Flexible preparation of PA6-based thermoplastic elastomer filaments with enhanced elasticity, melt spinnability and transparency enabled by highmolecular-weight soft segments

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Experimental section

1. Materials

Caprolactam (CPL) and PTMG ($M_n \sim 3000$ g/mol) were purchased from China Petroleum (Zhejiang, China) and Jia Ying Resin (Shandong, China) Co. Ltd. respectively. Both were used as received without further purification, even they are commercial products. Ethylene glycol (EG), terephthalic acid (PTA), Zinc acetate (Zn(CH₃COO)₂) and deuterated trifluoroacetic acid (TFA-D) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai branch, China).

2. Synthesis of HS-TPAEs

The synthetic route for HS-TPAEs is illustrated in Scheme 1. All the reactions were conducted in a 3.5 L high-temperature reaction vessel in stainless steel, which was equipped with a condensing device, a vacuum pump and a magnetic stirring. Further details are provided below.

Step 1: Synthesis of PA6 with dibasic carboxyl terminus (HOOC-PA6-COOH)

In a representative polymerization procedure, a combination of CPL (563 g, 5 mol), PTA (69.4 g, 0.42 mol) and deionized water (28.2 g, 1.56 mol) was placed into a reactor and agitated for 2 hours at a gas pressure of 0.8 MPa and 260 °C. The pressure was then gradually reduced to 0.1 MPa and maintained at 260 °C for another 1 hour. The resulting product was stored in the container for subsequent experiments.

Step 2: Synthesis of PA6 with dibasic ethylene glycol ester terminus (EG-PA6-EG)

After the first step, EG (31.1 g, 0.5 mol) was injected into the reactor, and the mixture was agitated for 2 hours at 0.2 MPa gas pressure and 240 °C. Similarly, the resulting products were retained for the synthesis of HS-TPAEs.

Step 3: Synthesis of HS-TPAEs

In a representative polymerization procedure, a mixture of PTMG 3000 (690 g, ~0.23 mol) and $Zn(CH_3COO)_2$ (2 g, 0.01 mol) was injected to the reactor through a high-pressure tube after the second step. The resulting mixture was maintained at 0.2 MPa gas pressure and a temperature of 240 °C for 1 hour. Then, the pressure was gradually dropped to less than 100 Pa, and the temperature was raised to 250 °C to eliminate the excess EG, before continuing the polycondensation process for another 2 hours. HS-TPAEs were obtained after quenching the resulting polymer melt in ice water.

3. Melt-spinning of HS-TPAE-based filaments

In this scenario, HS-TPAE-55 was used to prepare elastic filaments using a laboratory melt-spinning apparatus (**Fig.12a**) equipped with a spinneret of 24 holes, and the diameter of this orifices was 0.25 μ m. Fully dried HS-TPAE-55 chips, about 1.5 Kg, were added to the extruder with zones I, II and III set to 230 °C, 230 °C and 240 °C respectively. The filaments extruded from spinneret were quench and drawn at a temperature of 15 °C and 100 °C, respectively, and were wound on a rolled drum at a speed of 500 m/min. Finally, golden elastic filaments with a line density of 90 dtex were prepared.

4. Characterization

¹H NMR and FTIR. TFA-D was used as the organic phase of HOOC-PA6-COOH, EG-PA6-EG, and HS-TPAEs for ¹H NMR studies using an AVANCE-600 (Switzerland) spectrometer. FTIR spectra of all samples were determined with a Spectrum Two FTIR spectrometer (PerkinElmer, America). The scanning range was $4000 \sim 400 \text{ cm}^{-1}$.

Gel Permeation Chromatography (GPC). The polymer dispersity index (PDI) and molecular weight, M_n and M_w , of HS-TPAEs were determined using a GPC equipped with a refractive index detector and a PL gel column (5 µm mixed-C). Using polymethyl methacrylate as a reference, a calibration curve was created. Eluents were 1,1,1,3,3,3-hexafluoro-2-propanol, with a flow rate of 0.3 mL·min⁻¹.

