Supporting Information

Intrinsically stretchable, solution-processable functional poly(siloxane-imide)s for stretchable resistive memory applications

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Experimental section

Synthesis of poly(siloxane-imide)s

Synthesis of ODPA-A12 poly(siloxane-imide): As shown in Scheme 1, in a 50ml two-neck flask, dianhydride (ODPA, 2 mmol, 620.4mg) was dissolved and stirred in DMAc(5ml) under a nitrogen atmosphere. After 30 minutes, aminopropyl terminated polydimethylsilxoane (DMS-A12, 2 mmol, 1.9g) diluted with THF(5ml) was added dropwise with stirring to react with ODPA. After 2 days, the transparent and viscous reaction mixture was diluted by DMAc and dropped in MeOH/H_2O mixing solvent to achieve adhesive and viscous poly(amic-acid) precursor. Next, the PAA precursor was dissolved in chloroform and collected in glass petri dish by drop-casting. Finally, the PAA film on petri dish was converted to poly(siloxane-imide) via thermal imidization process at 100^{o}C for 1 hour, 200^{o}C for 1 hour, and 300^{o}C for 2 hours. The obtained polymer was brown jelly-like solid. GPC (DMF, 70 °C): Mn: 7300, PDI: 1.58

Synthesis of ODPA-A15 poly(siloxane-imide): The synthetic procedure was the same as ODPA-A12. ODPA(2 mmol, 620.4mg) as dianhydride, DMS-A15(2 mmol, 6g) as aminopropyl terminated polydimethylsiloxane, DMAc(5ml), and THF(5ml) were used. The obtained polymer was brown jelly-like solid. GPC (DMF, 70 °C): Mn: 7700, PDI: 1.47

Synthesis of BPDA-A12 poly(siloxane-imide): The synthetic procedure was the same as ODPA-A12, but the volume ratio of DMAc/THF was different. BPDA(2 mmol, 588.4mg) as dianhydride, DMS-A12(2 mmol, 1.9g) as aminopropyl terminated polydimethylsiloxane, DMAc (3ml) and THF (6ml) were used. The obtained polymer was brown jelly-like solid. GPC (DMF, 70 °C): Mn: 7700, PDI:

1.38

Synthesis of BPDA-A15 poly(siloxane-imide): The synthetic procedure was the same as ODPA-A12, but the volume ratio of DMAc/THF was different. BPDA(2 mmol, 588.4mg) as dianhydride, DMS-A15(2 mmol, 6g) as aminopropyl terminated polydimethylsiloxane, DMAc (3ml) and THF (6ml) were used. The obtained polymer was brown jelly-like solid. GPC (DMF, 70 °C): Mn: 7300, PDI: 1.44

Synthesis of PMDA-A12 poly(siloxane-imide): Only THF is used as solvent for the synthesis of PMDA-A12. In a 50ml two-neck flask, dianhydride (PMDA, 2 mmol, 436.2mg) was dissolved and stirred in THF (5ml) under a nitrogen atmosphere. After 30 minutes, aminopropyl terminated polydimethylsiloxane (DMS-A12, 2 mmol, 1.9g) diluted with THF (5ml) was added dropwise with stirring to react with PMDA. After 2 days, the transparent and viscous reaction mixture was diluted by THF and dropped in MeOH/H_2O mixing solvent to achieve adhesive and viscous poly(amic-acid) precursor. Next, the PAA precursor was dissolved in chloroform and collected in glass petri dish by drop-casting. Finally, the PAA film on petri dish was converted to poly(siloxane-imide) via thermal imidization process at 100^{o}C for 1 hour, 200^{o}C for 1 hour, and 300^{o}C for 2 hours. The obtained polymer was brown jelly-like solid. The obtained polymer was brown jelly-like solid. GPC (DMF, 70 °C): Mn: 6500, PDI: 1.27

Synthesis of PMDA-A15 poly(siloxane-imide): The synthetic procedure was the same as PMDA-A12. PMDA (2 mmol, 436.2mg) as dianhydride, DMS-A15 (2 mmol, 6g) as aminopropyl terminated polydimethylsiloxane and THF (totally 10ml) were used. The obtained polymer was brown jelly-like solid. GPC (DMF, 70 °C): Mn: 9200, PDI: 1.24

Synthesis of 6FDA-ODA polyimide as the reference experiment

The soluble 6FDA-ODA polyimide was synthesized according to the previous study.[1] 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 4,4'-oxydianiline (ODA) were purchased from Tokyo Chemical Industry company (Japan). 6FDA were purified by recrystallization from acetic anhydride and dried under vacuum at 140 °C for 24 hours before use.

