Poly(Urea Ester): A Family of Biodegradable Polymers with High Melting Temperatures

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As one of the environmental problems, 'white pollution' is caused by the accumulation of nondegradable polymer materials. Recycling is one solution, however, creating biodegradable polymers would be more feasible for many applications.[1–6] If those biodegradable polymers exhibit similar properties to the nonbiodegradable ones then they should be more commercially competitive.[7–9] Among those biodegradable polymers developed so far, aliphatic polyesters are the best-known and they are already widely utilized in many applications (e.g., drug delivery carriers, medical implants, and tissue scaffolding)[10–15] since the ester linkages in aliphatic polyesters are hydrolytically or enzymatically degradable.[16,17] However, most of the biodegradable aliphatic polyesters exhibit low melting temperatures (T_m) and subpar mechanical properties. For instance, the T_m of poly(ε-caprolactone) is around 60 °C.[18] On the contrary, aromatic polyesters have high T_m values (e.g., the T_m of polyethylene terephthalate is as high as 260 °C[19]) and show competitive mechanical properties but they are typically nonbiodegradable.

The aim of this study is to bridge the gap between the aliphatic and the aromatic polyesters and to create biodegradable polymers with higher T_m values. Inclusion of the urethane or urea group into polymer backbones can enhance the crystallization/aggregation of polymer chains.[20] Furthermore, urea groups can also be degraded by proteases, such as papain.[21,22] Therefore, we explored a class of polymer, namely poly(urea ester)s (PUEs), via polycondensation of dimethyl esters (DMEs) and di(hydroxyalkyl) urea (DHAU, Scheme 1). In a PUE polymer chain, the ester groups offer biodegradability while the urea groups provide hydrogen-bonding which should increase the T_m and/or enhance the performance. Mulhaupt and co-workers reported previously the preparation of PUEs based on polyether polyols through an *N*,*N*′-carbonyl*bis*caprolactam route but only crosslinked materials were prepared.[23] Du et al. also synthesized nonbiodegradable liquid crystalline PUEs.[24] To the best of our knowledge, this work would be the first one creating biodegradable thermoplastic PUE.

Since amino groups react with urea at elevated temperatures and hydroxy groups are much less reactive,[25] we posited that DHAUs could possibly be prepared from amino alcohols (AAs) and urea. A series of DHAUs with different alkylene lengths between the urea group and the hydroxy group were prepared: DHAU-4, DHAU-5, and DHAU-6 (Scheme 1). The reactions of urea with 4-amino-1-butanol (AA-4), 5-amino-1-pentanol (AA-5), and 6-amino-1-hexanol (AA-6) were performed at 150 °C. In all these reactions the conversions were essentially quantitative within 24 h. The crude products were precipitated in acetone to remove the mono-substituted by-products and the remaining AAs. The isolated yields of DHAUs were all around 80%. The melting points of these DHAUs range from 110 to 128 °C.

By transesterification polymerization, DHAUs react with DMEs to form PUEs (Scheme 1). It is of great importance to understand the effect of the length of alkylene group of both DHAU and DME moieties on the PUE properties. Therefore different DHAUs (e.g., DHAU-4, DHAU-5 and DHAU-6) and different DMEs (namely dimethyl succinate, DMSu; dimethyl adipate, DMAd; and dimethyl sebacate, DMSe) were used. The polymer nomenclature in this work starts with 'P' and ends with a number corresponding to the series number of

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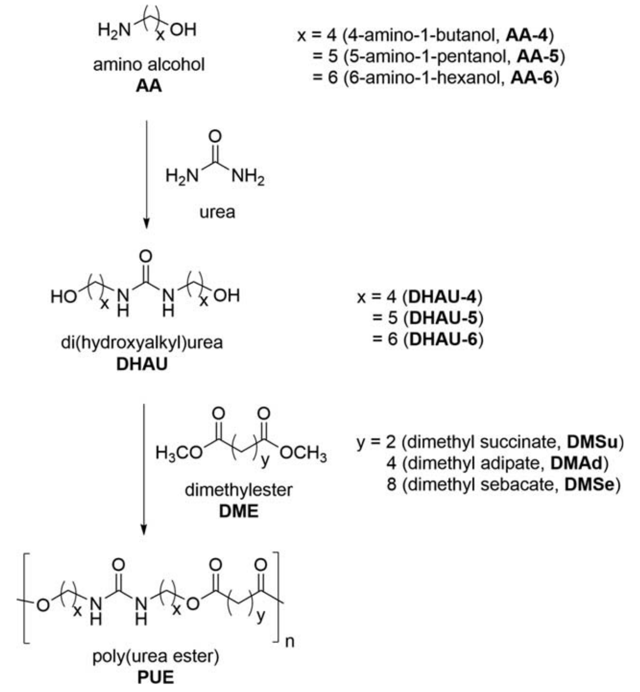

