Supporting information

Design and synthesis of mechanochromic poly(ether-ester-urethane) elastomer with high toughness and resilience mediated by crystalline domains

Wenwen Wang, Manli Li, Pengcheng Zhou, Zhong Yan, Dong Wang*

Key Laboratory of Textile Fiber and Products (Wuhan Textile University), Ministry of Education, Hubei International Scientific and Technological Cooperation Base of Intelligent Textile Materials & Application, Wuhan Textile University, Wuhan 430200, China

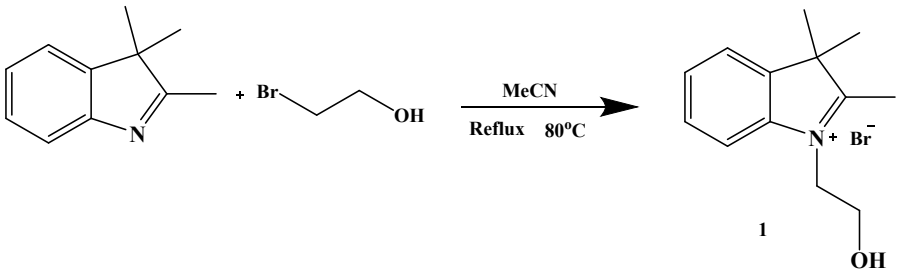
Chemicals

Poly(tetramethylene glycols) (PTMG, *M*n = 850 g/mol、1000 g/mol and 2000 g/mol), 2-bromoethanol (purity: 95%) and hexamethylene diisocyanate (HDI, purity: 99%) were purchased from Aladdin (China). 2,3,3-Trimethylindolenine (purity: 97%) and 3-chloromethyl-5-nitrosalicylaldehyde (purity: 97%) were purchased from TCI. Dimethyl terephthalate (DMT, purity: 99%) and zinc acetate solution (AR) were purchased from Sigma-Aldrich. 1,4-Butanediol (BDO, purity: 99%), tetrabutylorthotitanate (purity: 98%), acetonitrile (purity: 99.5%), potassium hydroxide (KOH, purity: 95%) and dibutyltin dilaurate (DBTDL, purity: 90%) were purchased from Sinopharm. PTMG was heated at 110 °C under vacuum and stirred for 2 h to remove the moisture before use. Other chemicals were used without further purification.

Synthesis of spiropyran diol. 2,3,3-Trimethylindolenine and bromoethanol were dissolved in acetonitrile solution, stirred and refluxed for 24 hours, then washed with ether to obtain **indole (1)**. Indole 1 reacted with potassium hydroxide and distilled water at room temperature for 2 hours to give **indole (2)**. Hydrolysis of 3-chloromethyl-5-nitrosalicylaldehyde gave methylhydroxy substituted **salicylaldehyde (3**) in good yield after recrystallization from water. **Spiropyran (4)** was prepared by condensation of 1and 3 in refluxing 50% aqueous ethanol, which gave the product as a precipitate. The photochrome was recrystallized from acetonitrile and water volume ratio of 7:3 as raw

*Corresponding author. Email: wangdon08@126.com.

material, which gave the pure photochrome.



Scheme S1 The synthesis route of indole (1).

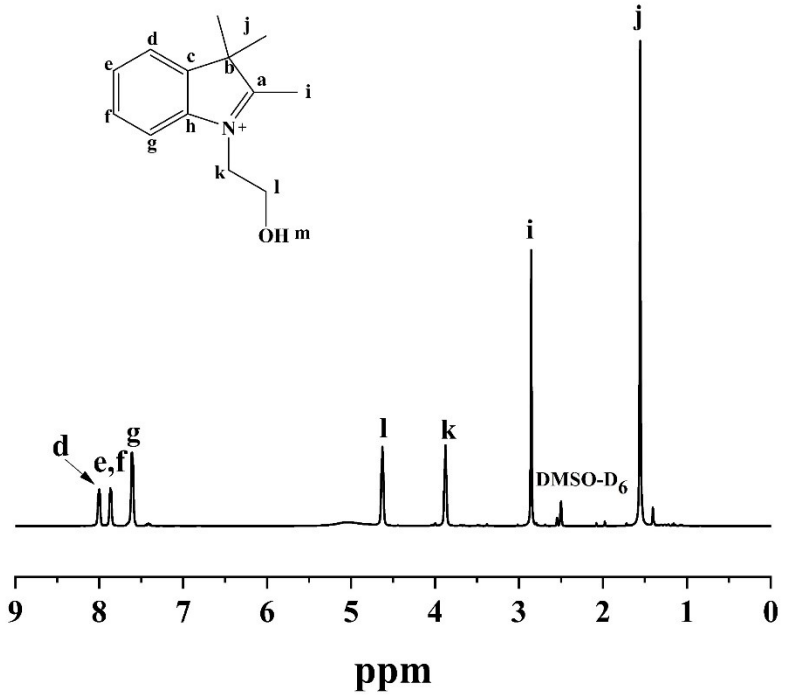
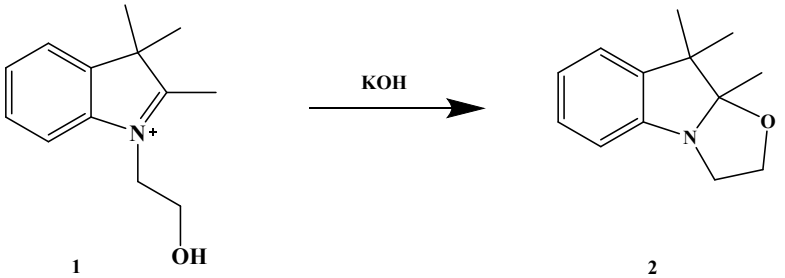


Figure S1 ^{1}H NMR spectrum of indole (1).