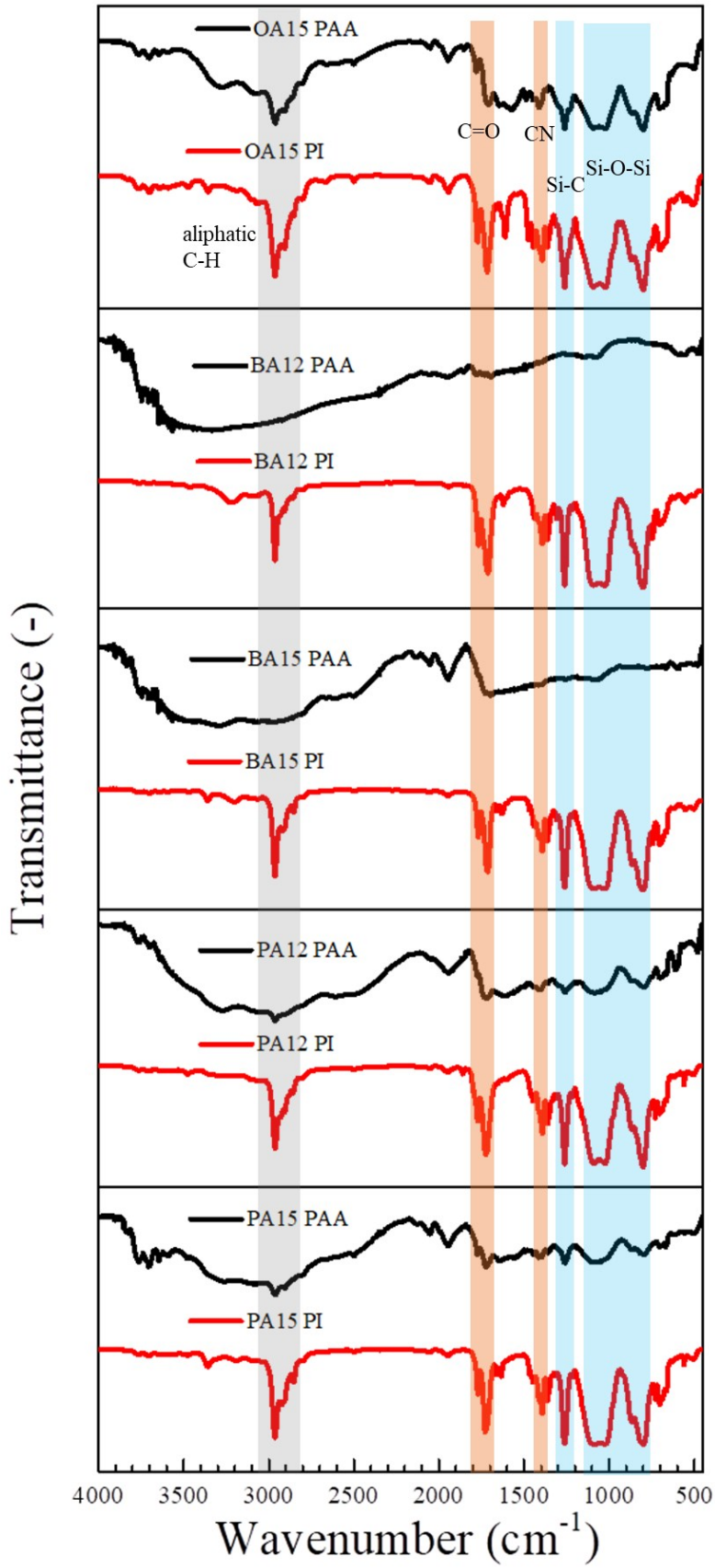
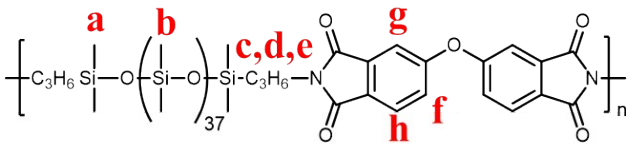
