Supplementary Information

Enabling Shape Memory and Healable Effects in a Conjugated Polymer by Incorporating Siloxane via Dynamic Imine Bond

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1. Materials and Instruments

9,9-dihexylfluorene-2,7 diboronic acid bis(1,3-propanediol) ester (97%), 4,7-dibromo-2,1,3-benzothiadiazole (98%), tetraethylammonium hydroxide (~ 40 wt% in water), tris(dibenzylideneacetone) dipalladium(0) (Pd$_2$(dba)$_3$, palladium content 15.0~22.0%) and tri(o-tolyl)phosphine (P(o-tol)$_3$, 97%) were purchased from Sigma-Aldrich. 5-bromoisophthalaldehyde (95%) was purchased from Combi-Blocks. Aminopropyl terminated polydimethylsiloxane (100-120 cSt) was purchased from Gelest. Solvents were purchased from VWR Singapore. All the reagents and solvents were used directly.

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker ARX 400 MHz spectrometer. Chemical shifts were recorded in parts per million (ppm) and referenced to the residual solvent (CDCl$_3$: 7.26 ppm) in $^1$H NMR.

Fourier transform infrared spectra (FT IR) were recorded on a Bruker vertex 70 using ATR mode by 40 scans from 4000 to 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

Gel permeation chromatography (GPC) analysis was performed in THF (1 mL/min) using Agilent PL mixed gel B 10 µm column with waters 1515 isocratic pump and 2414 refractive index detector. Polystyrene standards were used for calibration curve.

Solution UV-vis absorption spectra of the polymers were recorded on a Shimadzu UV-1700 spectrometer in THF solutions. Absorbance of films were recorded with spin-coated films on glass substrates. Solution photoluminescence (PL) spectra of the polymers were measured with the excitation wavelength of 450 nm on a Perkin-Elmer LS 55 spectrofluorometer in THF solutions. Curves were normalized by keeping the same amount of PFBT polymers.
Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG 60 AH with a heating rate of 20 °C/min from 20 °C till 800 °C under nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a Perkin Elmer DSC 8000. Samples were heated to 220 °C and then cooled to 20 °C with a scanning rate of 20 °C/min for 2 cycles. Results was taken from the second heating curve.

Uniaxial tensile test was performed on an Instron 3345 with an extension rate of 10 mm/min at room temperature (~ 20 ± 2 °C). Dynamic mechanical analysis (DMA) was performed on a TA Q800 machine using film tensile mode.

2. Methods

*Synthesis of the isophthalaldehyde end-capped poly(fluorene-co-benzothiadiazole) (PFBT) via one-pot Suzuki polymerizations*¹

\[
\begin{align*}
\text{CHO} & \quad \text{CHO} \\
\text{Br} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{Br} & \quad \text{Br} \\
\text{B} & \quad \text{B} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (256.0 mg, 0.51 mmol), 5-bromoisophthalaldehyde (4.3 mg, 0.02 mmol), 4,7-Dibromo-2,1,3-benzothiadiazole (147.0 mg, 0.50 mmol), Pd\(_2\)(dba)\(_3\) (9.0 mg, 0.01 mmol) and P(o-tol)\(_3\) (12.0 mg, 0.04 mmol) were charged into a schlenk tube. The tube was degassed and filled with Argon. A mixture of degassed toluene (8 mL), tetraethylammonium hydroxide (0.5 mL, 1.4 mmol), and deionized water (1.5 mL) was transferred to the tube. After three freeze-pump-thaw cycles, the tube was put in an oil bath of 70 °C for three days. Afterwards, the mixture was washed with water and extracted with toluene. The organic layer was collected and precipitated into methanol. The precipitates was collected and dissolved in toluene and precipitated into methanol twice. The obtained solids were then dried to get yellow powders as final product of the isophthalaldehyde end-capped PFBT (yield 95%, Mw 20400, PDI 3.16).

*Synthesis of the poly(fluorene-co-benzothiadiazole)-co-polydimethylsiloxane (PFBT-PDMS) copolymer via imine reactions*

Isophthalaldehyde end-capped PFBT (aldehyde content ~1/7k, 28.0 mg) and amino-terminated PDMS (amino content ~2/5k, 15.0 mg) were charged to a glass vial with toluene (0.5 mL). The vial was put in an oil bath for 20 hours under toluene reflux. Afterwards, the solution was added into methanol and the precipitates were collected and dried to obtain the copolymer. For film preparations, the solution was directly casted on a hand-made Teflon mode (40.0 x 10.0 x 0.5 mm). The mold was put in the fume hood overnight to evaporate remaining solvents to obtain the film.
DMA analysis of the copolymer film

The copolymer film size was 16.0 x 3.5 x 0.1 mm approximately for all tests. Before mechanical tests, films were heated on a hot plate (120 °C) for 20 mins of annealing. Heating rate was 3 °C/min for all tests. Oscillation modulus test within a temperature range was performed using multi-frequency-strain mode with a frequency 1 Hz and a strain 0.1%. Glass transition temperature ($T_g$) was recorded as the maximum value of loss factor tan $\delta$. The time and temperature dependent tests were performed after samples reached equilibrium temperature and kept isothermal for 2 mins. Creep recovery experiments were performed by monitoring strain changes of samples during a displace stress (creep) for 10 mins followed with stress free (recover) for 10 mins. Stress relaxation experiments were performed by monitoring stress relaxation modulus changes of samples after an original displace strain 1%. Stress relaxation activation energy $E_a$ was calculated by fitting the Arrhenius equation:

$$ln \tau^* (T) = ln\tau_0 + E_a/RT$$

Where $\tau^*$ is the characteristic relaxation time determined by when normalized stress relaxation modulus $G_r/G_0$ decreased to 1/e, and $R$ is the gas constant with the value 8.31446 J/K·mol. By fitting $\tau^*$ with $1000/T$ in a linear curve, the stress relaxation activation energy $E_a$ was calculated to be $80.0 \pm 0.2$ kJ/mol.

3. Supporting Data

Fig. S1 Sol-gel transition of the PFBT-PDMS reaction mixture.
Fig. S2 FT IR spectra of PFBT-PDMS during imine reaction.

Fig. S3 a) UV-vis absorption and b) PL spectra of PFBT and PFBT-PDMS.

Fig. S4 a) TGA and b) DSC analysis results of the copolymer PFBT-PDMS.
Fig. S5 A typical tensile curve of the copolymer film.

Fig. S6 A copolymer film at a) original and b) stretched state on a hot-plate (140 °C).

Fig. S7 Creep recovery results of a copolymer film under different stresses at 140 °C.
Fig. S8 A bulk film generated from two overlapped films after hot-pressing.

Fig. S9 A copolymer film a) before and b) after swelling in THF for 3 hours.

Fig. S10 GPC analysis of the benzaldehyde-induced polymer degradation.

4. References:
