

*Electronic Supplementary Information for*

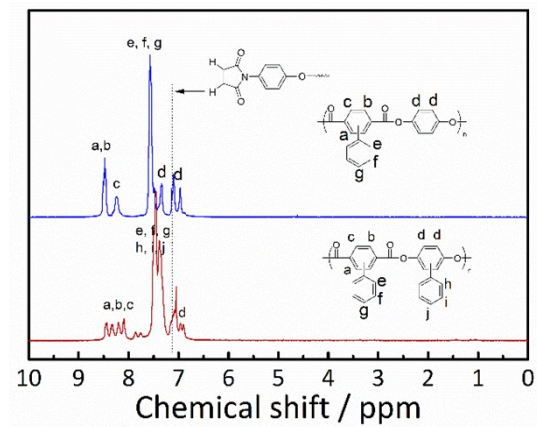
# **Synthesis and characterization of aromatic-PDMS segmented block copolymers and their shape-memory performance**

Hongli Xu,<sup>a,b</sup> Johan Bijleveld,<sup>b</sup> Maruti Hedge,<sup>c</sup> Theo Dingemans\*<sup>b, c</sup>

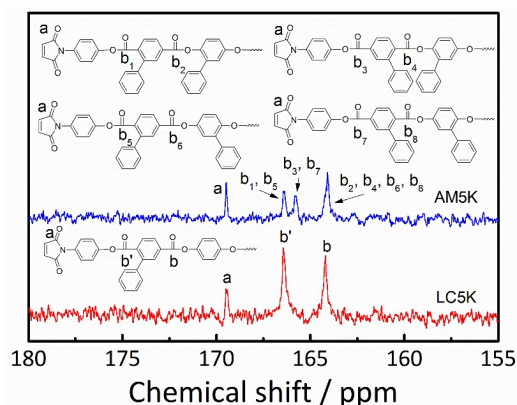
a. School of Innovation and Entrepreneurship, Southern University of Science and Technology, 518055 Shenzhen, China.

b. Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands.

c. Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Murray Hall 1113, Chapel Hill, North Carolina 27599-3050, United States.



**Fig. S1.**  $^1\text{H}$  NMR spectra of the AM5K and LC5K oligomers ( $M_n=5 \text{ kg}\cdot\text{mol}^{-1}$ ) were recorded in TFA-*d*. The spectra were offset for clarity. The assignment of protons of the oligomers is shown in the inset.



**Fig. S2.** Quantitative  $^{13}\text{C}$  NMR spectra of carbonyl groups of AM5K and LC5K. The integration can be used to calculate the molecular weight ( $M_n$ ) of the oligomers.

**$M_n$ s of all-aromatic oligomers:** Determination of the HPM end-group concentration is of great importance, as it provides information about the molecular weight and is critical for synthesis of high molecular weight polymer.  $^1\text{H}$  NMR spectroscopy is routinely employed for quantifying end-group concentration through reliable proton integrations that are directly related to specific proton ratios.<sup>1</sup> However, this technique is limited by spectral congestion of closely grouped proton peaks. In literature, polymers have alternatively been analyzed by quantitative solution  $^{13}\text{C}$  NMR spectroscopy, to determine the degree of polymerization ( $DP$ )<sup>2, 3</sup>. In our case, since proton peaks assigned to maleimide end-groups overlap with those of aromatic protons in the main-chain, as shown in Figure S1, quantitative  $^{13}\text{C}$  NMR was used to quantify the oligomer end-groups. This information can then be used to determine the molecular weight of the oligomers.<sup>3-6</sup> To achieve a good signal-to-noise ratio, long relaxation delays are required. Integration of carbon resonances of two different groups of carbon atoms can only be compared if the same number of hydrogen atoms are present in each group. This is to minimize differences in nuclear Overhauser effect.<sup>7</sup>

In order to calculate the number average molecular weight ( $M_n$ ) of our oligomers from quantitative  $^{13}\text{C}$  NMR data, the degree of polymerization ( $DP$ ) of the oligomers was determined using equation 1. For a dual end-capped ester-based oligomer, the number of carbonyl groups within the main-chain ( $N_{CO}$ ) corresponds to two carbonyl group in one repeating unit, while the number of maleimide end-groups ( $N_{end}$ ), corresponds to 4 carbonyl groups. Combined with  $DP$  a relationship is formed where  $I_{end}$  and  $I_{CO}$  represent the integrals of the peaks of the terminal end-group and the carbonyl groups within the polymer chain, respectively.