Scheme S2 The synthesis route of indole (2).

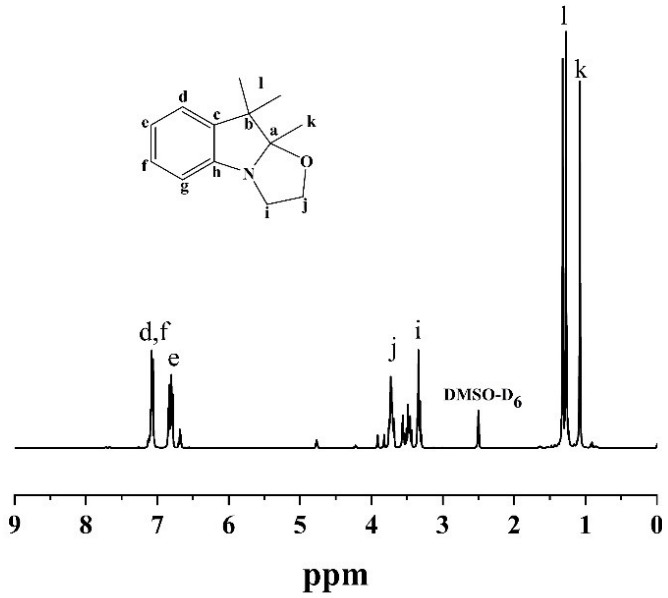
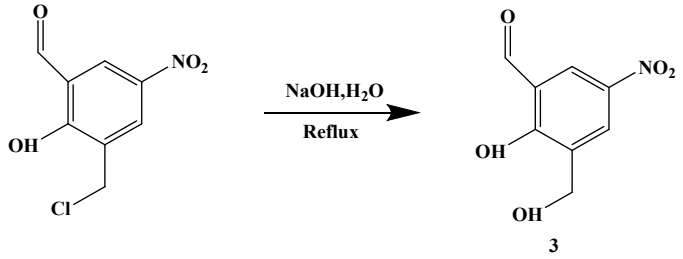


Figure S2 ^{1}H NMR spectrum of indole (2).



Scheme S3 The synthesis route of salicylaldehyde (3).

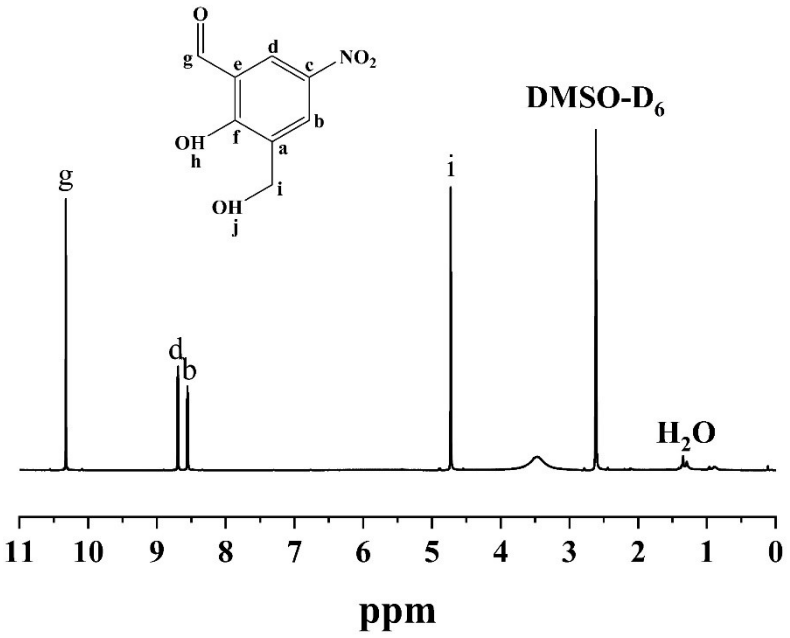
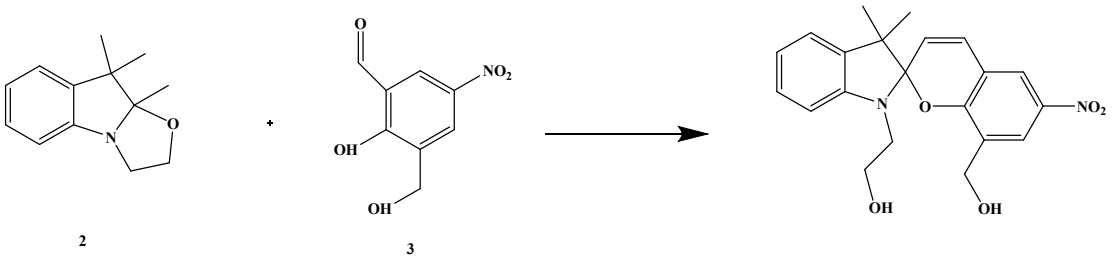


Figure S3 ^{1}H NMR spectrum of salicylaldehyde (3).



Scheme S4 The synthesis route of spiropyran (4).