SCHEME 1 Synthetic scheme for PUEs, from AA and urea, intermediated by DHAU.

DHAU and DME, respectively. For example, P-4Se represents the polymer synthesized from DHAU-**4** and DM**Se** (see Scheme 1 and Table 1). Since 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was reported to be a good catalyst for ring-opening and transesterification polymerizations,[26] we applied it as the catalyst. To achieve a polymer product with a high molar mass, the reaction needs to be stoichiometrically balanced. However, the DMEs are more volatile than the DHAUs upon heating. So the DMEs were used in slight excess (the feed ratio of [DME]/[DHAU] = 1.1) and the polymerizations were performed initially at lower temperatures to reduce evaporation. After 2 h at 90 °C the conversion of DME achieved 60%, then the temperature was raised to 130 °C and kept for another 2 h. Chain extension, which is the third step, was carried out at 130 °C under reduced pressure and was held for 4 h. For all PUEs except P-6Su, the number average molar masses (M_n) are around 20 kg/mol, by a gel permeation chromatography with DMF as an eluent (DMF-GPC) and calibrated by PS standards. P-6Su did not dissolve in DMF.

TABLE 1 Monomers for PUE Preparation and the Characterization Results of the Obtained PUEs

	DHAU[a]	DME[a]	M_n[b] (kg/mol)	Đ[b]	T_g (°C)	T_m[c] (°C)	ΔH_m[c] (J/g)
P-4Su	DHAU-4	DMSu	25.2	1.19	−10	103; 120	30.3
P-5Su	DHAU-5	DMSu	18.2	1.29	–	110; 123	56.0
P-6Su	DHAU-6	DMSu	ND[d]	ND	–	118; 131	42.1
P-4Ad	DHAU-4	DMAd	22.0	1.06	–	131	55.1
P-4Se	DHAU-4	DMSe	18.2	1.13	12	92	28.6

[a] DHAU = di(hydroxyl alkyl) urea; DME = dimethyl ester. Their chemical structures refer to Scheme 1.

[b] The number average molar mass (M_n) and the dispersity (Đ) of the PUEs were determined by gel permeation chromatography (GPC) with an eluent of *N,N*-dimethylformamide (DMF) and polystyrene standards.

[c] The ΔH_m values in the table are the sum ΔH_m values of all melting peaks for each sample.

[d] ND = not determined. P-6Su does not dissolve in DMF at 50 °C.