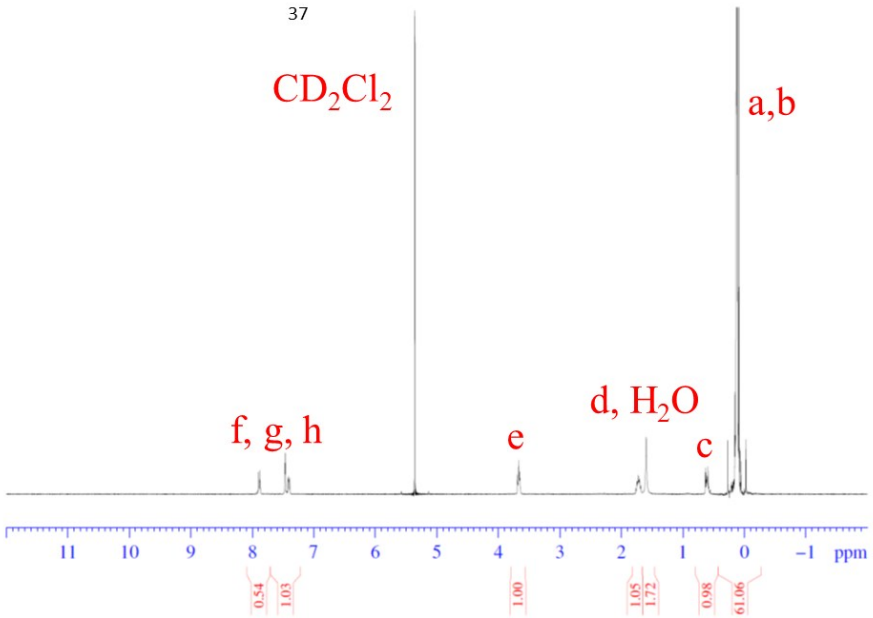


