{-1}^{\circ}C^{-1}$		Onset/°C	Maximum/°C	Offset/°C	$\Delta H_m/Jg^{-1}$					M _w /gmol ⁻¹	Equivalents	Name	M _w /gmol ⁻¹	Equivalents	Name	M _w /gmol ⁻¹	Equivalents
PU1	PCL850-MDI	-10	-6	-3	0.391	7	-	-	-	-	-	-	Moderate Yellow	Soft, Sticky	850	0.485	MDI	250.25	0.515	-	0	0
PU2	PCL850-MDI-BD	-10	-6	-3	0.395	7	-	-	-	-	-	-	Light Yellow	Hard	850	0.25	MDI	250.25	0.52	1,4 BD	90.12	0.23
PU3	PCL850-MDI-BD	-1	7	15	0.461	16	-	-	-	-	-	-	Moderate Yellow	Soft, Brittle	850	0.25	MDI	250.25	0.52	1,4 BD	62.07	0.23
PU4	PCL850-MDI-EG	-13	-5	3	0.501	16	-	-	-	-	-	$T_g = 47/57/58 - 0.163$	Moderate Yellow	Hard	850	0.25	MDI	250.25	0.52	EG	62.07	0.23
PU5	PCL850-MDI-EG	-2	8	19	0.420	21	-	-	-	-	-	-	Moderate Yellow	Hard	850	0.25	MDI	250.25	0.52	EG	62.07	0.23
PU6	PCL850-PDI	-77	-69	-59	0.277	18	16	55	73	80.0	57	-			850	0.485	PDI	160.1	0.515	-	0	0
PU7	PCL850-PDI-BD	-80	-68	-64	0.239	16	4	45	67	56.2	63	-			850	0.25	PDI	160.1	0.52	1,4 BD	90.12	0.23
PU8	PCL850-PDI-EG	-73	-59	-49	0.259	24	9	56	79	68.3	70	-			850	0.25	PDI	160.1	0.52	EG	62.07	0.23
PU9	PCL850-TDI	-42	-27	-25	0.493	17	-	-	-	-	-	-	Brown	Soft, Sticky	850	0.485	TDI	174.2	0.515	-	0	0
PU10	PCL850-TDI-BD	-53	-39	-25	0.517	28	-	-	-	-	-	-	Brown	Liquid	850	0.25	TDI	174.2	0.52	1,4 BD	90.12	0.23
PU11	PCL850-TDI-EG	-25	-17	-14	0.563	11	-	-	-	-	-	-	Orange	Soft, Sticky	850	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU12	PCL850-TDI-EG	-32	-22	15	0.690	47	-	-	-	-	-	-	Orange	Soft, Sticky	850	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU13	PCL850-TDI-EG	-25	-17	10	0.666	35	-	-	-	-	-	-	Orange	Soft, Sticky	850	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU14	PCL850-TDI-EG	-10	-3	0	0.289	10	-	-	-	-	-	$T_g = 93/102/114 - 0.137$	Orange	Soft, Sticky	850	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU15	PCL850-TDI-EG	-18	-10	5	0.561	23	-	-	-	-	-	-	Orange	Soft, Sticky	850	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU16	PCL850-HMDI	-	-	-	-	-	-18	29	84	15.1	102	$T_m = -60/-56/-44 - 6.65$	Light Yellow	Soft, Sticky	850	0.485	HMDI	262.34	0.515	-	0	0