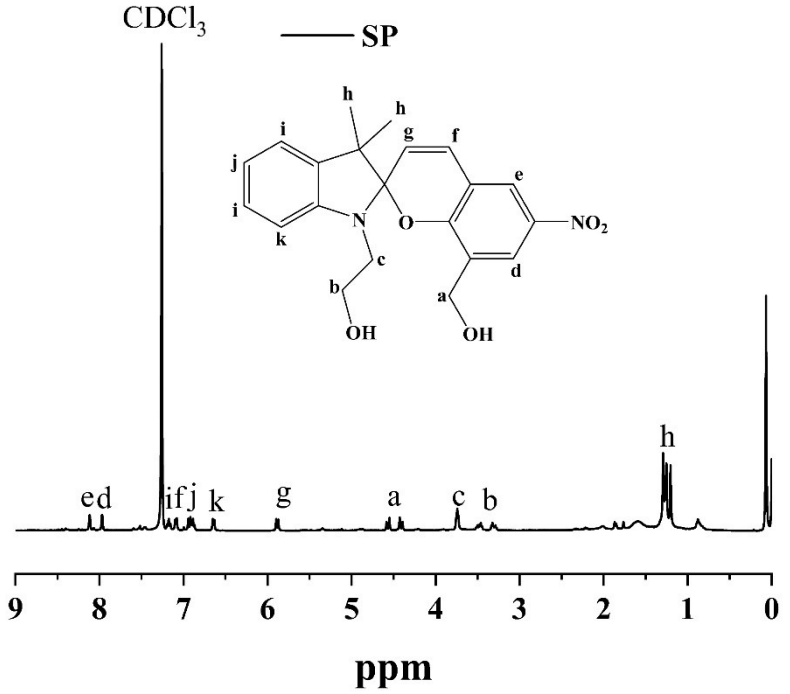
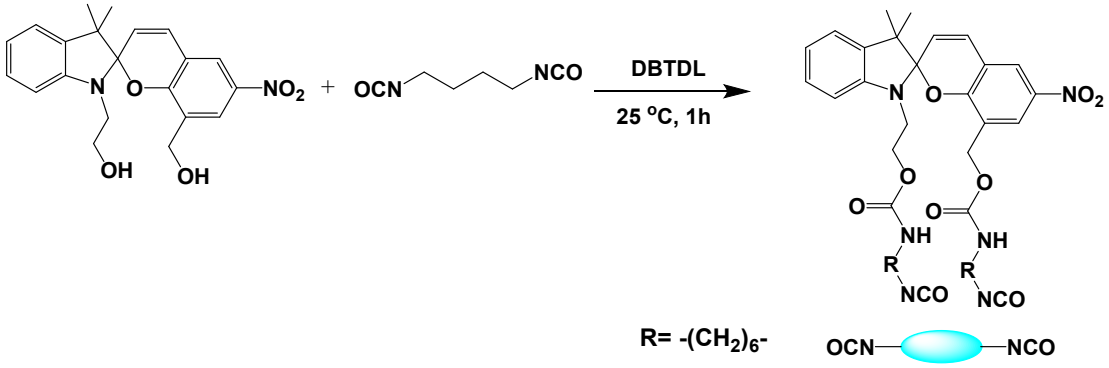


Figure S4 ^{1}H NMR spectrum of spiropyran (4).



Scheme S5 The synthesis route of NCO-SP-NCO.

