Origin of highly recoverable shape memory polyurethanes (SMPUs) with non-planar ring structures: A single molecule force spectroscopy investigation

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1 **The detailed information of the samples**

STable.1 The detailed information of the samples

	PTMG2000 / mol	PPDI /mol	Chain extender / mol	Non-planar structure content in HS mol %	HS wt%	Mn	PDI
PPDI-1	1	4.5	3.5	36.5 (43.8)	33 (38.0)	3.2×10^4	3.2
PPDI-2	1	3.5	2.5	73 (83)	37 (39.8)	3.1×10^4	3.1
PPDI-3	1	4	3	110 (128)	35 (38.1)	3.0×10^4	3.3
PPDI-4	1	2.4	1.4	126 (147)	34 (38.2)	3.5×10^4	3.0

Note: The ratio of the PTMG2000: PPDI: chain extender is the molar ratio. Non-planar structure content in hard segment (HS) is calculated by the following formula: mol%=

$$\frac{N1\times M_{Non-planar\ diisocyanate}+N2\times M_{Non-planar\ chain\ extender}}{M_{diisocyanate}+M_{chain\ extender}}\times 100\%,$$

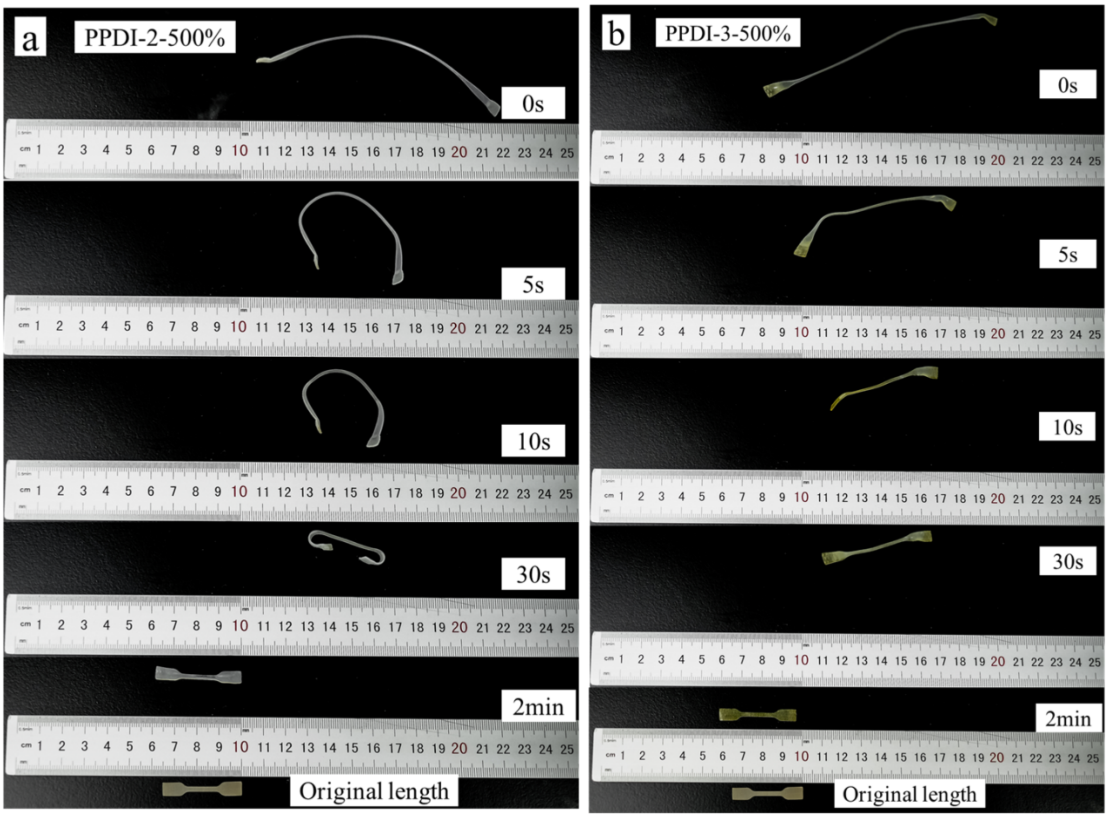
N1 and N2 are the ring numbers per non-planar diisocyanate and chain extender molecule. The HS wt% means the weight percent of hard segment, which is defined as the per cent by weight of the PPDI and chain *extender in the polyurethane. The values in the brackets are the theoretical value, the outside one is the practical value. M_n, number average molecular weight. PDI means the polydispersity index.*