$$\frac{N_{end}}{N_{CO}} = \frac{I_{end}}{I_{CO}} = \frac{4}{2 \times DP} \quad (\text{eqn. 1})$$

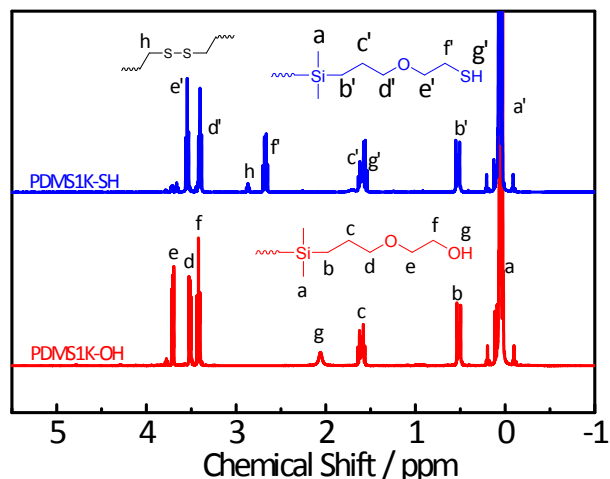
Therefore,  $M_n$ s of the oligomers can be calculated by equation 2,

$$M_n = DP \times M_0 + 2 \times M_{end} \quad (\text{eqn. 2})$$

Where  $M_0$  and  $M_{end}$  are molecular weights of the repeat units (316 and 392  $\text{g}\cdot\text{mol}^{-1}$  for LC and AM oligomers, respectively) and maleimide end-groups (188  $\text{g}\cdot\text{mol}^{-1}$ ).

In Figure S2 the quantitative  $^{13}\text{C}$  NMR spectra of both LC5K and AM5K are shown with the assignment of the oligomer carbonyl groups. The carbonyl carbons of the polymer gave rise to 2 (for LC oligomers) or 3 (for AM oligomers) distinct resonances covering a total chemical shift range of 4 ppm (ranging from 163 to 167 ppm). This is due to the random arrangements of the bulky phenyl groups at the backbone in consecutive repeating units along the polyester chain.<sup>8, 9</sup> The resonance at 169 ppm is assigned to the carbonyl carbon of maleimide end-groups. As an example, the calculation of  $M_n$  for the LC5K sample is further explained. Using equation 1,  $DP$  is calculated to be 21.28 using the integrals of carbonyl peaks from both maleimide and main-chain (peaks a and b at 169 ppm and 164/166 ppm in Figure S2, respectively). Using equation 2,  $M_n$  is calculated to be 7.1  $\text{kg}\cdot\text{mol}^{-1}$ .

The calculated  $M_n$  and experimental data is summarized in Table 1. The calculated  $M_n$ s of the oligomers are in close agreement with the targeted molecular weights and similar to the viscometry analysis.



**Fig. S3.**  $^1\text{H}$  NMR spectra and peak assignments of PDMS1K-OH and PDMS1K-SH oligomers. The labelling scheme of the peaks is included in the Figure. The spectra are offset for clarity.

**$M_n$ s of PDMS oligomers:** The average number of dimethylsiloxane repeating units ( $DP$ ) in PDMS can be calculated from the integration ratios of the  $\alpha$  protons in the methylene group adjacent to Si ( $I_{b'}$ , corresponding to 4 protons of  $b'$  peak at  $\delta = 0.5$  ppm in Figure S3) to that of the methyl group on Si in the PDMS main-chain ( $I_{a'}$ , corresponding to 6 protons of  $a'$  peaks at around 0 ppm in Figure S3), using the following Equation 3.