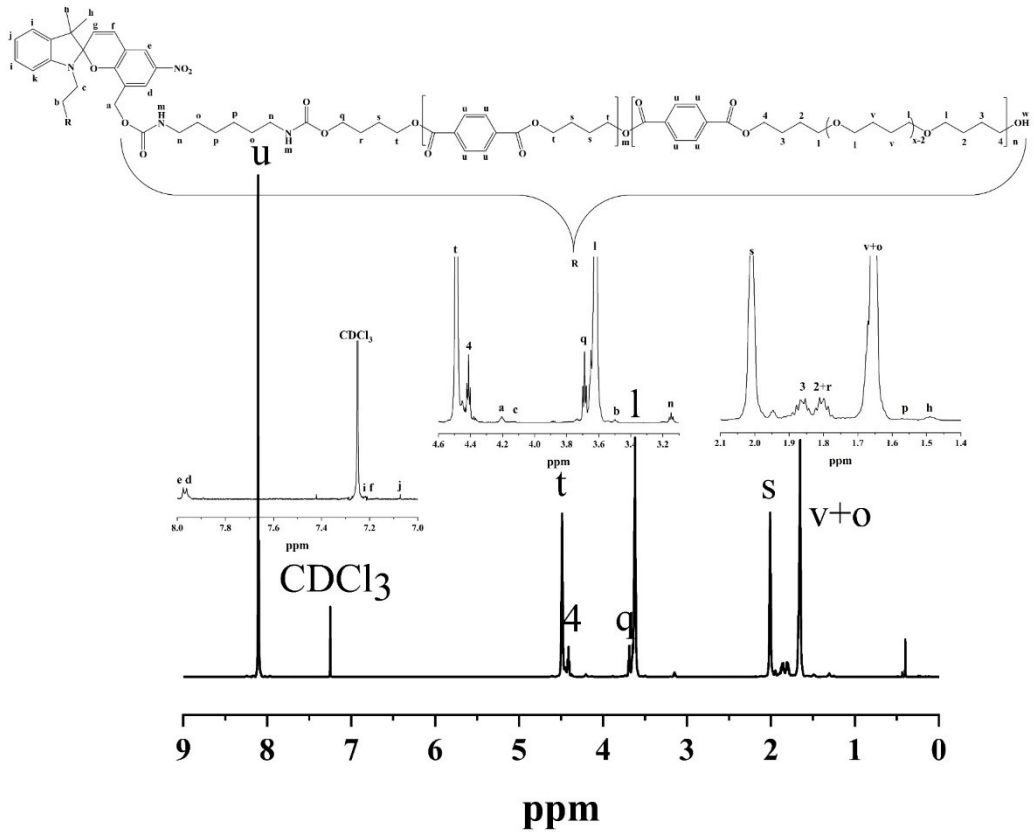


Figure S5 The ^{1}H NMR spectrum of PBT-SP-PTMG850-1

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm): 8.14 (d, 8H, H_u), 7.97 (s, 1H, H_e), 7.96 (s, 1H, H_d), 7.22 (m, 2H, H_i), 7.21 (m, 1H, H_f), 7.07 (d, 1H, H_j), 4.49 (m, 6H, H_t), 4.41 (m, 4H, H_4), 4.21 (s, 2H, H_a), 4.13 (m, 2H, H_c), 3.69 (m, 2H, H_q), 3.62 (m, 4H, H_l), 3.50 (m, 2H, H_b), 3.15 (m, 4H, H_n), 2.00 (m, 6H, H_s), 1.87-1.84 (m, 4H, H_3), 1.82-1.78 (m, 6H, H_{2+r}), 1.65 (m, 8H, H_{v+o}) , 1.54 (m, 4H, H_P) , 1.49 (s, 6H, H_h) .

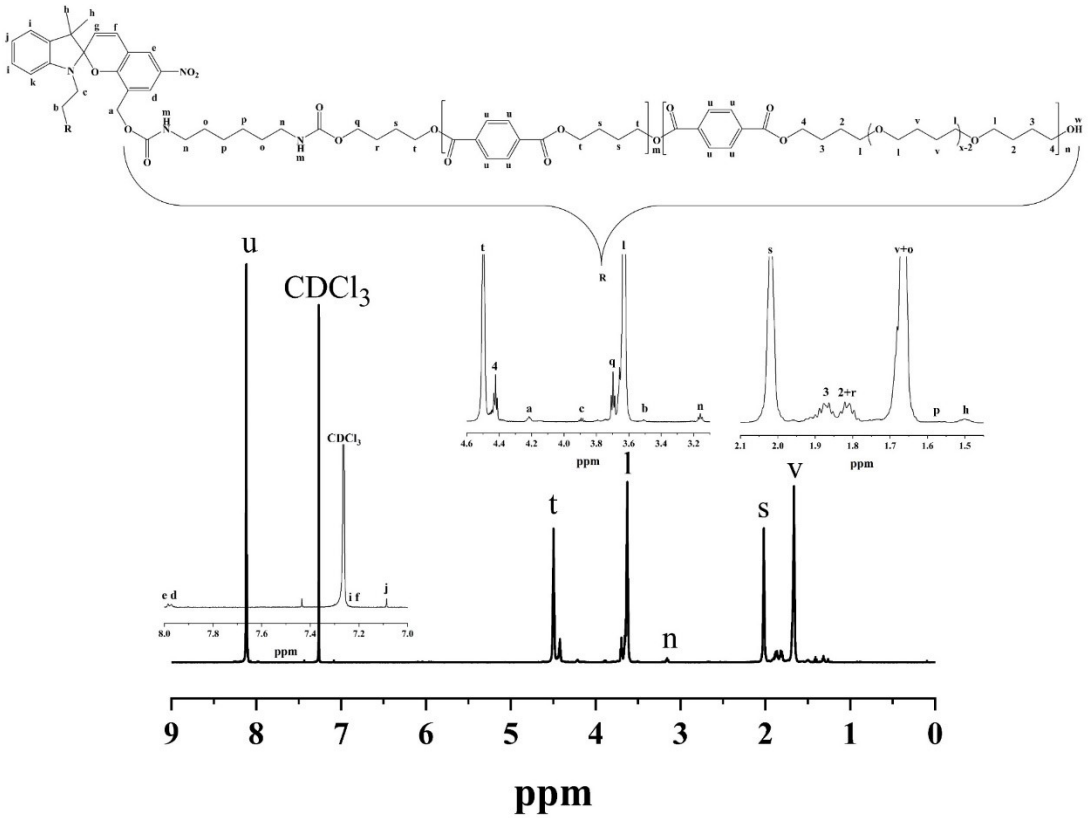


Figure S6 The ^{1}H NMR spectrum of PBT-SP-PTMG1000-1.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm): 8.14 (d, 8H, H_u), 7.98(s, 1H, H_e), 7.97 (s, 1H, H_d),7.23 (m, 2H, H_i), 7.22 (m, 1H, H_f), 7.09 (d, 1H, H_j), 4.50 (m, 6H, H_t), 4.42 (m, 4H, H_4), 4.22 (s, 2H, H_a), 4.14 (m, 2H, H_c), 3.70 (m, 2H, H_q), 3.63 (m, 4H, H_l), 3.51 (m, 2H, H_b), 3.16 (m, 4H, H_n), 2.02 (m, 6H, H_s), 1.89-1.85 (m, 4H, H_3), 1.82-1.80 (m, 6H, H_{2+r}), 1.66 (m, 8H, H_{v+o}) , 1.56 (m, 4H, H_P) , 1.50 (s, 6H, H_h).

