Electronic Supplementary Information (ESI)

Supplementary Table S1

Table S1. The mechanical properties and thermal properties for various WDPU (measured from bulk films).

Abbrev of WDPU	Mechanical properties (25°C)			T_{onset} (°C)	T_d (°C)	T_g (°C)		
	Young's modulus (MPa)	Tensile strength (MPa)	Elongation (%)			DMA (tan δ)	DMA (*E''*)	DSC
PCL100	10.0 ± 1.1	26.1 ± 2.7	778.3 ± 50.8	266.0	372.2	-39.0	-47.1	-52.0
PCL80EB20	24.3 ± 4.1	32.3 ± 6.5	537.4 ± 5.6	261.7	366.1	-35.1	-44.1	-47.3
PCL60EB40	33.4 ± 3.8	26.7 ± 5.9	520.3 ± 7.7	263.1	371.3	-34.7	-38.1	-49.8
PCL40EB60	16.0 ± 1.1	16.4 ± 0.4	619.5 ± 4.1	270.0	387.0	-32.7	-37.1	-44.9
PCL80LL20	23.2 ± 1.6	28.0 ± 3.4	581.1 ± 4.2	236.9	343.2	-19.6	-24.5	-54.5
PCL60LL40	35.0 ± 11.0	14.0 ± 0.4	405.1 ± 7.9	219.9	321.0	-15.5	-23.6	-46.6
PCL40LL60	125.4 ± 9.9	11.0 ± 0.8	282.1 ± 17.0	238.7	301.3	-6.5	-13.9	-33.2
PCL80DL20	4.6 ± 0.7	12.6 ± 3.9	655.5 ± 17.5	237.1	334.7	-18.5	-24.2	-60.8

* T_g evaluation based on maximum *E''* is recommended by ASTM D 4065-2001.

Thermal behavior: T_g values determined from DSC (–60.8 to –33.2°C) were lower han those from DMA (–47.1 to –6.5°C) and considered less proper to describe for PU in general. PCL40LL60 exhibited the highest T_g and PCL100 showed the lowest T_g, based on DMA. All T_g values were well below zero, typical of elastomers. No melting peak (T_m) was clearly observed in DSC analysis (Figure S3a) for most WDPU. For PCL80LL20, the peak was very small (low-crystalline ~3%). XRD analysis is provided in Figure S3b. PCL80LL20 was low-crystalline (~7%), consistent with DSC data. Taken together, these results indicate that WDPU is thermoplastic and thermally stable.

Supplementary Figures (S1, S2, S3, S4, and S5):

1. The hydrophilic properties of WDPU.

a

	Contact angle (°)
PCL100	83.4 ± 1.8
PCL80EB20	85.0 ± 0.7
PCL60EB40	86.8 ± 2.2
PCL40EB60	90.9 ± 1.4
PCL80LL20	80.6 ± 3.1
PCL60LL40	87.7 ± 3.4
PCL40LL60	93.4 ± 4.0
PCL80DL20	62.5 ± 3.8
PLA	95.3 ± 2.5

b

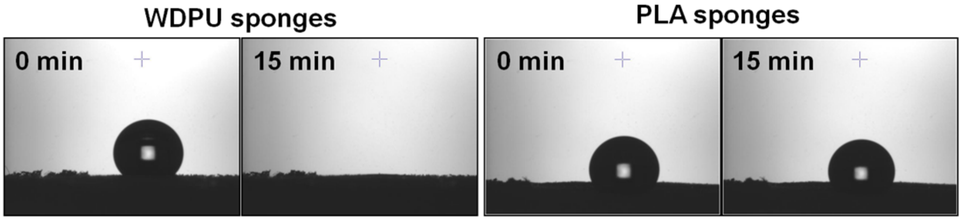

Figure S1. The hydrophilic properties of WDPU. (a) The water contact angle of WDPU films, as compared to PLA films. (b) The wetting properties of WDPU sponges (PCL40EB60 as an example) and conventional PLA sponges by sessile water droplets. The surface functional group of WDPU may be rearranged in response to the hydrophilic environment.

