Supplementary Information

New strategy to synthesize degradable polystyrene of ultra-high molecular weight.

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Experimental Section

Materials.

Sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) were supplied by Sinopharm Chemical Reagent Co., Ltd. (China). KPS was used after three recrystallizations using distilled water. Lipoic acid (α-LpA) was supplied by Shanghai Maclin Biochemical Technology Co., Ltd. (China), *Tert*-butanol (TBA), *N, N'*-dicyclohexyl carbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Shanghai Adamas-beta Reagent Co., LTD. Styrene (St) was supplied by Strong Functional Chemical Co., Ltd. (Jiangsu, China), which was washed three times with 8% sodium hydroxide (NaOH) water solution to remove the inhibitor, then washed with water to neutral, then dehydrated by calcium hydride (CaH_2), and then used after vacuum distillation. Deionized water was used for all washings. As-received solvents were used directly.

Synthetic procedure of *tert*-butyl lipoate (*t*-BLp).

The α-LpA (4.1264g, 0.02mol) was dissolved in tetrahydrofuran (THF, 30 mL) after they were added into a 250 mL three-mouth flask, and when fully dissolved, TBA (7.4120g, 0.1mol) was added by drops, and then stirred evenly using an ice bath. Then the DCC (4.1266g, 0.02 mol)-THF (20 mL) solution was added drop by drop using an eyedropper, and finally the DMAP (0.4887 g, 0.004 mol)-THF (10 mL) solution was slowly added (about 3~4 s/drop) using a constant pressure drip funnel. The reaction was carried out in the ice bath for 1 h, and then in a constant temperature water bath at 25 °C for 24 h. The liquid obtained from the reaction was evaporated by rotation to obtain a yellow thin oil liquid, which was dissolved in an appropriate amount of dichloromethane (50 mL), then washed with alkali (saturated sodium bicarbonate aqueous solution), pickling (5% hydrochloric acid aqueous solution), and water each three times in turn (the ratio of the aqueous phase to the dichloromethane phase is about 1:1.2), and finally dissolved in 20 mL THF after spin steaming, and left to rest overnight at -18 °C. The final target functional monomer *t*-BLp was obtained after filtration and spin steaming.

Polymerization process.

St (2.0830 g, 0.02mol) and *t*-BLp (0.0524 g, 0.0002 mol) were added successively into 100 mL Schlenk reaction bottle with a magnetic stirrer, stirred at a suitable speed until it was fully dissolved and then an aqueous (8.3320 g, 4 $m_{\text{.St}}$) solution of SDS (0.1042 g, 5% $m_{\text{.St}}$) was added. After the mixture was fully stirred and pre-emulsified for a period, the mixture was degassed by three cycles of vacuuming-argon gas filling process in ice water bath. Then KPS was added into the reaction bottle under the protection of argon gas, and degassed by two cycles of vacuuming-argon gas. After sealing, the reaction was carried out in a water bath at 25 °C. After 1-24 hours of polymerization, the reaction was finished. According to the needs, the emulsion was demulsified in anhydrous ethanol, and the copolymer was repeatedly rinsed with water. Then, the copolymer was extracted by anhydrous ethanol in a Soxhlet extractor. Finally, the obtained copolymer was dried in an oven at 80 °C.

Degradation process of PS-*co*-*t*BLp was catalysed by DTT.

The above copolymer (0.1 g) and dioxane (10 g) were added to a three-necked reaction bottle containing a magnetic stirrer and stirred at a suitable speed until it was fully dissolved. Then appropriate amount of dithiothreitol (DTT, 0.02g) was added, stirred thoroughly until it was dissolved, then reacted in a constant temperature oil bath at 80 °C. The reaction liquid gradually changed from colorless and transparent to cloudy yellow liquid, accompanied by yellow solid precipitation. At the end of the reaction, the obtained sample was passed over neutral alumina column and precipitated in anhydrous ethanol. Finally, the resulting degraded polymer was dried in a vacuum oven at 30 °C to constant weight.

Degradation process of PS-*co*-*t*BLp by UV.

The above copolymer (0.05 g) and THF (5 g) were added to a small sealed glass bottle containing a magnetic stirrer and stirred at a suitable speed until it was fully dissolved. After sealing, it was irradiated under 365 nm ultraviolet lamp for different times using different samples were diluted and directly tested by gel permeation chromatography.

Characterization.

The molecular weight and polydispersity ($Đ$) of obtained copolymer (PS-*co*-*t*BLp) were detected by gel permeation chromatography (GPC) using polystyrene as the standard sample. And the HPLC-grade THF was used as the eluent at a flow rate of 1 $mL \cdot min^{-1}$ at 35 °C. The GPC analysis results were determined on a Waters system (Waters Corporation, U.S.A,) equipped with Waters 1515 isocratic HPLC pump, Styragel HR5 GPC column (7.8×300 mm, molecular weight range: 5.0×10^4-4.0×10^6 Da), Styragel HR4 GPC column (7.8×300 mm, molecular weight range: 5.0×10^3-6.0×10^5 Da), Styragel HR3 GPC column (7.8×300 mm, molecular weight range: 5.0×10^2-3.0×10^4 Da), Styragel HR1 GPC column (7.8×300 mm, molecular weight range: 1.0×10^2-5.0×10^3 Da) and Waters 2414 refractive index detector.

The monomer conversion was detected by gas chromatography (GC) using toluene as the external standard. The carrier gas was hydrogen flowing at 1 mL min^{-1}, and the column temperature was increased from a starting value of 80 °C from sample injection to the maximum of 220 °C with an increasing rate of 20 °C min^{-1}.

The purity of the functional monomer was detected by the high- performance liquid chromatography (HPLC) using model 1515 of Waters Corporation. The mobile phase was a mixed solution of water and acetonitrile, and the set flow rate was 1 $mL \cdot min^{-1}$.