PU17	PCL850-HMDI-BD	-46	-41	-36	0.548	10	9	45	84	9.5	75	-	Off-White	Soft, Brittle	850	0.25	HMDI	262.34	0.52	1,4 BD	90.12	0.23
PU18	PCL850-HMDI-EG	-50	-47	-43	0.321	7	23	39	59	25.2	36	$T_g = -2/8/12 - 0.159$	Moderate Yellow	Hard	850	0.25	HMDI	262.34	0.52	EG	62.07	0.23
PU19	PCL850-HMDI-EG	-47	-40	-34	0.401	13	-3	34	68	16.8	71	-	Light Yellow	Soft, Brittle	850	0.25	HMDI	262.34	0.52	EG	62.07	0.23
PU20	PCL3050-MDI	-57	-53	-52	0.054	5	26	50	67	60.4	41	-			3050	0.485	MDI	250.25	0.515	-	0	0
PU21	PCL3050-MDI	-42	-35	-27	0.214	15	22	43	76	33.9	54	-	Orange	Soft, Brittle	3050	0.485	MDI	250.25	0.515	-	0	0
PU22	PCL3050-MDI-BD	-67	-57	-48	0.338	19	-12	40	59	46.6	71	-	Orange	Soft, Brittle	3050	0.25	MDI	250.25	0.52	1,4 BD	90.12	0.23
PU23	PCL3050-MDI-BD	-68	-59	-52	0.186	16	19	58	83	75.5	64	-	Orange	Soft, Brittle	3050	0.25	MDI	250.25	0.52	1,4 BD	90.12	0.23
PU24	PCL3700-MDI-BD	-50	-40	-31	0.307	19	23	45	60	52.9	37	-	Moderate Yellow	Hard	3700	0.25	MDI	250.25	0.52	1,4 BD	90.12	0.23
PU25	PCL3050-MDI-EG	-56	-50	-45	0.104	11	14	49	65	44.6	51	-			3050	0.25	MDI	250.25	0.52	EG	62.07	0.23
PU26	PCL3700-MDI	-56	-52	-45	0.125	11	13	53	94	59.1	81	-			3700	0.485	MDI	250.25	0.515	-	0	0
PU27	PCL3700-MDI	-52	-44	-35	0.092	17	19	70	118	31.9	99	-			3700	0.485	MDI	250.25	0.515	-	0	0
PU28	PCL3700-MDI	-54	-46	-39	0.183	15	23	56	80	50.7	57	-	Moderate Yellow	Hard	3700	0.485	MDI	250.25	0.515	-	0	0
PU29	PCL3700-MDI	-50	-44	-36	0.209	14	25	52	75	46.4	50	-			3700	0.485	MDI	250.25	0.515	-	0	0
PU30	PCL3700-MDI	-52	-48	-32	0.155	20	15	47	65	34.8	50	$T_c = -10/-21/1 - 4.328$			3700	0.325	MDI	250.25	0.675	-	0	0
PU31	PCL3700-MDI-EG	-66	-60	-53	0.158	13	25	58	77	75.6	52	-	Off-White	Soft, Brittle	3700	0.25	MDI	250.25	0.52	EG	62.07	0.23

Table S1. Continue

PU	Composition	Glass Transition				Width/°C	Melting Transitions				Width/°C	Other Transitions	Colour	Mechanical Strength	PCL-diol		Diisocyanate			Chain Extender		
		Onset/°C	Midpoint/°C	Offset/°C	$\Delta C_p/Jg^{-1}^{\circ}C^{-1}$		Onset/°C	Maximum/°C	Offset/°C	$\Delta H_m/Jg^{-1}$					$M_w/gmol^{-1}$	Equivalent s	Name	$M_w/gmol^{-1}$	Equivalents	Name	$M_w/gmol^{-1}$	Equivalents