Figure S1. FTIR spectra of ODPA-A15, BPDA-A12, BPDA-A15, PMDA-A12, and PMDA-A15, and their precursors.

(a)


a
b
c,d,e
g
f
h
37
n


37
CD2Cl2
a,b
f, g, h
e
d, H2O
c
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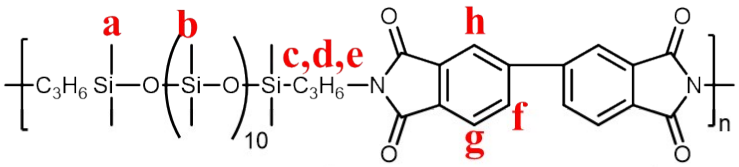
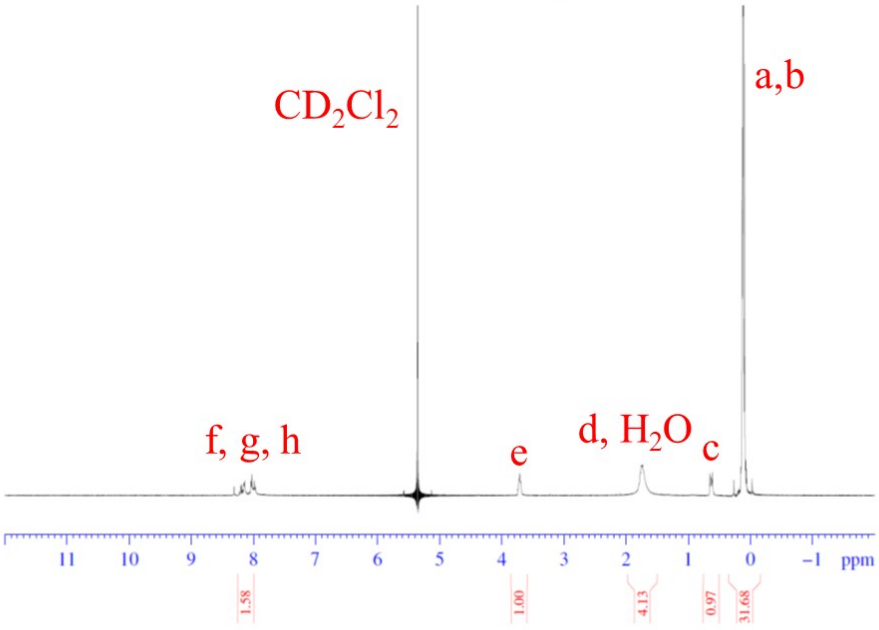
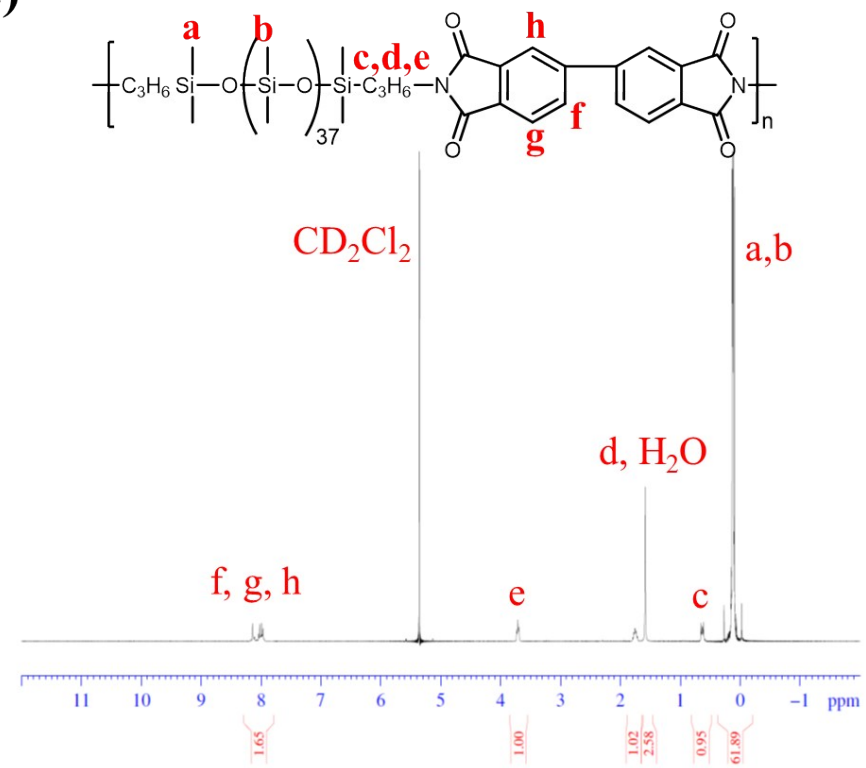
0.54
1.03
1.00
1.05
1.72
0.98
61.06

(b)