The concentration of carboxylic end-groups. Titration analysis was employed to assess the concentration of carboxylic end-groups [-COOH] in HOOC-PA6-COOH,

EG-PA6-EG and HS-TPAE-55. Samples weighing 0.50 ± 0.01 g were dissolved in a mixture of *m*-cresol and ethanol. The carboxyl end-group concentration was determined by titrating the solution with a standard sodium hydroxide solution (0.02 mol L⁻¹). The automated titrimetry system (T50, Mettler Toledo Co., Switzerland) was used to record the change in voltage levels during the titration process.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF-MS). In this study, the measurements were conducted using a MALDI-ToF-MS (Bruker rapiflex MALDI Tissuetyper) analyzer with a laser wavelength of 355 nm. Data acquisition was carried out in positive ion mode. The ionizing agent used was NaI, which was dissolved in formic acid at a concentration of 1 mg mL⁻¹. As for the substrate, 2,5-dihydroxybenzoic acid (DHB) was utilized and prepared as a substrate solution. The sample and the substrate solutions were mixed at a 1:1 volume ratio. Then, 1 μ L of the well-mixed solution was applied for spotting the target. The substrate and the sample were co-crystallized on the target plate, and the target was inserted into the instrument for the subsequent test after the drying process.

Atomic Force Microscopy (AFM). The morphology of HS-TPAE-55 was investigated using Atomic Force Microscopy (AFM) (Bruker AXS, Germany). To prepare the sample solution, 3 mg/mL of HS-TPAE-55 was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol. Subsequently, a film with a thickness of approximately 100 nm was obtained by spin-coating the solution onto a silicon wafer at 2000 rpm for 30 seconds.

Small-angle X-ray scattering (SAXS). Solid films, approximately 30 µm in thickness, were cast from 3 wt% solutions in 1,1,1,3,3,3-hexafluoro-2-propanol. To promote the establishment of equilibrium morphologies, the samples were annealed at 60 °C for 12 hours. SAXS profiles were obtained using Ni-filtered Cu K_a radiation with a wavelength (λ) of 1.542 Å, at 40 kV and 50 mA, employing a SAXSess mc² apparatus (Anton Paar, Austria). All patterns were adjusted for air scattering, background scattering, and beam fluctuations. The scattering intensity (*I*) was calculated as a function of the magnitude of the scattering wave vector ($q = (4\pi / \lambda) \sin(\theta/2)$), where λ represents the wavelength and θ denotes the scattering angle.

Dynamic mechanical analysis (DMA). DMA spectra were collected from a DMA Q800 apparatus (TA Instruments, America) fitted with a liquid nitrogen chilling device. Rectangular specimens measuring dimensions of $20 \times 8 \times 0.3$ (length × width × thickness) mm³ were employed, and temperature sweeps were taken from -100 °C to

100 °C at 3 °C \cdot min⁻¹ heating rate and 1 Hz frequency.

Differential scanning calorimetry (DSC). DSC measurements were performed using a DSC 4000 (Perkin Elmer, America) apparatus calibrated with an indium standard. All samples were measured under a nitrogen environment. For the HS-TPAEs, samples weighing approximately 5-10 mg were heated to 250 °C to eliminate thermal history, then cooled to -50 °C, and reheated to 250 °C at a ramping rate of 5 °C/min. The second heating scan was selected to investigate the thermal characteristics. In the case of the HS-TPAE-55 filaments, samples weighing about 5-10 mg were cooled from ambient temperature to -30 °C, followed by an increase to 220 °C at a ramping rate of 5 °C/min. The first scan was chosen to investigate the thermal characteristics.

Transparency of HS-TPAEs. The chips of HS-TPAEs were molded into dumbbell-shaped films with a thickness of approximately 2 mm. Subsequently, the films were thermally annealed at 100 °C for 1 hour to achieve equilibrium morphologies. The transparency of prepared films was assessed by measuring the transparence curves using the UV-3600 ultraviolet spectrophotometer (Shimadzu, Japan), with an integrating sphere attachment.