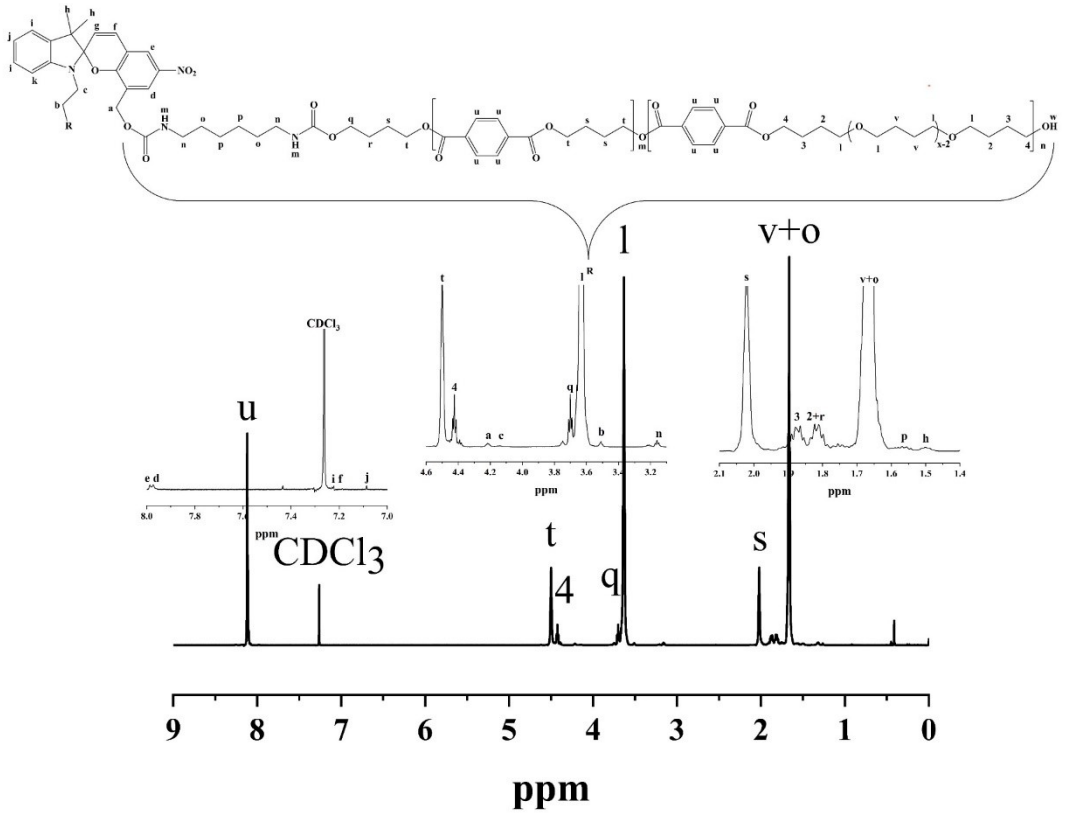


Figure S7 The ^{1}H NMR spectrum of PBT-SP-PTMG2000-1

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm): 8.14 (d, 8H, H_u), 7.98 (s, 1H, H_e), 7.97 (s, 1H, H_d), 7.23 (m, 2H, H_i), 7.22 (m, 1H, H_f), 7.09 (d, 1H, H_j), 4.50 (m, 6H, H_t), 4.42 (m, 4H, H_4), 4.22 (s, 2H, H_a), 4.14 (m, 2H, H_c), 3.70 (m, 2H, H_q), 3.63 (m, 4H, H_l), 3.51 (m, 2H, H_b), 3.16 (m, 4H, H_n), 2.02 (m, 6H, H_s), 1.89-1.85 (m, 4H, H_3), 1.82-1.80 (m, 6H, H_{2+r}), 1.66 (m, 8H, H_{v+o}) , 1.56 (m, 4H, H_P) , 1.50 (s, 6H, H_h) .

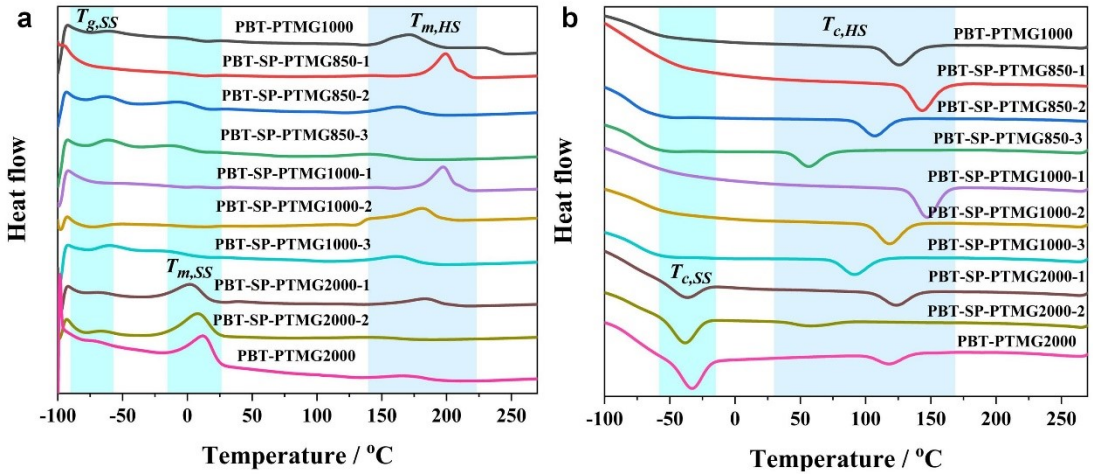


Figure S8 DSC thermograms for elastomers with SP and without SP; (a) heating ramp and (b) cooling (crystallization) ramp.