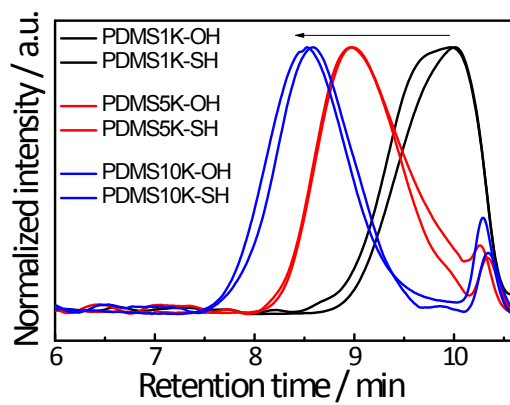
$$\frac{I_{a'}}{I_{b'}} = \frac{4}{6 \times DP} \quad (\text{eqn. 3})$$

Therefore,  $M_n$  can be calculated by Equation 4.

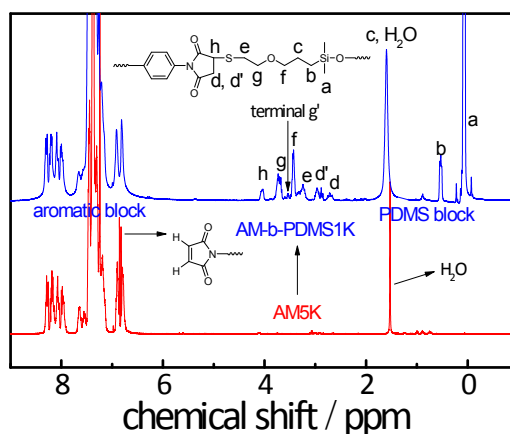
$$M_n = (DP \times M_0) + M_{end} \times 2 \quad (\text{eqn. 4})$$

Where  $M_0$  is the molar mass of the dimethylsiloxane repeating unit (equals 74 for PDMS),  $M_{end}$  is the molecular weight of end-groups (equals 119 in this case). Using this method, all the  $M_n$ s were calculated and summarized in Table 2.

$^1\text{H}$ -NMR was also used to follow the progress of the reactions and to confirm conversion of hydroxyl functionalities into thiol functionalities. In Figure S3, the  $^1\text{H}$  NMR spectra of PDMS1K-OH and PDMS1K-SH are shown. The  $\alpha$  protons of hydroxyl group at  $\delta = 3.41$  ppm ( $f$  triplets in Figure S3) shifted to 2.67 ppm ( $f'$  triplets in Figure S3) of the thiol  $\alpha$  protons, clearly showing the conversion to telechelic thiol-terminated PDMS. The observed peaks at  $\delta = 2.9$  ppm (*i.e.* peaks  $h$  in Figure S3) arise from a slight and almost unavoidable formation of disulfide in the telechelic dithiol when exposed to atmospheric oxygen during work-up, which is reported to occur in similar systems.<sup>10, 11</sup>



**Fig. S4.** GPC traces of PDMS-OH and PDMS-SH oligomers. All curves are normalized to maximum intensity. The small increase in molecular weight and PDI observed for the PDMS-SH oligomers is due to the formation of disulfides.



**Fig. S5.**  $^1\text{H}$  NMR of the AM5K oligomer and resulting multiblock copolymer AM5K-*b*-PDMS1K, as a representative example. The assignment of peaks is shown in the Figure. The spectra are offset for clarity. The maleimide peak at  $\delta = 6.84$  ppm has disappeared after the thiol-ene click reaction. The proton peak of *g'* at 3.53 ppm in the terminal end-groups are integrated to calculate the molecular weights of the block copolymers.

**$M_n$ s of multiblock copolymers:** For  $^1\text{H}$  NMR analysis, different deuterated solvents were selected depending on the solubility of the prepared block copolymers. All the AM5K-*b*-PDMS series were measured in  $\text{CDCl}_3$ , whereas the LC5K-*b*-PDMS analogs were measured in a 50/50(v) mixture of  $\text{CDCl}_3$  and  $\text{TCE-}d_2$ . In Figure S5, the  $^1\text{H}$  NMR spectra of the AM5K oligomer and AM5K-*b*-PDMS1K are shown as examples to verify the thiol-ene click reaction. A dramatic decrease in the proton signal of the maleimide (at  $\delta = 6.84$  ppm) was observed, while at the same time the appearance of peaks *h*, *d* and *d'*, assigned to protons in the hydrothiolated maleimide, imply a successful thiol-ene Michael addition.