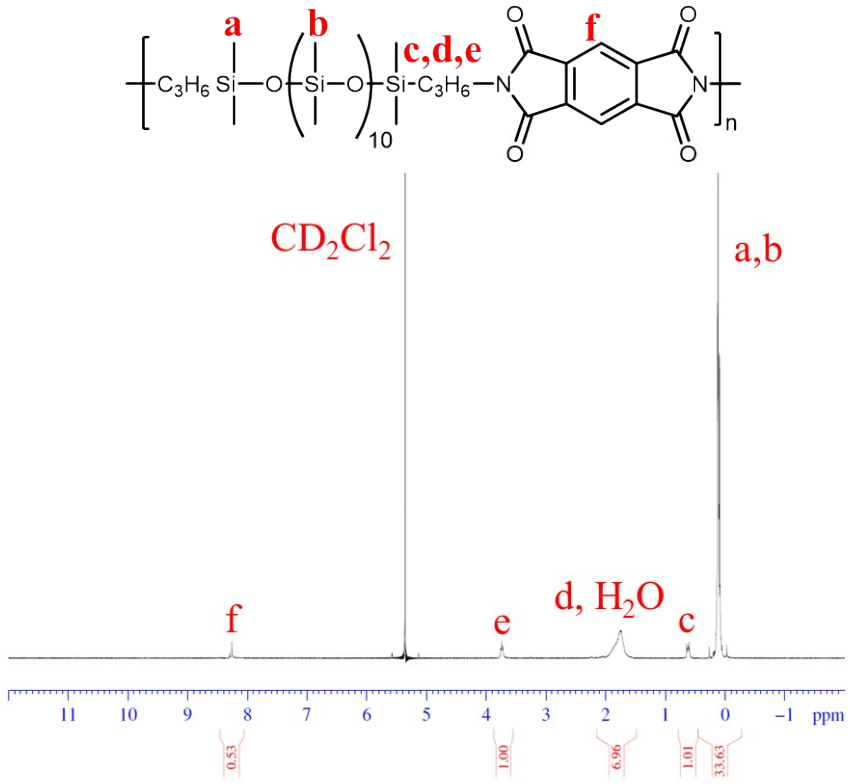

a
b
c,d,e
h
f
g
10
n


CD2Cl2
a,b
f, g, h
e
d, H2O
c
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm
1.58
1.00
4.13
0.97
31.68

(c)


a
b
c,d,e
h
f
g
37
n
CD2Cl2
a,b
d, H2O
f, g, h
e
c
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm
1.65
1.00
1.02
2.58
0.95
61.89

(d)


a
b
c,d,e
f
10
n
CD2Cl2
a,b
f
e
d, H2O
c
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0.53
1.00
6.96
1.01
33.63