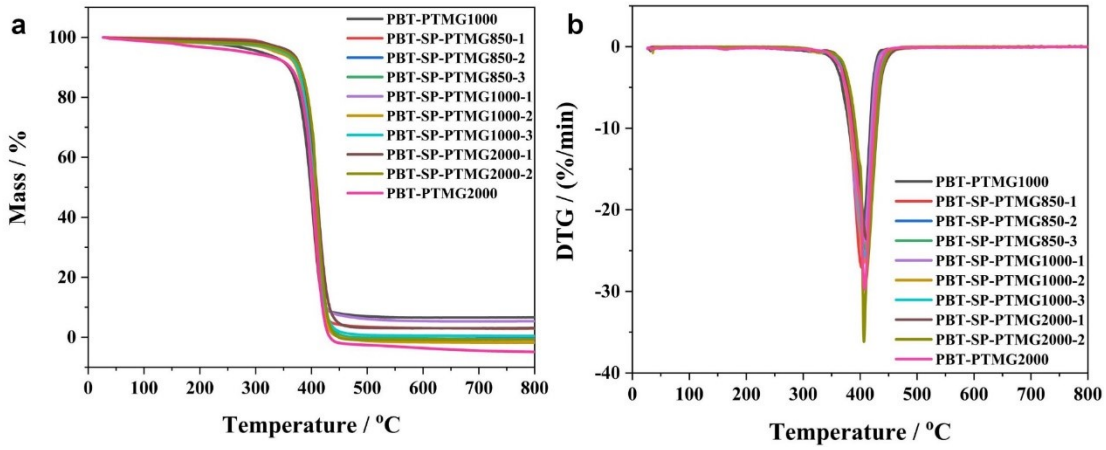


Figure S9 Thermogravimetric analysis (TGA) of elastomers.

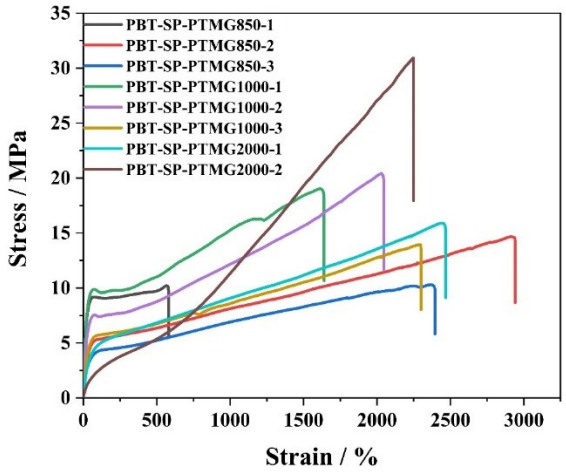


Figure S10 Representative stress-strain curves of elastomers.

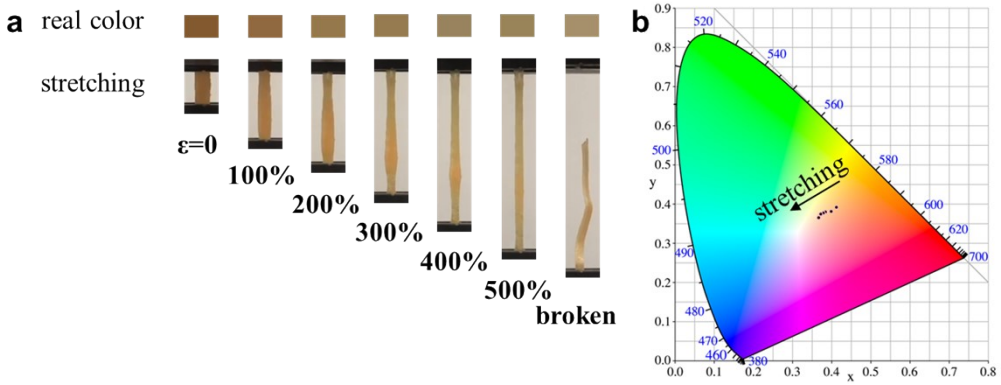


Figure S11 (a) Snapshots of PBT-SP-PTMG850-1 during tensile testing. (b) The strain-induced color changes in the CIE *xy* chromaticity diagram during the elastomer stretching.

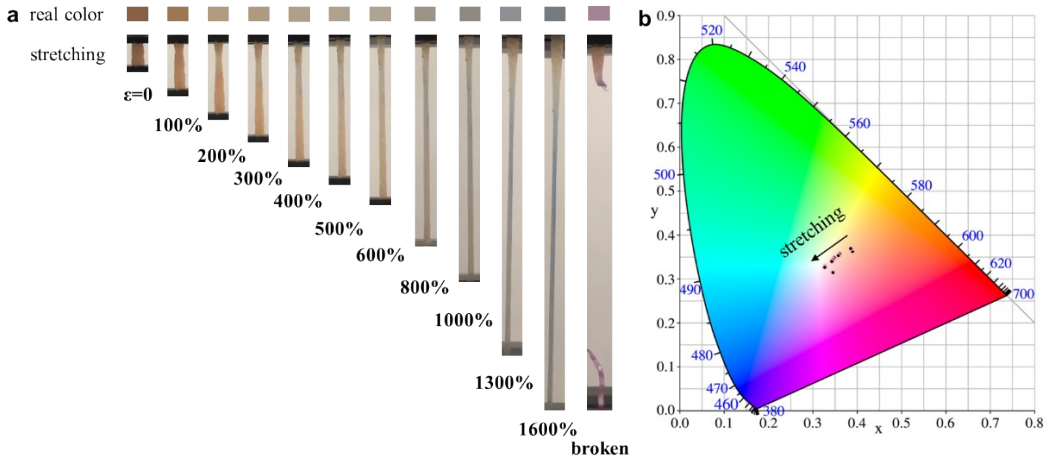


Figure S12 (a) Snapshots of PBT-SP-PTMG850-2 during tensile testing. (b) The strain-induced color changes in the CIE *xy* chromaticity diagram during the elastomer stretching.

