Electronic Supplementary Information (ESI)

Tuning Chain Extenders Structure to Prepare High-Performance Thermoplastic Polyurethane Elastomers

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Table of contents:

1. Supplementary Table (Table S1)
2. Supplementary Figures (Fig. S1–S10)
1. Supplementary Table

Table S1 Comparison of thermal stabilities and mechanical properties of BDO-PU, monoFc-PU, and bisFc-PU.

| Samples  | $T_{5\%}$ ($^\circ$C) | $T_{\text{max}}$ ($^\circ$C) | $E_a$ (KJ/mol) | Young's modulus (MPa) | Stress, $\sigma_{\text{max}}$ (MPa) | Strain, $\varepsilon_{\text{max}}$ (%) | Toughness (GJ m$^{-3}$) |
|----------|-----------------------|-------------------------------|----------------|-----------------------|-------------------------------------|--------------------------------------|------------------------|
| BDO-PU   | 298                   | 300                           | 110.6          | 7.3                   | 27.5                               | 932                                  | 10.6                   |
| monoFc-PU | 321                  | 350                           | /              | 6.0                   | 6.0                                | 758                                  | 2.4                    |
| bisFc-PU | 345                   | 369                           | 214.9          | 13.9                  | 42.3                               | 1018                                 | 19.6                   |

2. Supplementary Figures

Fig. S1 Gel permeation chromatograph curves of BDO-PU, monoFc-PU and bisFc-PU were performed on a Waters-1515 using DMF-LiBr as an eluent and polystyrene (PS) as standards, the sample concentration was 2 ~ 3 mg mL$^{-1}$, and the flow rate was 0.800 mL min$^{-1}$ at 40 $^\circ$C. The BDO-PU ($M_n = 3.6 \times 10^4$ g/mol, $M_w/M_n = 2.0$), monoFc-PU ($M_n = 3.0 \times 10^4$ g/mol, $M_w/M_n = 1.6$), and bisFc-PU ($M_n = 2.9 \times 10^4$ g/mol, $M_w/M_n = 1.5$).
Fig. S2 (a) TGA and (b) DTG thermograms of BDO-PU, monoFc-PU and bisFc-PU, at the heating rate of 10 °C min⁻¹ from 50 to 700 °C under nitrogen atmosphere.

Fig. S3 The thermal behaviors of hard segments for BDO-PU, monoFc-PU and bisFc-PU. The curves were derived from differential scanning calorimeter (DSC) of the second heating processes between 80 to 240 °C.
Fig. S4 Fourier transform attenuated total reflection infrared spectroscopy (ATR-FTIR) spectra at various temperature (150, 250, 325, 375 °C) of BDO-PU, monoFc-PU and bisFc-PU at the region of 3600 – 3000 cm$^{-1}$, 1780 - 1580 cm$^{-1}$ and 890 - 700 cm$^{-1}$.
Fig. S5 (a) Differential scanning calorimeter (DSC) curves of first cooling and second heating processes and (b) The crystallinity ($X_c$) for BDO-PU, monoFc-PU and bisFc-PU; Dynamic mechanical analysis to show (c) the storage modulus and (d) $\tan \delta$ of BDO-PU, monoFc-PU and bisFc-PU from at a heating rate at 3 °C min$^{-1}$ from -100 to 80 °C. The degree of crystallinity ($X_c$) for those PUs were calculated via the equation of $X_c = \Delta H / \Delta H_0$ where $\Delta H$ is the heat fusion of PUs and $\Delta H_0$ is the enthalpy of fusion of the fully crystalline material of $\Delta H_0 = 172.2$ J g$^{-1}$.

Fig. S6 (a) WAXD and (b) SAXS profiles of BDO-PU, monoFc-PU and bisFc-PU.
Fig. S7 SEM images of BDO-PU, monoFc-PU and bisFc-PU, and partial enlargements of the marked positions.
Fig. S8 (a) $^1$H-NMR and (b) $^{13}$C-NMR spectra for monoFc (600 Hz, CDCl$_3$).
Fig. S9 (a) $^1$H-NMR and (b) $^{13}$C-NMR spectra for bisFc (600 Hz, CDCl$_3$).
Fig. S10 A) $^1$H-NMR and B) $^{13}$C-NMR spectra for (a) BDO-PU, (b) monoFc-PU, and (c) bisFc-PU (600 Hz, DMF-$d_7$). (*) Signals of solvent.