2. Thermal degradation curves of WDPU.

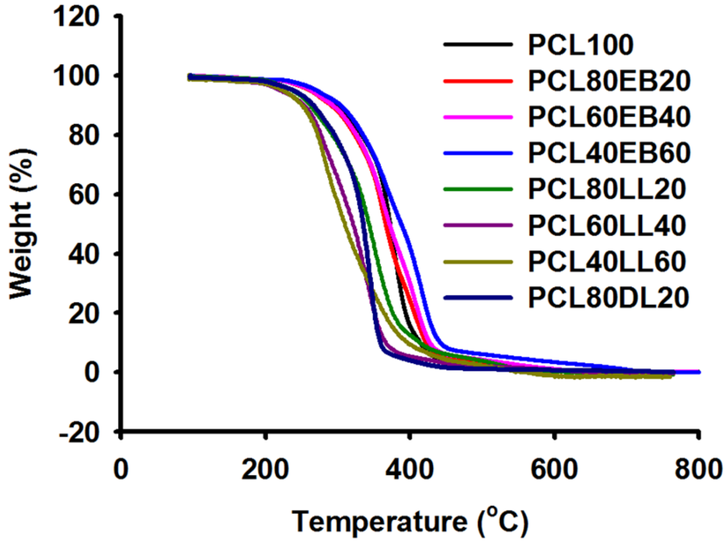

Figure S2. Thermal degradation curves of WDPU. The pyrolytic temperature (at 50% weight loss) was >300°C for all WDPU samples.

3. Crystallization behavior of WDPU.

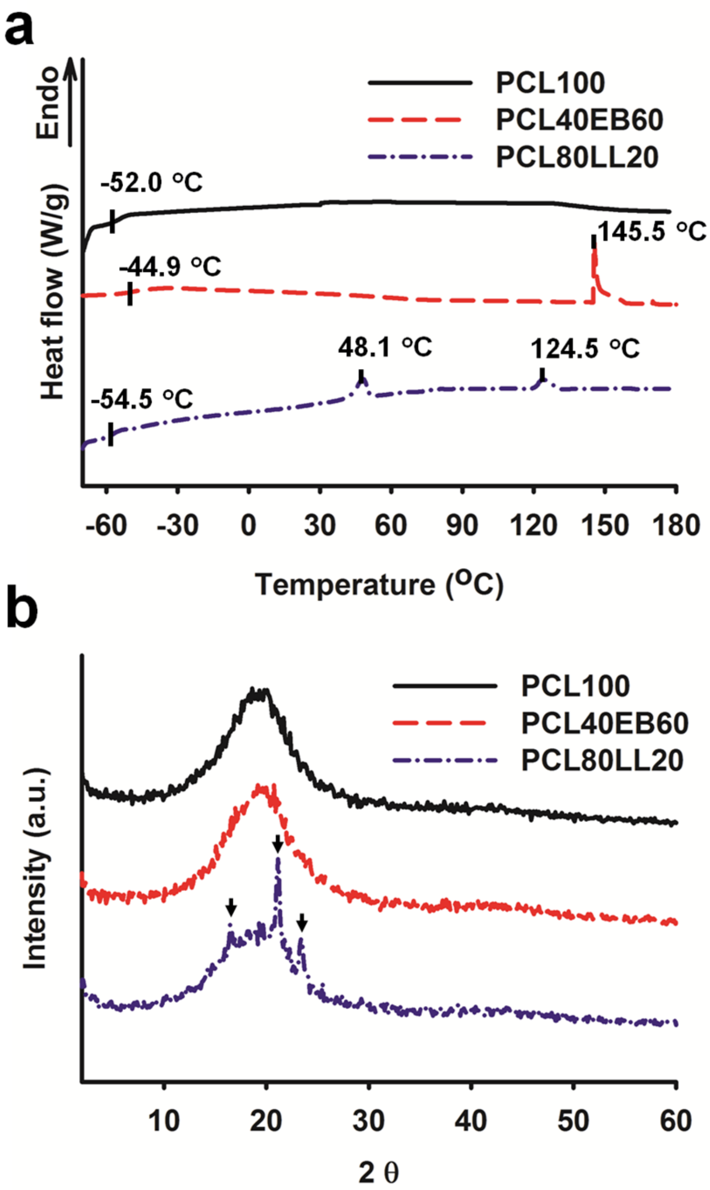

Figure S3. Crystallization behavior of WDPU. (a) DSC curves of WDPU, showing the glass transition temperature and melting temperature. The heating rate was 10°C/min for all measurements. No melting peak was clearly observed for PCL100, PCLEB, and PCLDL series except for the small peak in PCL40EB60 (~1%). For PCL80LL20, there were two small peaks (low-crystalline ~3%). (b) XRD patterns of WDPU, showing amorphous broad band (structureless). According to literature, the (110) plane and (200) plane of PCL crystal are at (2θ=) 21.4 and 23.6°, respectively. The (110) plane of PLA crystal is at 16.6°. PCL80LL20 revealed PCL peaks and a small PLLA peak. The calculated degree of crystallinity was 7%.