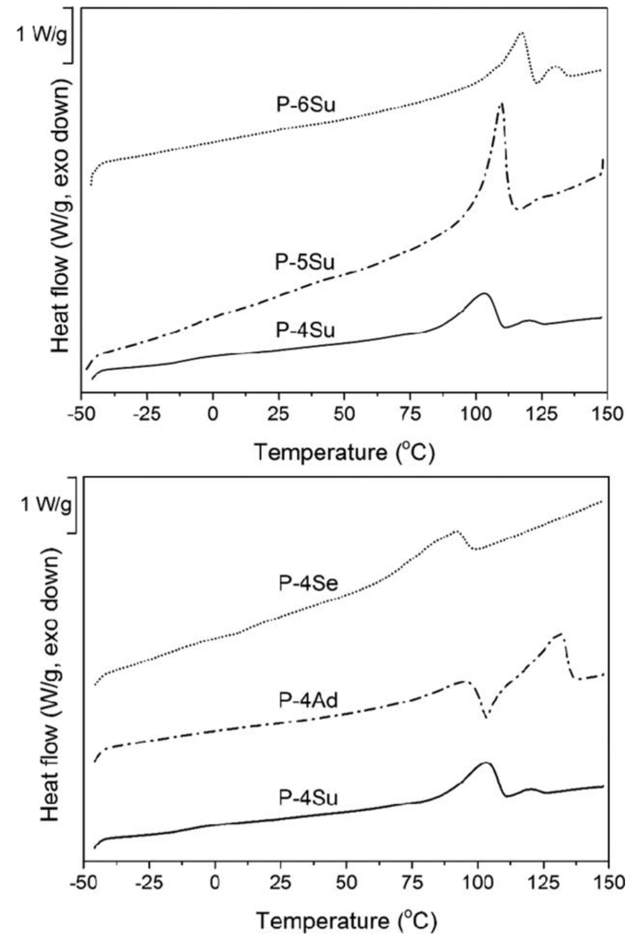

FIGURE 1 DSC traces of PUEs. (Top) PUEs based on dimethyl succinate and different di(hydroxyalkyl) urea and (bottom) PUEs based on di(hydroxybutyl) urea (DHAU-4) and different dimethyl esters. All traces are the second heating cycles with a heating rate of 20 °C/min.

The T_m of the PUEs was measured by differential scanning calorimetry (DSC) and the results are shown in Figure 1 and Table 1. All the PUEs are semicrystalline. Two melting peaks can be observed for both samples of P-4Su and P-6Su. In the DSC trace of P-4Ad, an exothermic peak existing at about 100 °C is designated as a cold crystallization peak. It was reported[27] that aliphatic polyesters always crystallize slowly and different crystallites can be found. If they are cooled with a rate of 5 °C/min or higher, there is not enough time for them to crystallize during cooling. The PUEs exhibit similar crystallization behavior to aliphatic polyesters, in terms

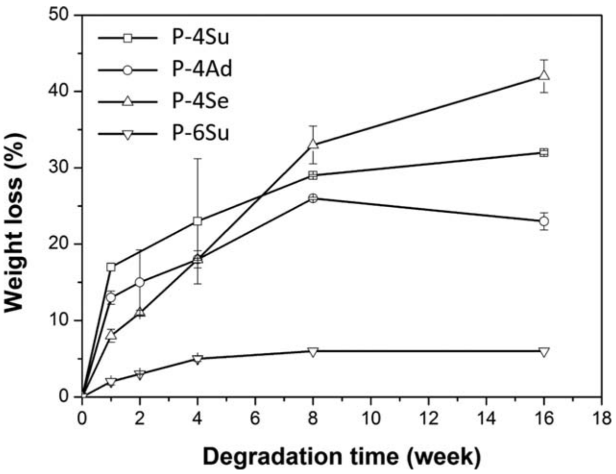

FIGURE 2 The weight loss of the PUEs as a function of degradation time (37 °C in a PBS buffer, pH 7.4 under the catalysis of lipase PS).

of cold crystallization and multiple crystallites. As shown in Table 1, the T_m values for all PUEs are above 100 °C, except P-4Se ($T_m \approx 92$ °C). Incorporation of the urea group in the backbone generally leads to higher T_m than the corresponding aliphatic polyesters with the same alkylene groups in the backbones. For example, T_m [poly(butylene succinate)] = 114 °C[18] versus T_m (P-4Su) = 120 °C; T_m [poly(butylene adipate)] = 60 °C[18] versus T_m (P-4Ad) = 131 °C; T_m [poly(butylene sebacate)] = 67 °C[18] versus T_m (P-4Se) = 92 °C. The existence of urea groups in aliphatic polyesters allows for intermolecular hydrogen bonds (see Supporting Information the temperature-dependent infra-red spectra), which results in a higher T_m. For those PUEs based on the same DME (dimethyl succinate in this case) and different DHAU, the difference among those polymers, in terms of chemical structure, is the methylene (CH_2) number between urea and ester groups. As one can conclude from Figure 1 and Table 1, the T_m of PUE increases with the expansion of methylene number from 4 to 6. This is similar to the behavior of the corresponding aliphatic polyesters.[18]

BIODEGRADATION OF PUEs

Lipases are known to be the best enzymes for biodegradation of aliphatic polyesters. Therefore, *pseudomonas cepacia* Lipase (Lipase PS) was selected as the enzyme for the biodegradation studies of PUEs in this work. The biodegradation was measured at 37 °C, in a phosphate buffered saline (PBS) solution. Samples were weighed and the weight loss (WL) values were calculated as a function of degradation time. Normally, biodegradation of polymers takes place with a two-step process which includes 'adsorption stage' and 'hydrolysis stage'.[28] To achieve the adsorption of lipase onto the surface of polymer materials, the polymer chains should be flexible for the binding of lipase.[29] In this case, the polymers that have more flexible backbones would degrade faster. Among the PUEs from the same DHAU (e.g., P-4Su, P-4Ad, and P-4Se), P-4Se, which is the most flexible and exhibits the lowest T_m (see Table 1), should degrade faster than the other two. The biodegradation results (in terms of WL, see Fig. 2) confirm this prediction. P-4Se indeed degrades the fastest; 42% weight loss is achieved after 16 weeks. The WL values for P-4Su and P-4Ad are 32% and 23%, respectively. A higher T_m value for P-4Ad, when compared with P-4Su, results in a lower WL value. P-5Su films were transformed into milky dispersions when they were dipped into the buffer solution, therefore, it was impossible to get WL data. Since P-6Su is insoluble in DMF, we suspect that it should also show poor biodegradability since it could also be difficult to adsorb buffer solution and even more difficult for the permeation of enzyme into the bulk of material. The WL of P-6Su keeps consistent (see Fig. 2) and only a WL of 6% can be achieved even after 16 weeks of degradation. The poor biodegradability of P-6Su can also be concluded from the SEM images before and after degradation. Even after 16 weeks, the surface of P-6Su film did not significantly change (see Fig. 3). But for other PUEs, significant erosion can be found on the surface, especially for P-4Su and P-4Se. The degradation, either enzymatic or nonenzymatic, prefers to take place in the amorphous region of polymeric materials.[30] Morphologically, there is always crystalline regions left after degradation, which was also observed in our study (see Fig. 3).

CONCLUSIONS

A novel idea is proposed to increase the melting temperature of biodegradable aliphatic polyester, by introducing urea

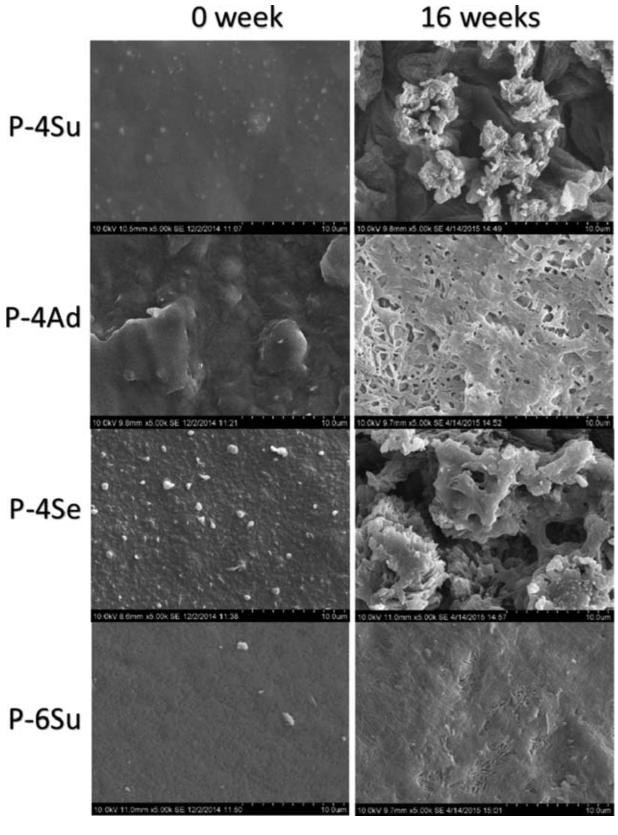

FIGURE 3 SEM images of PUE films before and after biodegradation (scale bar: 10 μm).

groups into the polyester backbones. These poly(urea ester)s (PUEs) were fabricated by polycondensation of di(hydroxyalkyl)ureas (DHAUs) with dimethyl esters. Such DHAUs are the products from amino alcohols and urea. The PUEs obtained were found to exhibit higher melting temperatures than their corresponding aliphatic polyester counterparts and most of them proved to be biodegradable. PUEs are a new family of biodegradable polymers with higher melting points and may show interesting potential applications.

EXPERIMENTAL

Materials

5-Amino-1-pentanol, urea, dimethyl succinate, dimethyl adipate, dimethyl sebacate were purchased from Aladdin Industrial Corporation (Shanghai, China). 4-amino-1-butanol was obtained from 9-Ding Chemistry (Shanghai, China) while 6-amino-1-hexanol was from J&K Chemicals (Guangzhou, China). The catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from TCI Shanghai (China). All solvents were purchased from Guangzhou Chemical Reagent Factory. All chemicals were used as received without further treatment.

Synthesis of Di(Hydroxyalkyl)Urea (DHAU)

In a three-necked flask equipped with a mechanical stirrer, argon inlet and vigreux column, urea and 2 eq. of amino alcohol were added. The flask was then immersed in an oil bath preheated to 150 °C. The reaction started and the ammonia released was removed from the flask by argon flow and was absorbed in water. The reaction was performed for 24 h before being dissolved in DMSO. The solution was poured into acetone to allow the precipitation of the product. After filtration and washing with acetone, the residue was collected and dried *in vacuo* at 70 °C overnight.

DHAU-4: yield: 82%; m. p. 128.3 °C (by DSC); ^{1}H-NMR (400 MHz, *d*6-DMSO, δ): 5.75 ppm (t, 2H, $\mathrm{N}\mathit{H}$), 4.42 (t, 2H, $\mathrm{O}\mathit{H}$), 3.38 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{OH}$), 2.97 (m, 4H, $\mathrm{NHC}\mathit{H}_2$), 1.33-1.41 (m, 8H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2}$); ^{13}C-NMR (400 MHz, *d*6-DMSO, δ): 158.66 ppm ($\mathrm{NH}\mathit{C}\mathrm{ONH}$), 61.02 ($\mathit{C}\mathrm{H_2OH}$), 39.64 ($\mathrm{NH}\mathit{C}\mathrm{H_2}$), 30.34 ($\mathrm{NHCH_2}\mathit{C}\mathrm{H_2}$ $\mathit{C}\mathrm{H_2CH_2}$); ESI-MS (m/z) $[M+\mathrm{Na}]$ $C_9H_{20}N_2O_3Na$, calculated: 227.1372, found: 227.1370.

DHAU-5: yield: 76%; m. p. 110.1 °C (by DSC); ^{1}H-NMR (400 MHz, *d*6-DMSO, δ): 5.73 ppm (t, 2H, $\mathrm{N}\mathit{H}$), 4.37 (t, 2H, $\mathrm{O}\mathit{H}$), 3.37 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{OH}$), 2.95 (m, 4H, $\mathrm{NHC}\mathit{H}_2$), 1.19–1.44 (m, 12H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$); ^{13}C-NMR (400 MHz, *d*6-DMSO, δ): 159.22 ppm ($\mathrm{NH}\mathit{C}\mathrm{ONH}$), 61.81 ($\mathit{C}\mathrm{H_2OH}$), 40.41 ($\mathrm{NH}\mathit{C}\mathrm{H_2}$), 33.44 ($\mathit{C}\mathrm{H_2CH_2OH}$), 31.12 ($\mathrm{NHCH_2}\mathit{C}\mathrm{H_2}$), 24.09 ($\mathit{C}\mathrm{H_2CH_2}$ $\mathrm{CH_2OH}$); ESI-MS (m/z) $[M+\mathrm{Na}]$ $C_9H_{20}N_2O_3Na$, calculated: 255.1685, found: 255.1688.

