Synthesis of fluorinated diol (FDO). FDO was synthesised as illustrated in Figure S1. Using 2,2,3,3,4,4,5,5-octafluoro-1-pentanol and 2-(chloromethyl)oxirane as raw materials in a round bottom flask, then tetrabutylammonium bromide (TBAB) was added as a catalyst for the ring-opening etherification reaction. 2-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)oxirane was synthesized by adding sodium hydroxide, and further purified by distillation under reduced pressure. The epoxy product 2-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)oxirane was dissolved in tetrahydrofuran, then dilute sulfuric acid was added to carry out normal temperature hydrolysis reaction for 24 h followed by sodium hydroxide powder introducing to adjust to neutral. After liquid separation, the lower layer liquid is dried with anhydrous sulfuric acid and the salt was removed by suction filtration together with the solvent removed by rotary evaporation. The product was purified by distillation under reduced pressure to give the 1-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)ethane-1,2,-diol (FDO).
Synthesis of polyurethanes. A series of fluorinated silicon-based polyether urethanes (FSPEU) were synthesised using a two-step bulk polymerization method as indicated by Figure S2. PTMO and PDMS were accurately weighed, added to a three-necked flask, and dehydrated under vacuum at 100 °C for 2 h. Formula amount of FDO was added and mixed evenly after temperature cooling to 60 °C. After the temperature dropped to 40 °C, the accurately weighed MDI liquid and trace organic bismuth were added to further react and the temperature was controlled at 60 °C. After 40 minutes of reaction, the temperature was cooling down to 50 °C and BDO was added then quickly stirred followed by being poured into a Teflon plate. The mixture was placed in an oven at 100 °C for 6 h to continue carry out the polymerization.
Figure S2. Synthesis of fluorinated silicon-containing polyether urethanes (FSPEU).

Figure S3. SEM images of samples for hydrolyzing 0, 8, 16, 24 weeks. The scale bars on low resolution images are 200μm, on enlarged images are 10μm.
Figure S4. GPC result curves for (a) PEU, (b) FPEU (c) SPEU-10 and (d) FSPEU-10. The black lines are calibration curves of PMMA.

Figure S5. (a) Ultimate tensile strength (UTS) of samples. E2A, P35\(^1\) and a silicon rubber\(^2\) were selected as controls. (b) Elongation at break of samples. (c) Stress at 100% strain of samples.
Figure S6. The backbone hydrolysis product of PEU detected by \textsuperscript{1}H NMR. Peaks at 7.18 ppm and 7.50 ppm are attributed to protons on the benzene ring attached to urethane bond while peaks at 6.60 ppm and 6.90 ppm are ascribed to protons on the benzene ring near amine groups.

\textsuperscript{1}H Nuclear Magnetic Resonance (\textsuperscript{1}H-NMR) Spectroscopy was used to detect the degree of the hydrolysis of urethane bond and date spectra were acquired on a Bruker AV II 400MHz at room temperature. The samples control and aged were dissolved in DMF-d\textsubscript{7} at a concentration of \textasciitilde{}20 mg mL\textsuperscript{-1}. 
Figure S7. The adjacent urethane bond hydrolysis product of PEU for 16 weeks denoted as MDA. The peak located in about 6.2 min with an area intensity of 165690 was determined by total ion current (TIC) with LCMS.

Liquid Chromatography Mass Spectrometry (LCMS) was used to check the water phase of closed degradation system and find out the concentration of 4,4'-methyleneedianiline (MDA) which was liberated via the cleavage of adjacent urethane linkage. The Shimadzu LCMS-2020 was consisted of an autosampler SIL-20, binary high pressure gradient pump LC-20AD (×2), a system controller, a column oven CTO-20A with a temperature of 25 °C as well as the MS detector. Samples with a volume of 20 μL were injected through the autosampler, separated by a Phenomenex® C18 column (150 × 4.60 mm, 5 micron), passed by the Electrospray Inoization (ESI) generator finally monitored by the MS. Solvent A was water while B was acetonitrile with a concentration of 35%. The elution rate was 1 mL min⁻¹ and the mass-to-charge ratio detection range was 188 to 225 m/z. The mass peak of MDA was located at 199.10 m/z which should be interpreted as [M + H]⁺, accompanied by
an isotope peak of 200.1 m/z. In order to establish the standard curve, a series of gradient concentrations of chromatographic pure MDA was injected.

Figure S8. (a) LCMS calibration curve of MDA standard samples with a few known concentrations. (b) MDA concentration in water phase for samples detected by LCMS.

Figure S9. Representative curves of DSC for samples. The temperature range is from -160 °C to 230 °C.

The glass transition temperature of hard segments for MDI-BDO system is long-term confused. In the late 1990s, Teng Ko Chen et al. presented an experimental method to access the reliable hard segment Tg from a series of complete phase-mixed polyurethanes. The obtained Tg was 108 °C which was close to the experimental reported value. MDSC was used when we start the characterization of melting behaviors. This experimental method separates the normal heat flow into reversing and non-reversing
parts and thus enables separation of transition occurring in close proximately such as glass transition and enthalpy relaxation. The Glass transition and melting can be obtained using the reversing heat flow curves. This is more precise compared to values measured from the total heat flow curves due to enthalpic relaxation are not present in the reversing heat flow. The temperature was modulated by 1.27 °C per 60 seconds and the range was also from -160 to 230 °C with a warming rate of 2 °C min⁻¹. The samples used were PEU and FPEU, about 180 days after extrusion. As can be seen in Figure S10, the reversing heat flow curves only have a Tg of PTMO and an endothermic peak above 100 °C. Therefore, it is inferred that the peak above 100 °C is a combination of Tg and Tm for hard segments. However, as the heat capacity of the hard segments is generally very small or almost undetectable, we claimed the peaks as “thermal transitions” for more accurate expression.

Figure S10. Representative curves of MDSC for (a) PEU and (b) FPEU.

The thermodynamic behavior of polyurethanes is very interesting for few reasons. Firstly, as mentioned above, the endothermic peaks above 100 °C are likely to be a combination of Tg and Tm for hard segments. Secondly, thermoplastic polyurethane exhibits multiple melting behaviors with several melting peaks can be obtained in heating curves. Finally, the extent of phase separation always relates to multiple factors e.g. storage time and temperature. As illustrated in Figure S11, the solid lines represent for as-prepared samples while the dotted lines represent for samples storing for 6 months at room
temperature (RT). As time goes by, the endothermic peaks above 100 °C shifted to higher temperatures denoting obvious phase separation. Besides, the temperature tends to play a more significant role in phase demixing. In a word, the thermodynamic behavior of polyurethanes is very complicated. Since the focus of our research is not to elucidate the thermodynamic behavior of polyurethane, but to prove the change of thermal transition before and after hydrolysis from one aspect. Thus the detailed analysis of the DSC endotherm as discussed above is not presented in the text.

![DSC heating curves](image)

Figure S11. DSC heating curves of samples of initial and stored at room temperature (RT) for 6 months.
Figure S12. The results of ATR-FTIR for samples hydrolysed for up to 24 weeks.

Figure S13. The percentage of strongly hydrogen-bonded carbonyl group in C=O stretching region of samples detected by IR over a temperature range from 25 °C to 155 °C. Carbonyl group could be divided into 3 peaks on IR spectrum using the software PeakFit 4.0. 1735 cm$^{-1}$ belongs to the free-bonded carbonyl, 1715 cm$^{-1}$ is attributed to loosely hydrogen-bonded carbonyl groups and 1700 cm$^{-1}$ is caused by strongly hydrogen-bonded fraction.
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REFERENCE