STable.2 The transition temperature (T_{gS}) and mechanical properties of the samples

	T_{gS} / °C	Elongation at break / %	Modulus / MPa	Tensile strength / MPa
PPDI-1	-30	680±10	7.5±0.4	45.3±3.4
PPDI-2	-32	750±50	12.2±0.6	54.7±5.1
PPDI-3	-18	1000±20	8.3±1.6	32.5±1.8
PPDI-4	-22	1200±60	4.5±1.2	23.2±2.1

Note: The glass transition temperature of soft segment (T_{gS}) is determined by DMA method.

2 The shape memory process of PPDI-2 and PPDI-3 with 500% strain



SFig. 1 The shape memory process of PPDI-2 (a) and PPDI-3 (b) with 500% strain at

room temperature (23°C).

3 Characterization

Fourier transform infrared spectroscopy (FTIR) characterization was performed on a Thermo Nicolet 6700 Fourier transform infrared spectrometer from Thermo-Fisher Scientific, scanning from 500 to 4000 cm^{-1}, and 32 scans were collected for each sample. The sample was prepared by casting the polyurethane solution on KBr disk.

The shape recoverability after tensile break of the samples in 15s was performed on Instron 5567 apparatus with a deformation rate of 1.7mm/s and five specimens were used to determine the mean values and standard deviation for recovery rate and elongation at break. In this part of the experiment, we started timing when the sample was fractured.

The shape memory property of the samples with 500% strain was performed on the same dynamometer with the aid of liquid nitrogen. At first, the sample was stretched at room temperature (23°C) up to 500% deformation (strain rate, 100mm/min; gauge length=20mm). Without releasing the sample from the grips, the elongated sample was frozen by liquid nitrogen to temperatures lower than glass transition. Then the sample was removed from the dynamometer clamps, and allowed for free recovery at room temperature (23°C). We started timing when the frozen sample was removed from the clamps.

4 Single molecule force spectroscopy (SMFS)

We first dissolved the samples in N, N-dimethyl-formamide (DMF) and then diluted the solution to 1.0×10^{-4} mg/mL. Silicon wafers were treated with hot piranha solution (70:30 v/v 98% H_2SO_4/30% H_2O_2) for 1h, sonicated in large amounts of deionized water several times, rinsed with ethanol, and dried in a steam of nitrogen. (*Caution! Piranha solution is very corrosive and can react violently with organics, so security measures should be taken.*) A clean silicon wafer was immersed in the sample solution (1.0×10^{-4} mg/mL) overnight, and then the silicon wafer was flushed thoroughly with the solvent to remove any unstable molecules.

Commercially available V-shaped Si_3N_4 AFM cantilevers (Agilent, Santa Clara, US) with a sharp tip (radius of curvature ~20 nm) at the end of a soft cantilever and a spring constant ~0.06 N/m were utilized in the SMFS experiment. The thermal tune method is used to calibrate the spring constant of the cantilever in this work. The SMFS experiments were carried out at room temperature. Details of the SMFS experiment have been described elsewhere[2-4]. In brief, when an AFM tip was brought into contact with a polymer that had been physical absorbed on the substrate, the polymer could absorb onto the AFM tip as well as on the substrate, thus forming the so-called polymer bridge between the tip and the substrate. With the tip separated from the substrate, the polymer bridge was elongated, resulting in the bending of the cantilever toward the substrate. The deflection of the cantilever and the extension were recorded and converted to force−extension curves (in brief, force curves).

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