PU32	PCL3700-PDI	-65	-60	-51	0.170	14	28	62	85	72.0	57	-			3700		PDI	160.1		-	0	
PU33	PCL3700-PDI-BD	-75	-65	-59	0.173	16	25	46	64	50.5	39	-			3700		PDI	160.1		1,4 BD	90.12	
PU34	PCL3700-PDI-EG	-55	-48	-40	0.193	15	23	53	81	57.5	58	-			3700		PDI	160.1		EG	62.07	
PU35	PCL3700-HMDI	-64	-59	-53	0.216	11	25	53	69	62.5	44	-	Off-White	Soft, Brittle	3700	0.485	HMDI	262.34	0.515	-	0	0
PU36	PCL3700-HMDI-BD	-60	-58	-50	0.179	10	25	46	64	67.2	39	-	Light Yellow	Hard	3700	0.25	HMDI	262.34	0.52	1,4 BD	90.12	0.23
PU37	PCL3700-HMDI-EG	-60	-56	-50	0.165	10	27	54	69	67.2	42	-	Off-White	Hard	3700	0.25	HMDI	262.34	0.52	EG	62.07	0.23
PU38	PCL3700-TDI	-59	-53	-46	0.158	13	26	57	75	73.4	49	-	Orange	Soft, Brittle	3700	0.485	TDI	174.2	0.515	-	0	0
PU39	PCL3700-TDI-BD	-50	-44	-37	0.189	13	26	50	72	61.0	46	-	Orange	Hard	3700	0.25	TDI	174.2	0.52	1,4 BD	90.12	0.23
PU40	PCL3700-TDI-EG	-51	-45	-37	0.300	14	24	49	62	60.6	38	-	Orange	Hard	3700	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU41	PCL7000-MDI	-58	-53	-47	0.132	11	21	55	78	65.7	57	-	Orange	Soft, Brittle	7000	0.485	MDI	250.25	0.515	-	0	0
PU42	PCL7000-MDI	-51	-47	-39	0.160	12	18	52	73	55.4	55	-	Moderate Yellow	Hard	7000	0.325	MDI	250.25	0.675	-	0	0
PU43	PCL7000-MDI-BD	-57	-59	-45	0.193	12	16	51	62	52.4	46	-	Moderate Yellow	Soft, Brittle	7000	0.25	MDI	250.25	0.52	1,4 BD	90.12	0.23
PU44	PCL7000-MDI-BD	-48	-40	-28	0.267	20	18	48	74	45.4	56	-	Light Yellow	Hard	7000	0.25	MDI	250.25	0.52	1,4 BD	90.12	0.23
PU45	PCL7000-MDI-EG	-59	-53	-44	0.168	15	17	54	74	68.3	57	-			7000	0.25	MDI	250.25	0.52	EG	62.07	0.23
PU46	PCL7000-MDI-EG	-54	-48	-36	0.252	18	21	53	70	60.7	49	-	Moderate Yellow	Soft, Brittle	7000	0.25	MDI	250.25	0.52	EG	62.07	0.23
PU47	PCL7000-MDI-EG	-53	-49	-41	0.146	12	20	53	72	58.0	52	-	Moderate Yellow	Hard	7000	0.25	MDI	250.25	0.52	EG	62.07	0.23
PU48	PCL7000-PDI-BD	-72	-59	-53	0.190	19	25	55	77	85.6	52	-			7000		PDI	160.1		BD	90.12	