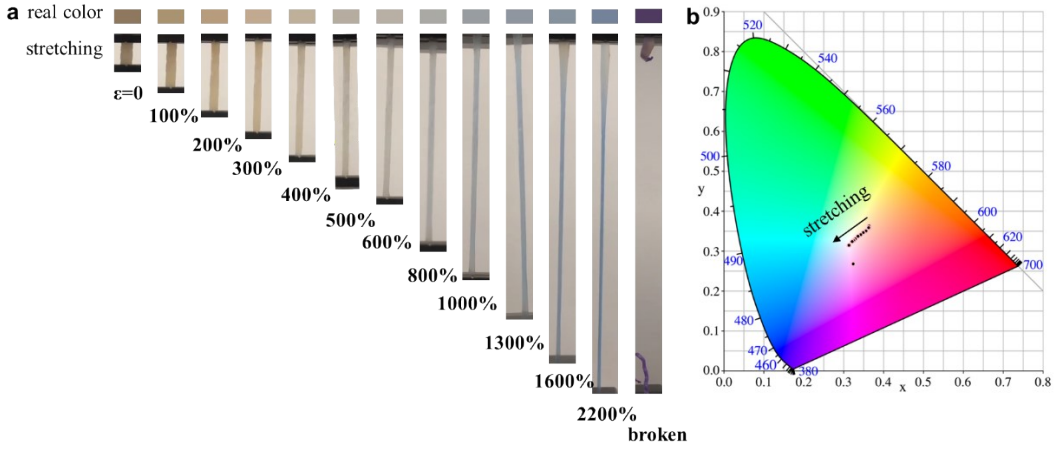


Figure S13 (a) Snapshots of PBT-SP-PTMG850-3 during tensile testing. (b) The strain-induced color changes in the CIE *xy* chromaticity diagram during the elastomer stretching.

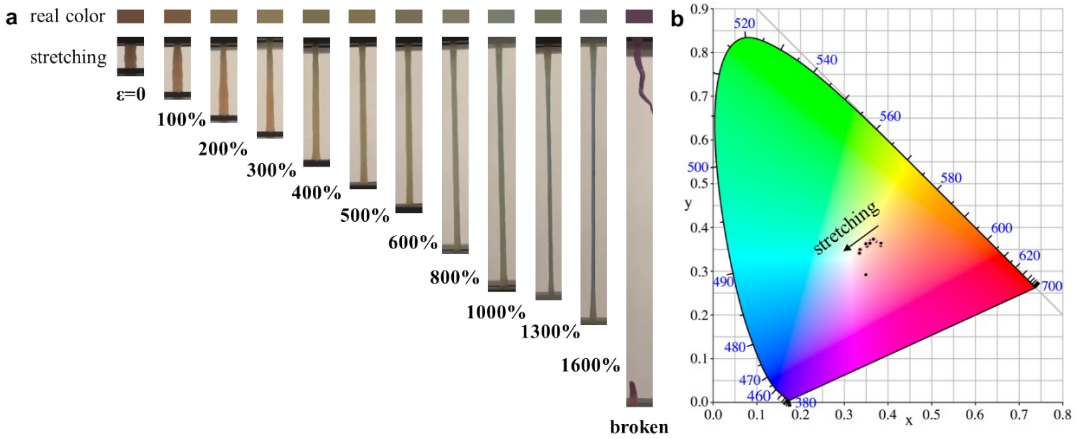


Figure S14 (a) Snapshots of PBT-SP-PTMG1000-2 during tensile testing. (b) The

strain-induced color changes in the CIE *xy* chromaticity diagram during the elastomer stretching.

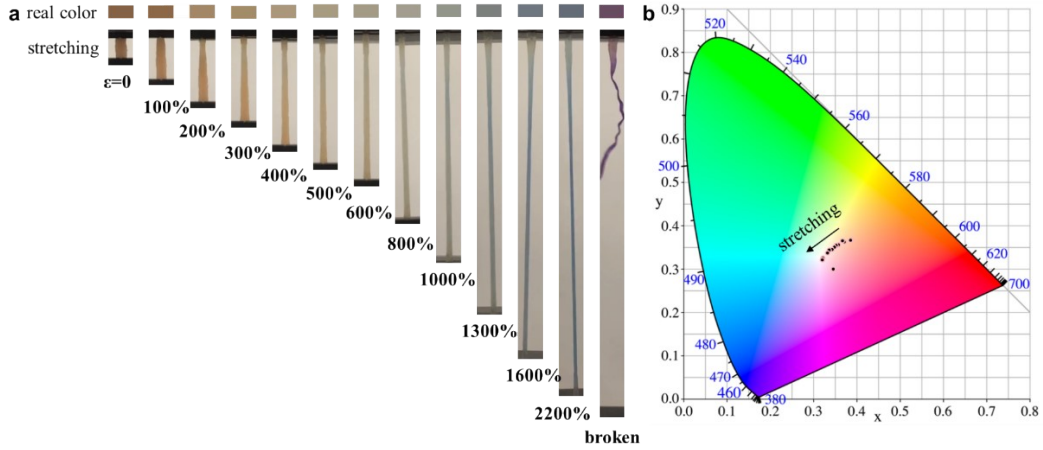


Figure S15 (a) Snapshots of PBT-SP-PTMG1000-3 during tensile testing. (b) The strain-induced color changes in the CIE *xy* chromaticity diagram during the elastomer stretching.