DHAU-6: yield: 80%; m. p. 119.6 °C (by DSC); ^{1}H-NMR (400 MHz, *d*6-DMSO, δ): 5.72 ppm (t, 2H, $\mathrm{N}\mathit{H}$), 4.33 (t, 2H, $\mathrm{O}\mathit{H}$), 3.38 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{OH}$), 2.95 (m, 4H, $\mathrm{NHC}\mathit{H}_2$), 1.40 (m, 4H, $\mathrm{NHCH_2C}\mathit{H}_2$ $\mathrm{CH_2}$), 1.34 (m, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$ OH), 1.22–1.30 (m, 8H, $\mathrm{NHCH_2CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2$); ^{13}C-NMR (400 MHz, *d*6-DMSO, δ): 158.59 ppm ($\mathrm{NH}\mathit{C}\mathrm{ONH}$), 61.14 ($\mathit{C}\mathrm{H_2OH}$), 39.68 ($\mathrm{NH}\mathit{C}\mathrm{H_2}$), 33.00 ($\mathit{C}\mathrm{H_2CH_2OH}$), 30.59 ($\mathrm{NHCH_2}\mathit{C}\mathrm{H_2}$), 26.78 ($\mathit{C}\mathrm{H_2CH_2}$ $\mathrm{CH_2OH}$), 25.76 ($\mathrm{NHCH_2CH_2}\mathit{C}\mathrm{H_2}$); ESI-MS (m/z) $[M+\mathrm{Na}]$ $C_9H_{20}N_2O_3Na$, calculated: 283.1998, found: 283.1992.

Synthesis of Poly(Urea Ester)s (PUEs)

PUEs were prepared by transesterification polymerization of different DHAUs with different dimethyl esters and similar procedures. A typical example: dimethyl succinate (4.82 g, 33 mmol), DHAU-5 (6.96 g, 30 mmol) and TBD (0.2085 g, 1.5 mmol) were added in a three-neck flask equipped with an argon inlet, mechanical stirrer and vigreux column connected to a Dean–Stark trap. The reaction was performed at 90 °C for 2 h to allow the formation of oligomers. The reaction temperature was then increased to 130 °C for another 2 h before vacuum was applied for further chain-extension. The polymerizations normally were run for 8 h. Once the polymerizations completed, DMSO was added to dissolve the crude polymers and the formed solutions were cooled and then poured into acetone to allow the precipitation of the polymer products. After filtration which was followed by washing with acetone three times, the residue was collected and dried *in vacuo* at 70 °C.

Characterization

^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra were collected using a Bruker AVANCE III HD 600 (600 MHz) spectrometer. All measurements were recorded at 25 °C. The chemical formula and the exact molar mass of DHAUs were determined by electrospray ionization mass spectroscopy (ESI-MS) on a Bruker maXis impact mass spectrometer. The molar mass of the PUEs were estimated by size exclusion chromatography (SEC) in *N*, *N′*-dimethyl formamide (DMF) on a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and three Styragel HR DMF columns (7.8 × 300 mm) in series at 50 °C. DMF containing lithium bromide (2 g/L) was used as eluent at a flow rate of 1.0 mL/min. The molar masses were calculated against polystyrene standards (Polymer Standards Service—USA, Inco. $\mathrm{Mp} = 890$ g/mol up to $\mathrm{Mp} = 2.63 \times 10^6$ g/mol). Differential scanning calorimetry (DSC) was used to measure the melting point (m.p.) of the DHAUs, as well as the glass transition temperatures (T_g) and the melting temperature (T_m) of the PUEs. Using a DSC 204 F1 from Netzsch, the measurements were carried out at a heating rate of 20 °C/min from −50 to 150 °C and a cooling rate of 10 °C/min.

The PUE film samples were prepared by compression molding (1 mm thick) at 150 °C and cut into pieces with weights of around 0.1 g. The samples were weighed accurately and added into vials together with 4 mL of a 0.01M phosphate buffered saline (PBS buffer) solution (pH = 7.4) and 0.4 mg *pseudomonas cepacia* Lipase (Lipase PS). The vials were then placed in a shaking bath at 37 °C. The buffer solution in the vials was replaced once per week and in the meantime, new enzyme was added. The samples were taken out, washed, dried and weighed after 1, 2, 4, 8, and 16 weeks. The weight loss (WL) was calculated by the equation as shown below.

$$\mathrm{WL}=\frac{m_0 m_\mathrm{t}}{m_0}\times 100\%$$

where m_0 is the initial mass of the samples and m_t is the mass of the samples after degrading for a certain time (1, 2, 4, 8, or 16 weeks).

The surface morphology of the PUEs during biodegradation was studied by scanning electron microscopy (SEM). SEM images were recorded by a Hitachi S-3700N instrument (Japan) which was performed at 0.3–30 kV.

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