PU49	PCL7000-PDI-EG	-77	-64	-53	0.298	24	21	55	74	86.0	53	-			7000	0.25	MDI	250.25	0.515	EG	62.07	0.23
PU50	PCL7000-TDI	-61	-56	-49	0.155	12	21	55	81	74.3	60	-	Moderate Yellow	Soft, Brittle	7000	0.485	TDI	174.2	0.515	-	0	0
PU51	PCL7000-TDI	-61	-57	-48	0.148	13	15	57	85	66.0	70	-	Moderate Yellow	Hard	7000	0.325	TDI	174.2	0.675	-	0	0
PU52	PCL7000-TDI-BD	-53	-46	-33	0.269	20	-1	49	72	52.8	73	-	Orange	Hard	7000	0.25	TDI	174.2	0.52	1,4 BD	90.12	0.23
PU53	PCL7000-TDI-BD	-55	-49	-41	0.202	14	29	51	69	55.7	40	-	Moderate Yellow	Soft, Brittle	7000	0.25	TDI	174.2	0.52	1,4 BD	90.12	0.23
PU54	PCL7000-TDI-EG	-62	-50	-44	0.229	18	31	58	75	70.6	44	-	Light Yellow	Soft, Brittle	7000	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU55	PCL7000-TDI-EG	-53	-48	-41	0.177	12	23	58	77	57.1	54	-	Moderate Yellow	Liquid	7000	0.25	TDI	174.2	0.52	EG	62.07	0.23
PU56	PCL7000-HMDI	-62	-60	-51	0.152	11	23	55	75	64.1	52	-	Light Yellow	Soft, Brittle	7000	0.485	HMDI	262.34	0.515	-	0	0
PU57	PCL7000-HMDI	-60	-58	-50	0.161	10	19	51	66	58.9	47	-	Off-White	Hard	7000	0.325	HMDI	262.34	0.675	-	0	0
PU58	PCL7000-HMDI-BD	-62	-58	-50	0.106	12	26	58	79	44.8	53	-	Moderate Yellow	Liquid	7000	0.25	HMDI	262.34	0.52	1,4 BD	90.12	0.23
PU59	PCL7000-HMDI-BD	-60	-57	-53	0.100	7	24	51	69	61.0	45	-	Light Yellow	Hard	7000	0.25	HMDI	262.34	0.52	1,4 BD	90.12	0.23
PU60	PCL7000-HMDI-EG	-66	-59	-52	0.244	14	29	59	76	78.5	47	$T_g = -8/-4/-1 - 0.284$	Light Yellow	Soft, Brittle	7000	0.25	HMDI	262.34	0.52	EG	62.07	0.23
PU61	PCL7000-HMDI-EG	-65	-57	-49	0.251	16	29	59	77	82.1	48	-	Light Yellow	Hard	7000	0.25	HMDI	262.34	0.52	EG	62.07	0.23

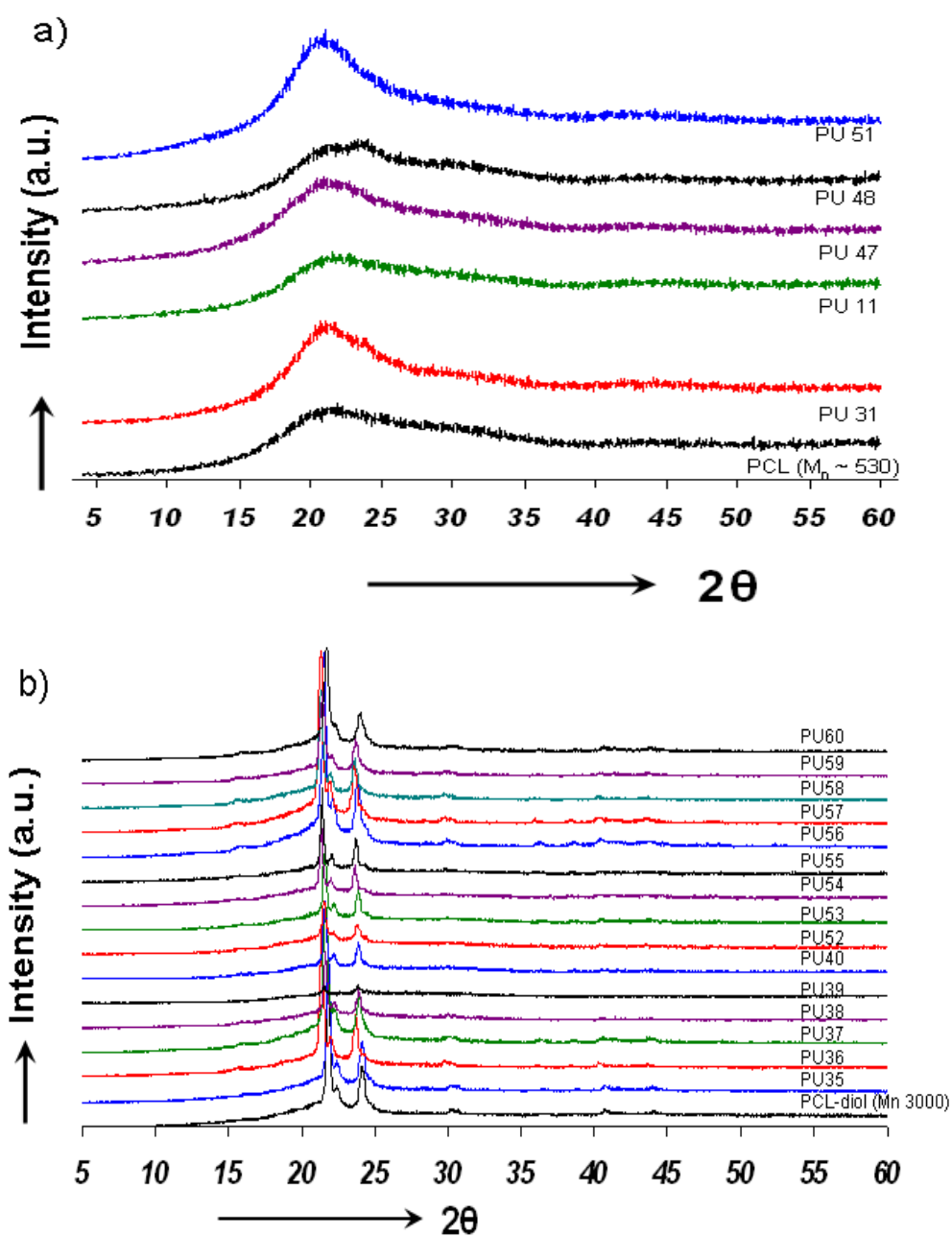


Figure S3. Wide-angle x-ray diffraction (WAXRD) spectra of a series of amorphous and semi-crystalline PU copolymers synthesised with PCL-diols. (a) Spectra of different PU's synthesized with PCL-diol of $M_n = 530$ and $M_w = 850$ Da, show amorphous broad band. (b) Spectra of several polyurethanes synthesized with higher molecular weights (PCL-diol of $M_n = 3000$ Da and $M_w = 7000$ Ds), show resolved crystalline peaks.