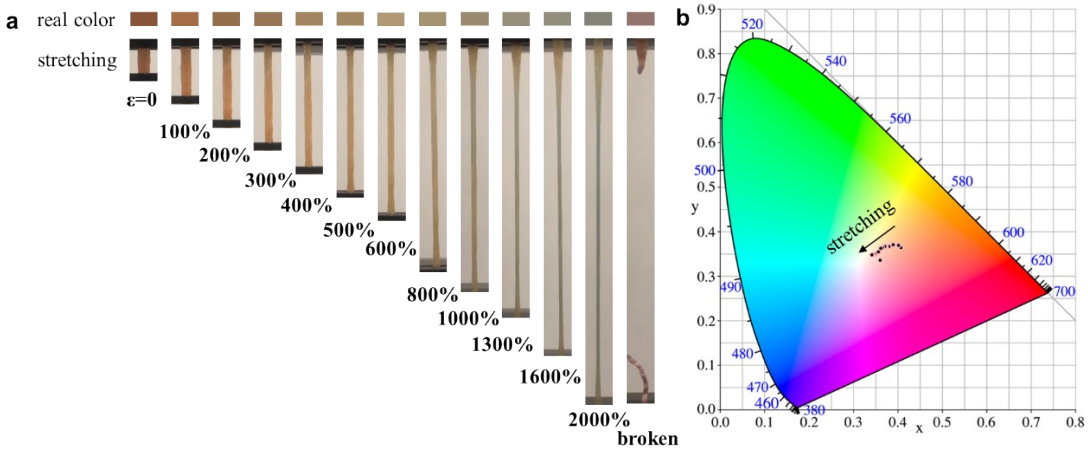


Figure S16 (a) Snapshots of PBT-SP-PTMG2000-1 during tensile testing. (b) The strain-induced color changes in the CIE *xy* chromaticity diagram during the elastomer stretching.

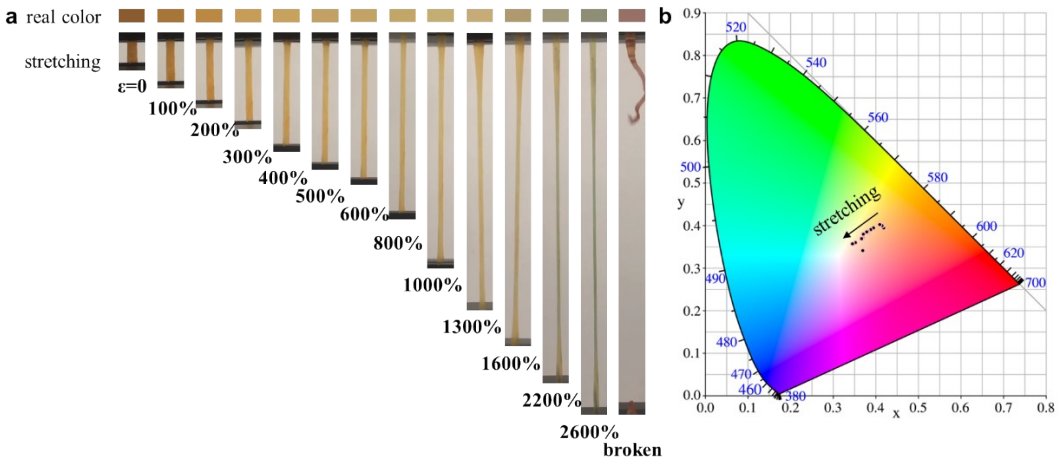


Figure S17 (a) Snapshots of PBT-SP-PTMG2000-2 during tensile testing. (b) The strain-induced color changes in the CIE *xy* chromaticity diagram during the elastomer stretching.

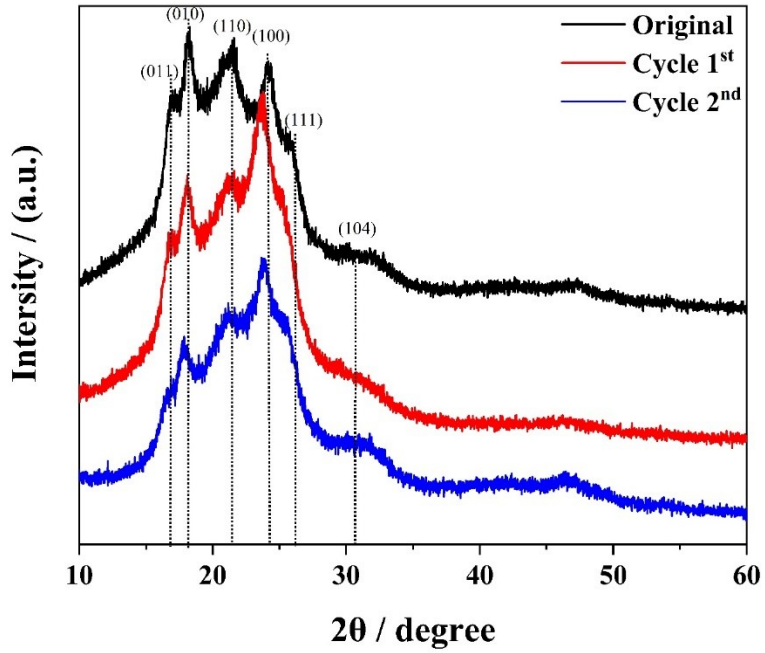


Figure S18 X-ray diffraction (XRD) profiles of PBT-SP-PTMG1000-1 before being stretched (Original), after the first (Cycle 1st) and the second (Cycle 2nd) cyclic stretching.