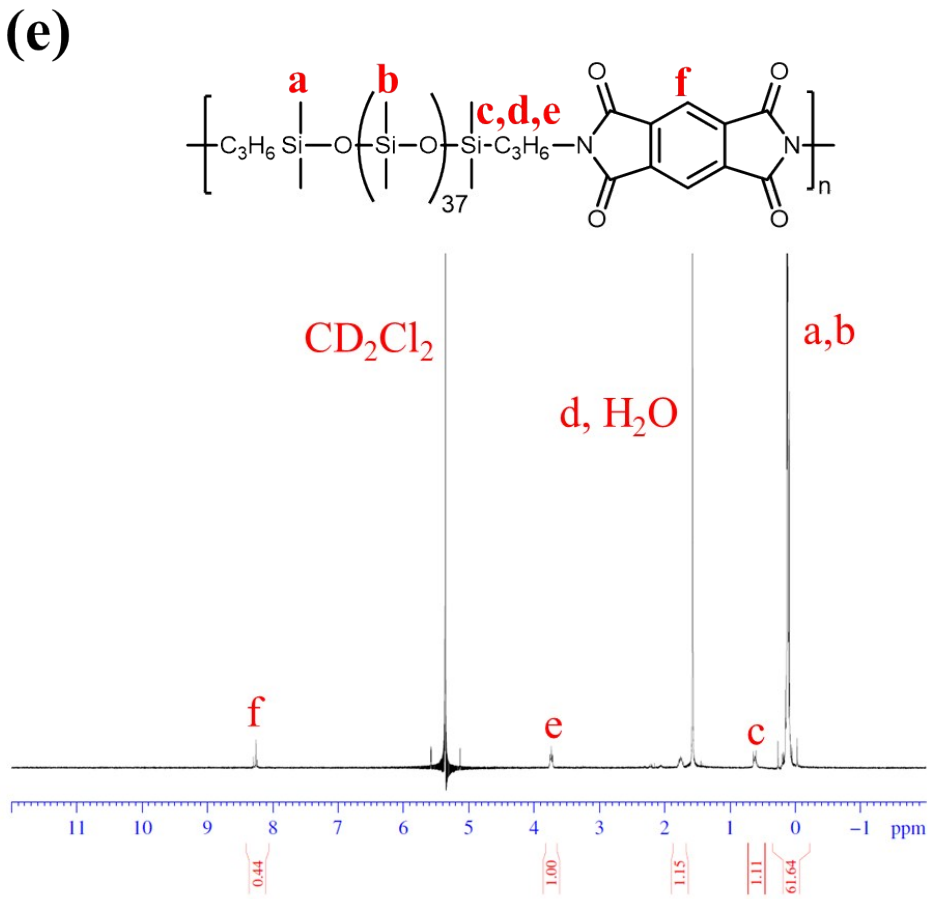

Figure S2. ^{1}H NMR spectra of (a) ODPA-A15, (b) BPDA-A12, (c) BPDA-A15, (d) PMDA-A12, and (e) PMDA-A15 PIs.

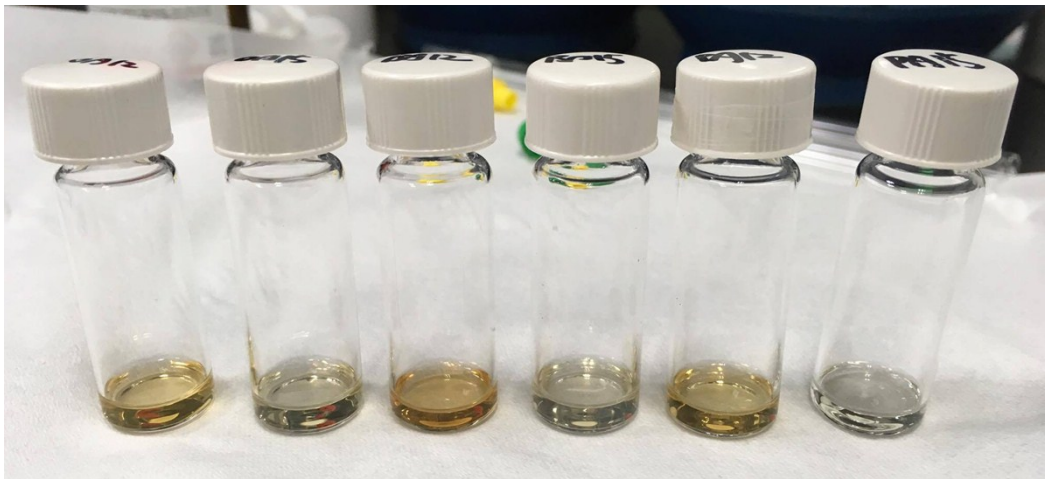

Figure S3. Solution of ODPA-A12, ODPA-A15, BPDA-A12, BPDA-A15, PMDA-A12, and PMDA-A15 PIs (from left to right) in DCM.