4. Degradation properties of WDPU.

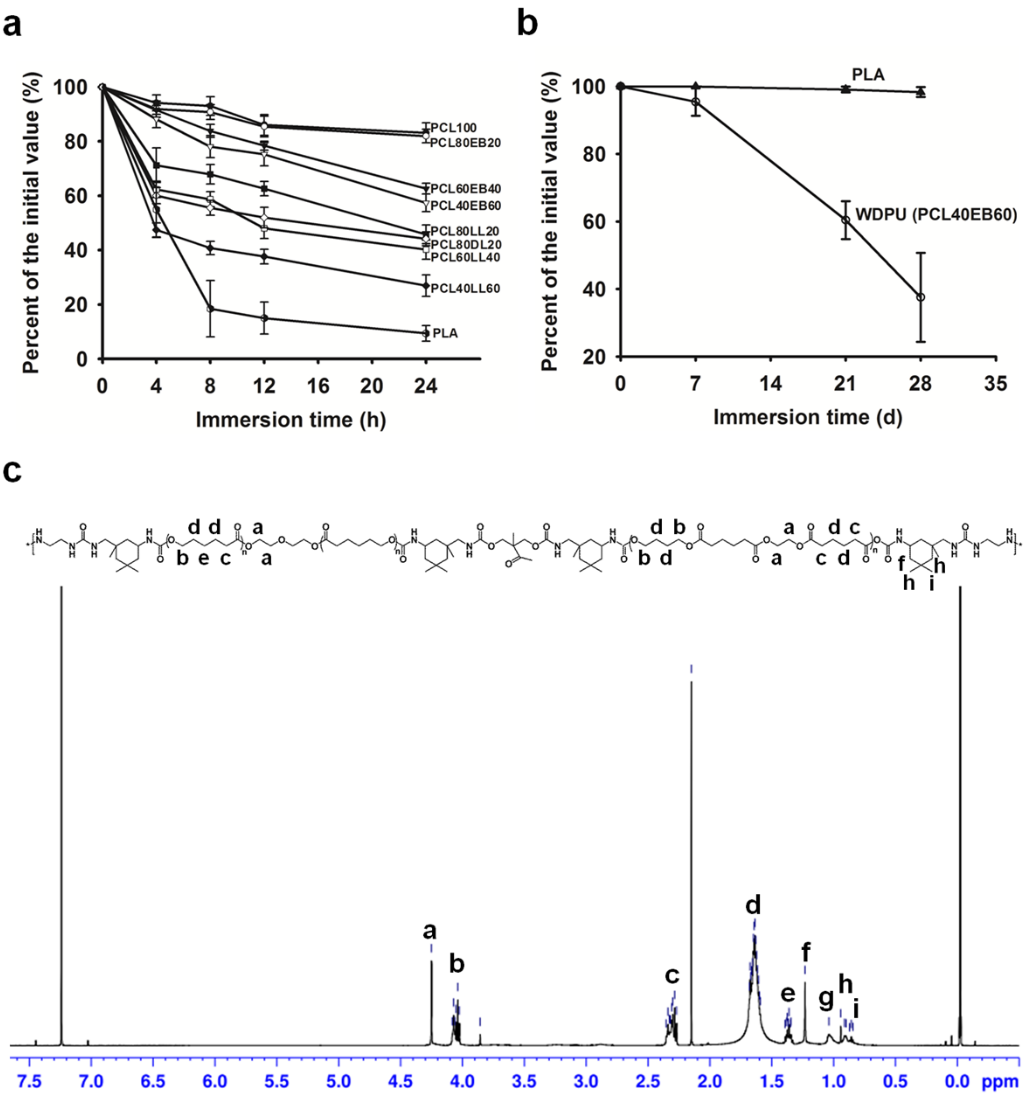

Figure S4. Degradation properties of WDPU. (a) The accelerated degradation of WDPU films immersed in 3% NaOH at 37°C. The degradation rate was PLA> PCL40LL60> PCL60LL40> PCL80DL20> PCL80LL20> PCL40EB60> PCL60EB40> PCL80EB20> PCL100. (b) Comparison of the degradation of PLA and WDPU (PCL40EB60) in PBS at 37°C. (c) ^{1}H-NMR analysis of the degradation products (collected after immersion at 50°C water for 3 weeks). The degradation products contained mostly soft segment. Amines were not observed, consistent with literature.[34,35]