With the aim of estimating the molecular weight ( $M_n$ ) of the final  $(\text{AB})_n$  multiblock copolymers, the starting materials, *i.e.*, AM5K and PDMS oligomers are treated as difunctional macromonomers in the calculation for the sake of simplicity. The number of macromonomer segments in the final  $(\text{AB})_n$  multiblock copolymers can be determined by end-group analysis from  $^1\text{H}$  NMR data. For a well-defined structured  $(\text{AB})_n$  main-chain type multiblock copolymer, the number of repeat units (*n*) and the number of unreacted end-groups at block **A** ( $N_t$ ) and main-chain linkage ( $N_c$ ) of the reacted end-group has a relationship<sup>12, 13</sup> of:

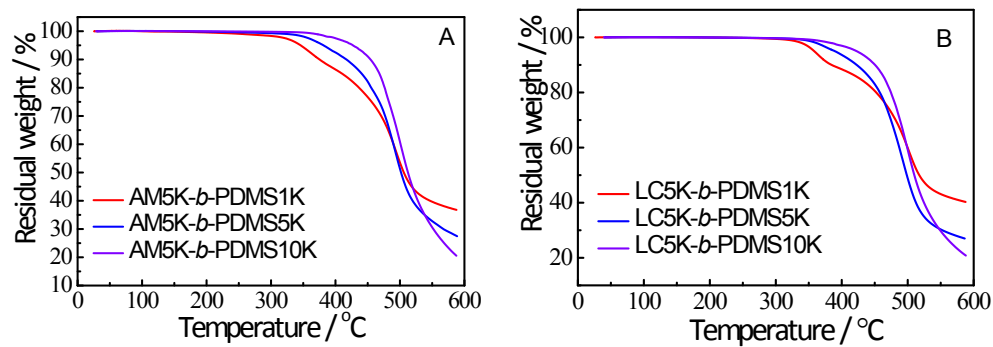
$$\frac{N_t}{N_c} = \frac{I_t}{I_c} = \frac{1}{2 \times n - 1} \quad (\text{eqn. 5})$$

Where  $I_t$  and  $I_c$  represent the integrals of the peaks of the terminal end-group and the linkage within the polymer chain, respectively. Therefore  $M_n$  of the  $(\text{AB})_n$  multiblock copolymer can be calculated by Equation 6,

$$M_n = (M_A + M_B) \times n \quad (\text{eqn. 6})$$

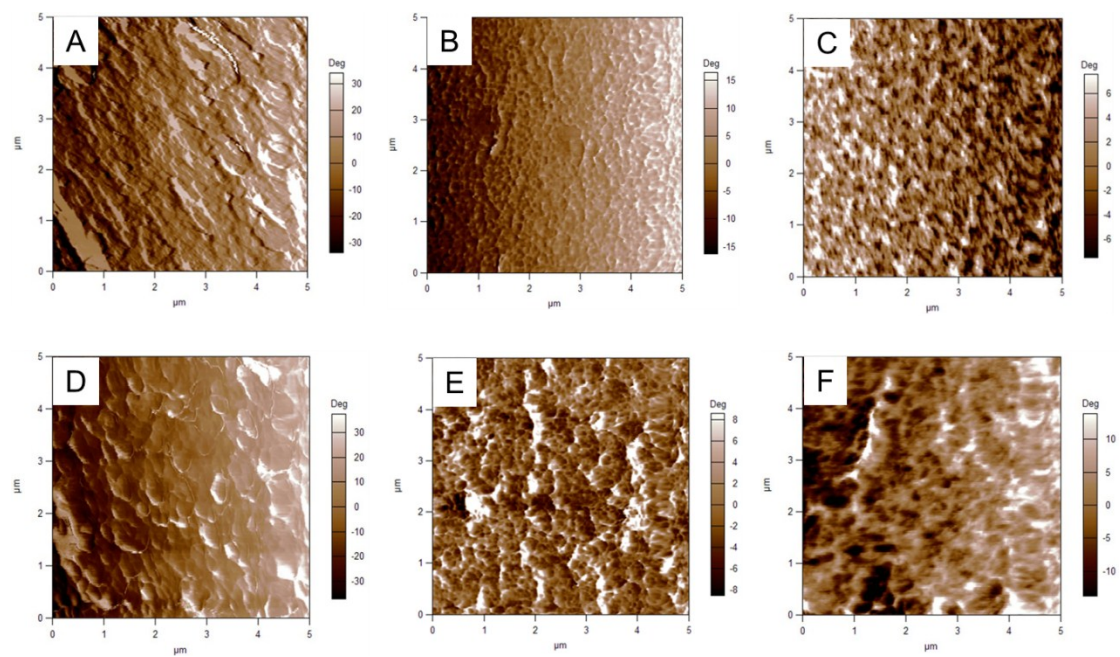
Where  $M_a$  and  $M_b$  are number average molecular weights ( $M_n$ ) of each block **A** and **B**, respectively.