Structure of functional monomers and copolymers was measured by NMR spectra using Bruker 400 MHz spectrometer at room temperature with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard.

Structure of functional monomers and copolymers was measured by the NEXUS670 mid-infrared spectrometer (FT-IR) of Nicolet Company in the United States. The sample was evenly mixed with KBr and pressed with YP-2 tablet press. The measuring wavelength range was 400 ~ 4000 cm^{-1}. The resolution was set to 4 cm^{-1} and the number of scans was 32 times.

The glass transition temperature (T_g) of the copolymer was measured by a differential scanning calorimeter (DSC) from Perkin-Elmer at a heating rate of 20 K/min in nitrogen atmosphere.

The thermal decomposition temperature of the copolymer was determined by TG209-F1 Libra® thermogravimetric analyzer (TGA) made by Neotchi Company. The test temperature was 30 ~ 650 °C, N_2 was used as the inert shielding gas, the gas flow rate was 20 $mL \cdot min^{-1}$, and the sample dosage was 3 ~ 8 mg.

Supplementary tables.

Table S1. Results of polymers obtained under different conditions.

Sample	Feed ratio $[St]_0/[t\text{-}BLp]_0/[KPS]_0$	T (°C)	t (h)	$Conv._{St}$ (%)	$M_{w,\ GPC}{}^{a}$ (g / mol)	$Đ^{a}$
PS	100/0/2	25	24	92.0	2020000	1.96
PS-*co*-*t*BLp-1	100/2/2	25	24	73.3	460000	2.97
PS-*co*-*t*BLp-2	100/1/2	25	24	64.8	900000	2.89
PS-*co*-*t*BLp-3	100/1/1	25	8	66.9	1410000	3.25
PS-*co*-*t*BLp-4	100/0.4/2	25	24	64.6	1380000	2.32
PS-*co*-*t*BLp-5	100/0.4/1	25	24	66.6	1910000	2.13
PS-*co*-*t*BLp-6	100/0.2/2	25	24	63.0	1760000	2.44
PS-*co*-*t*BLp-7	100/0.2/1	25	24	67.2	2500000	2.01
PS-*co*-*t*BLp-8	100/1/1	60	4	100	890000	4.30
PS-*co*-*t*BLp-9	100/1/1	80	1	100	550000	6.48
PS-*co*-*t*BLp-10	100/1/0.2	80	1	100	1210000	3.70
PS-*co*-*t*BLp-11	100/5/0.2	80	1	76.5	640000	3.31

$m_{.H2O}/m_{.St}/m_{.SDS}$ = 4/1/0.05; [a] It was measured by a gel permeation chromatograph at 35 ºC.

Supplementary figures

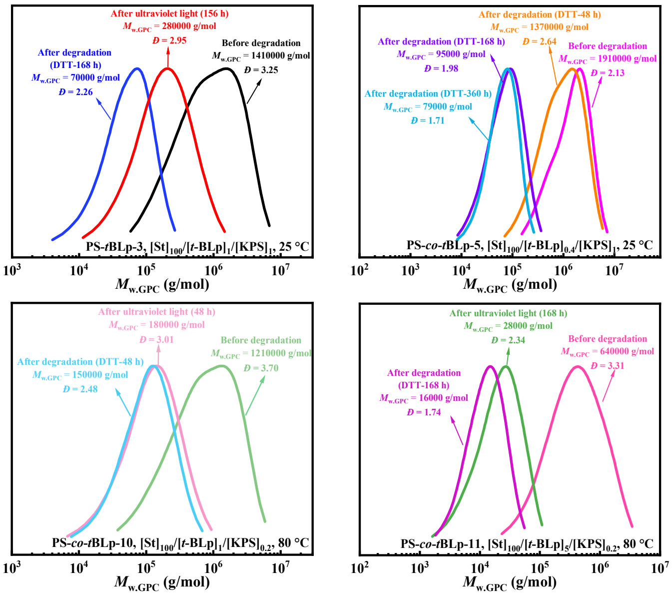

Fig. S1. Molecular weight differential distribution curves of PS-*co*-*t*BLp before and after degradation obtained under different conditions.

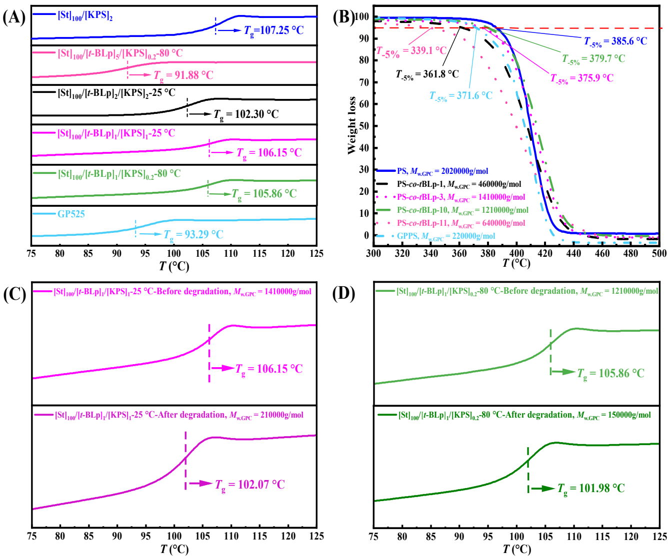

Fig. S2: (A) DSC curves of PS-*co*-*t*BLp obtained under different conditions. (B) TGA curves of PS-*co*-*t*BLp obtained under different conditions. (C) DSC of PS-*co*-*t*BLp-3 before and after degradation. (D) DSC of PS-*co*-*t*BLp-10 before and after degradation.