5. The responses of vascular endothelial cells and macrophages to WDPU films.

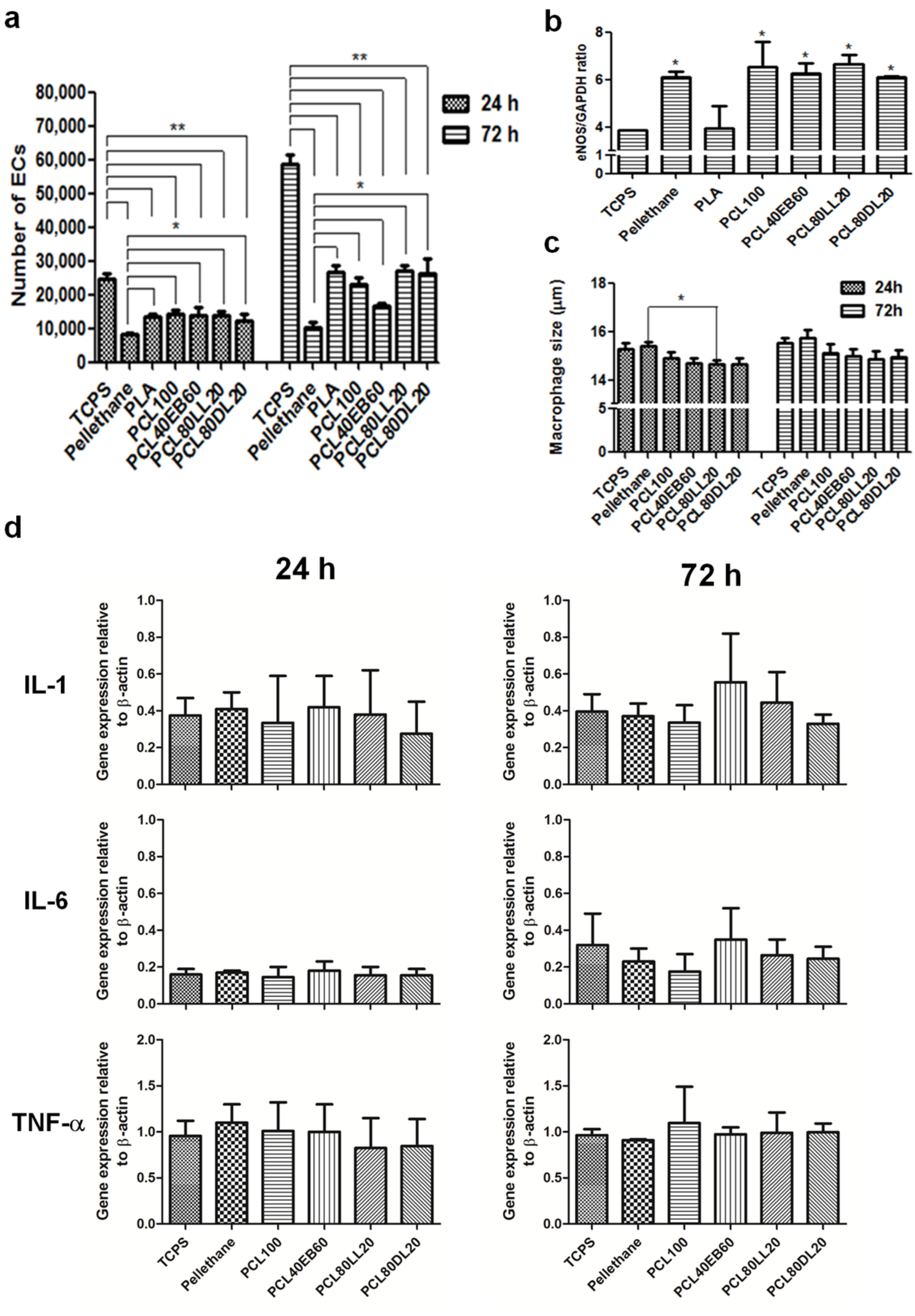

Figure S5. Additional biocompatibility data showing the responses of vascular endothelial cells (a, b) and macrophages (c, d) to WDPU films. (a) The attachment (24 h) and proliferation (72 h) of vascular endothelial cells (ECs). * $p < 0.05$, greater than Pellethane; ** lower than TCPS. (b) The endothelial nitric oxide synthase (eNOS) gene expression of ECs. * $p < 0.05$, greater than TCPS. The eNOS gene expression on WDPU was significantly greater than that on tissue culture polystyrene (TCPS, control) and PLA, indicating a positive cellular response. Observations in (a, b) also suggest that culture of ECs on WDPU may not require pre-coating with adhesion proteins such as fibronectin or laminin. (c) The average size of macrophages on WDPU was slightly lower than those on TCPS and Pellethane at both 24 and 72 h. (d) The proinflammatory gene (IL-1, IL-6, and TNF-α) expression was similar for J774A.1 macrophages on TCPS, Pellethane, and WDPU. * $p < 0.05$, lower than Pellethane. Observations in (c, d) indicate low immune reactions of WDPU.