As an example, the number of repeat units (*n*) of AM5K-*b*-PDMS1K is calculated using Equation 5, based on the NMR spectrum of integrated areas of the peaks of the terminal end-group (*g'* peak at 3.53 ppm in Figure S5) and the aliphatic bridge (*g* peak at 3.70 ppm in Figure S5), equals 5.07. The  $M_n$ s of the AM5K oligomer ( $M_a$ ) and the PDMS-SH-1K precursor ( $M_b$ ) are 4.9 and 1.5  $\text{kg}\cdot\text{mol}^{-1}$ , respectively, as determined previously. Therefore, the  $M_n$  of AM5K-*b*-PDMS1K is calculated to be approximately 32  $\text{kg}\cdot\text{mol}^{-1}$ .

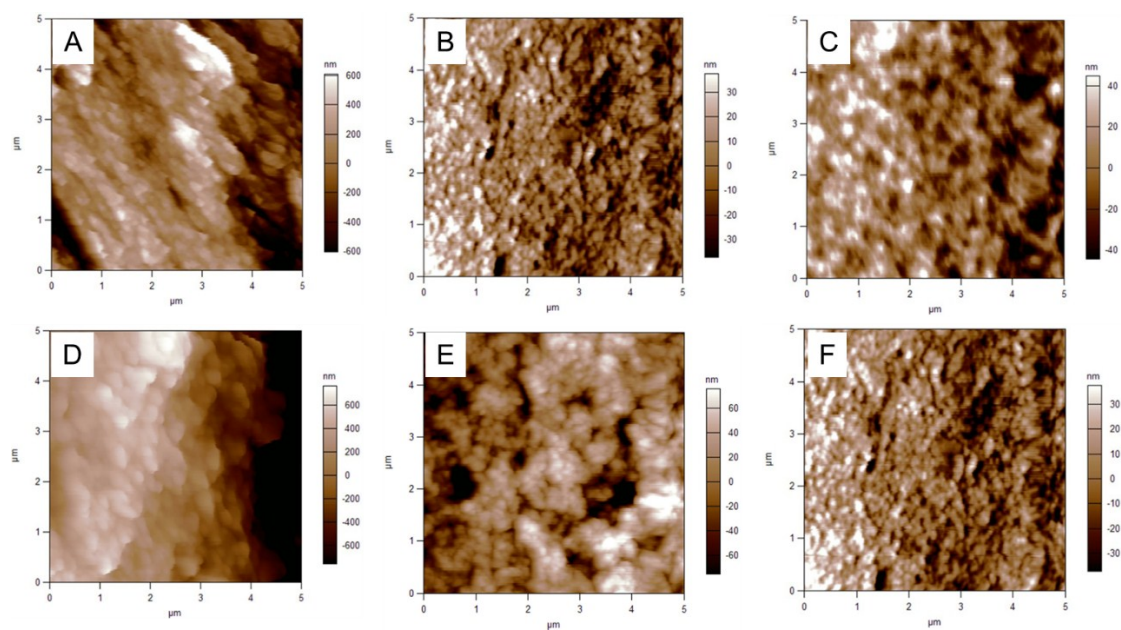


**Fig. S6.** TGA thermograms of the (AB)<sub>n</sub> block copolymers recorded under nitrogen atmosphere with a heating rate of 10 °C·min<sup>-1</sup>.