Tensile Hysteresis test of HS-TPAEs. Cyclic tensile tests were used to assess the tensile Hysteresis of HS-TPAEs. A dumbbell-shaped specimen with a thickness of about 0.4 mm was stretched repeatedly under constant elongation placed in a WDW 3020 universal tensile tester (Sansi, Shanghai), and a constant tensile speed of 100 mm/min was adopted.

Tensile measurements of HS-TPAE-based filament. The stress-strain curves of HS-TPAE-based filament were collected using an LLY-06E electronic single fiber strength tester (Laizhou electron instrument, China). During the tensile measurements, a drawing gauge of 20 mm and a drawing speed of 20 mm/min were carried out during the tensile measurements.

Tensile Hysteresis properties of HS-TPAE-based filament. Tensile hysteresis behavior of HS-TPAE-based filament was characterized via cyclic tensile testing in an LLY-06E electronic single fiber strength tester (Laizhou electron instrument, China). The drawing ratio (ε_0) was chosen as 30%, 50%, 80% and 100% respectively during this test.

The wide-angle X-ray Diffraction (WAXD) and tensile measurements of HS-TPAEs were carried out according to the procedures previously reported.¹



Fig. S1 GPC curves of HS-TPAEs.

Table S1 M_{obs} , M_{end} and M_{ion} values of HOOC-PA6-COOH and EG-PA6-EC	j
calculated from MALDI-ToF-MS results and eqn(1).	

Samples		n	$M_{ m the}{}^{ m a}$	$M_{ m obs}$	$M_{ m ion}$	$M_{ m end}$
НООС-РА6-СООН	A	9	1184	1184.7	1	166
		10	1297	1297.8	1	166
		11	1410	1410.9	1	166
		12	1523	1523.9	1	166
	В	9	1206	1206.7	23	166
		10	1319	1319.8	23	166
		11	1432	1432.9	23	166
		12	1545	1545.9	23	166
	С	6	706	705.5	28 ^b	/
		7	819	818.6	28 ^b	/
		8	932	931.6	28 b	/
		9	1045	1044.7	28 ^b	/
EG-PA6-EG	Е	8	1158	1157.8	0	254
		9	1271	1270.9	0	254
		10	1384	1383.9	0	254
		11	1497	1497.0	0	254
	F	8	1204	1203.8	46	254
		9	1317	1316.9	46	254
		10	1430	1430.0	46	254
		11	1543	1543.0	46	254

^a M_{the} represents the theoretical mass value associated with varying numbers of repeat units. ^b The M_{ion} value of [M+ 28]⁺ could potentially be attributed to the presence of formic acid during the MALDI-ToF-MS test.²

Samples	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)	Tensile toughness (×10 ⁷ J · m ⁻³)
TPAE-0	163.3 ± 12	20.5 ± 2.0	6 ± 2	9.1 ± 6
HS-TPAE-20	94.5 ± 8	7.4± 1.2	60 ± 20	33.7 ± 14
HS-TPAE-40	47.1 ± 7	7.5 ± 0.8	290 ± 30	172.6 ± 30
HS-TPAE-55	38.6 ± 6	10.0 ± 1.1	590 ± 40	370.5 ± 44
HS-TPAE-60	15.1 ± 4	6.1 ± 0.6	$245{\pm}45$	160.8 ± 28
HS-TPAE-70	11.5 ± 2	3.6 ± 0.5	80 ± 30	20.3 ± 8

Table S2 Mechanical Properties of HS-TPAEs.

Notes and references

- S1. R. C. Yuan, S. Fan, D. Q. Wu, X. L. Wang, J. Y. Yu, L. J. Chen and F. X. Li, *Polym. Chem.*, 2018, 9, 1327-1336.
- S2. D. Chionna, C. Puglisi, F. Samperi, G. Montaudo and A. Turturro, Macromolecular Rapid Communications, 2001, 22, 524-529.