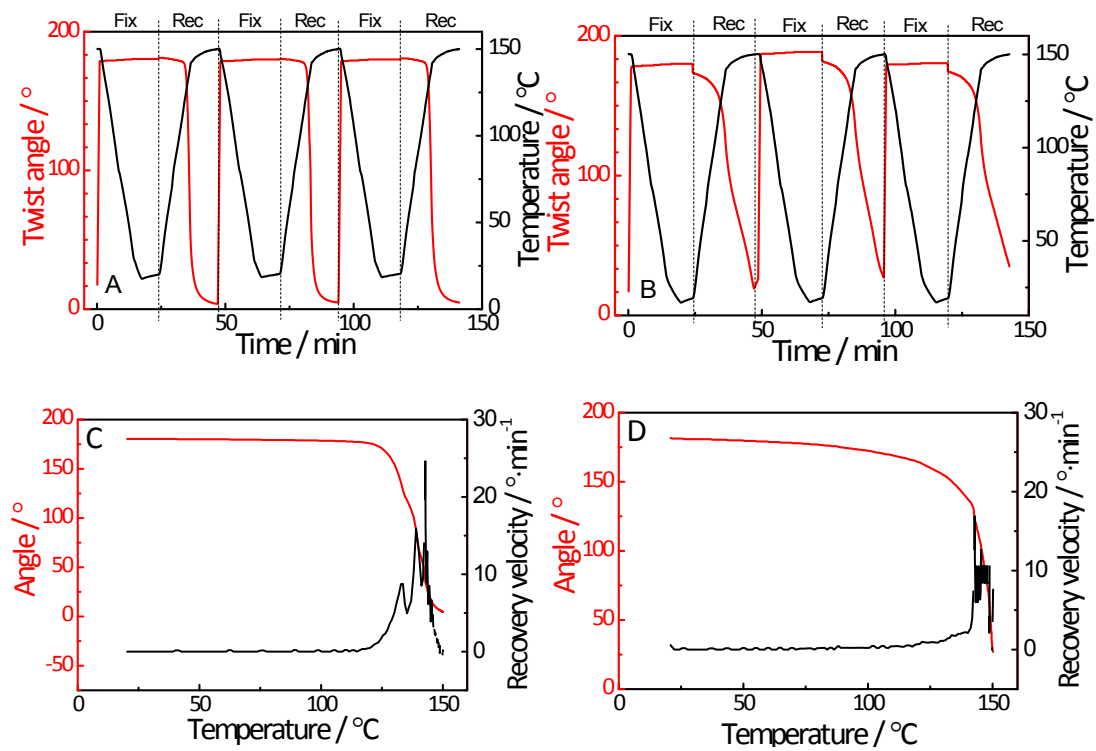




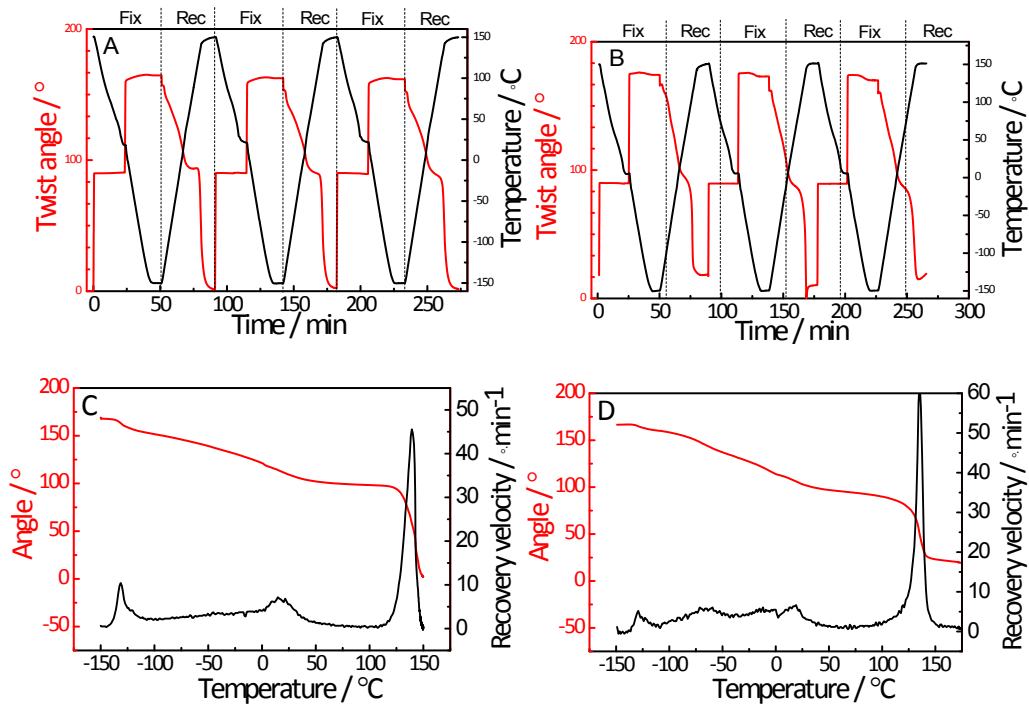
**Fig. S7.** AFM phase maps from the cross-sections of the segmented block copolymers. **A-** AM5K-*b*-PDMS1K; **B-** AM5K-*b*-PDMS5K; **C-** AM5K-*b*-PDMS10K; **D-** LC5K-*b*-PDMS1K; **E-** LC5K-*b*-PDMS5K; **F-** LC5K-*b*-PDMS10K.



**Fig. S8.** AFM height maps from the cross-sections of the segmented block copolymers. **A-** AM5K-*b*-PDMS1K; **B-** AM5K-*b*-PDMS5K; **C-** AM5K-*b*-PDMS10K; **D-** LC5K-*b*-PDMS1K; **E-** LC5K-*b*-PDMS5K; **F-** LC5K-*b*-PDMS10K.



**Fig. S9.** Dual SM torsion test of the multiblock copolymer films with a rotation angle of  $180^\circ$ . **A-** AM5K-*b*-PDMS1K; **B-** LC5K-*b*-PDMS1K. Shape recovery velocity as a function of temperature in the second cycle for **C-** AM5K-*b*-PDMS1K; **D-** LC5K-*b*-PDMS1K. The heating and cooling rates are  $10^\circ\text{C}\cdot\text{min}^{-1}$ .



**Fig. S10.** Triple SM torsion test of the multiblock copolymer films with a total rotation angle of  $180^\circ$ . **A-** AM5K-*b*-PDMS5K; **B-** LC5K-*b*-PDMS5K. Shape recovery velocity as a function of temperature in the second cycle for **C-** AM5K-*b*-PDMS5K; **D-** LC5K-*b*-PDMS5K. Test conditions in the experiment: the degree of rotation =  $90 + 90^\circ$ ,  $T_{prog (A \rightarrow B)} = 150^\circ\text{C}$ ,  $T_{prog (B \rightarrow C)} = 20^\circ\text{C}$ , the heating and cooling rates are  $10^\circ\text{C}\cdot\text{min}^{-1}$ .

## References

- 1 F. Malz and H. Jancke, *J. Pharm. Biomed. Anal.*, 2005, **38**, 813-823.
- 2 M. R. Seger and G. E. Maciel, *Anal. Chem.*, 2004, **76**, 5734-5747.
- 3 J. N. Shoolery, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1977, **11**, 79-93.
- 4 T. H. Mareci and K. N. Scott, *Anal. Chem.*, 1977, **49**, 2130-2136.
- 5 D. J. Cookson and B. E. Smith, *J. Magn. Reson.*, 1984, **57**, 355-368.
- 6 E. Caytan, G. S. Remaud, E. Tenailleau and S. Akoka, *Talanta*, 2007, **71**, 1016-1021.
- 7 D. A. L. Otte, D. E. Borchmann, C. Lin, M. Weck and K. A. Woerpel, *Org. Lett.*, 2014, **16**, 1566-1569.
- 8 P. K. Bhowmik, E. D. T. Atkins, R. W. Lenz and H. Han, *Macromolecules*, 1996, **29**, 3778-3786.
- 9 P. K. Bhowmik and H. Han, *Macromolecules*, 1993, **26**, 5287-5294.
- 10 O. van den Berg, L.-T. T. Nguyen, R. F. A. Teixeira, F. Goethals, C. Özdilek, S. Berghmans and F. E. Du Prez, *Macromolecules*, 2014, **47**, 1292-1300.
- 11 R. Mahou and C. Wandrey, *Polymers*, 2012, **4**, 561.
- 12 W. Huang, Y. Wan, J. Chen, Q. Xu, X. Li, X. Yang, Y. Li and Y. Tu, *Polym. Chem.*, 2014, **5**, 945-954.
- 13 H. Li, S. Thanneeru, L. Jin, C. J. Guild and J. He, *Polym. Chem.*, 2016, **7**, 4824-4832.