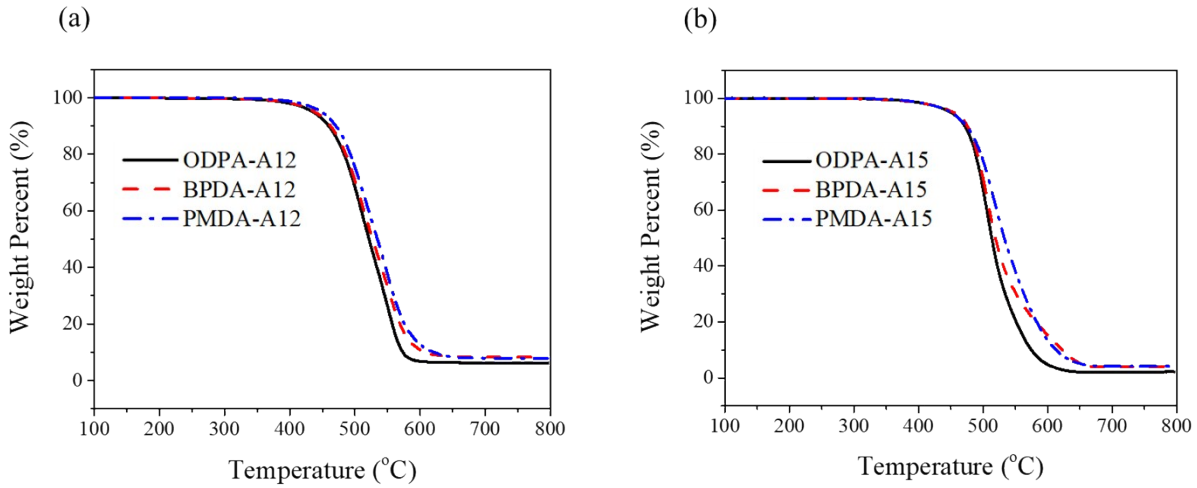

Figure S4. The TGA curves of (a) ODPA-A12, BPDA-A12, PMDA-A12, (b) ODPA-A15, BPDA-A15, and PMDA-A15 PIs. (from 100 to 800 °C, ramp rate: 10 °C min^{-1})

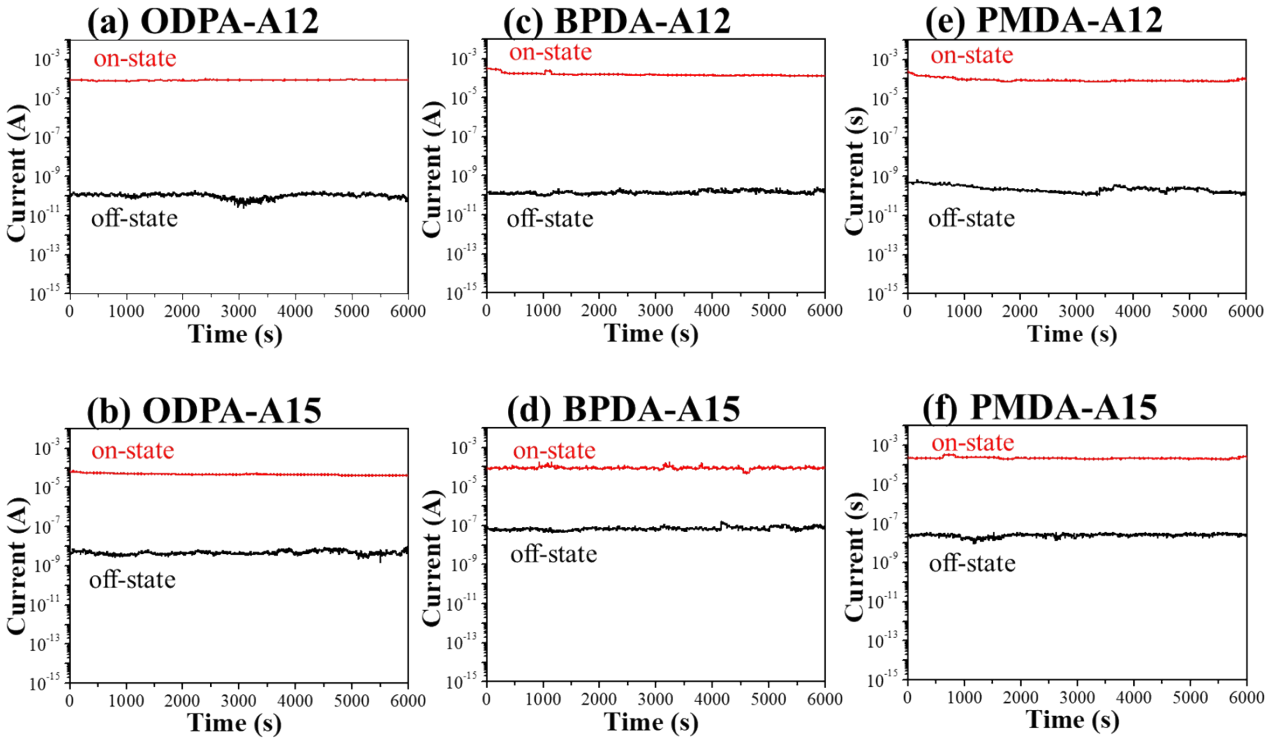

Figure S5. Retention time measurements of the memory devices made by (a) ODPA-A12, (b) ODPA-A15, (c)BPDA-A12, (d) BPDA-A15, (e) PMDA-A12 and (f) PMDA-A15.

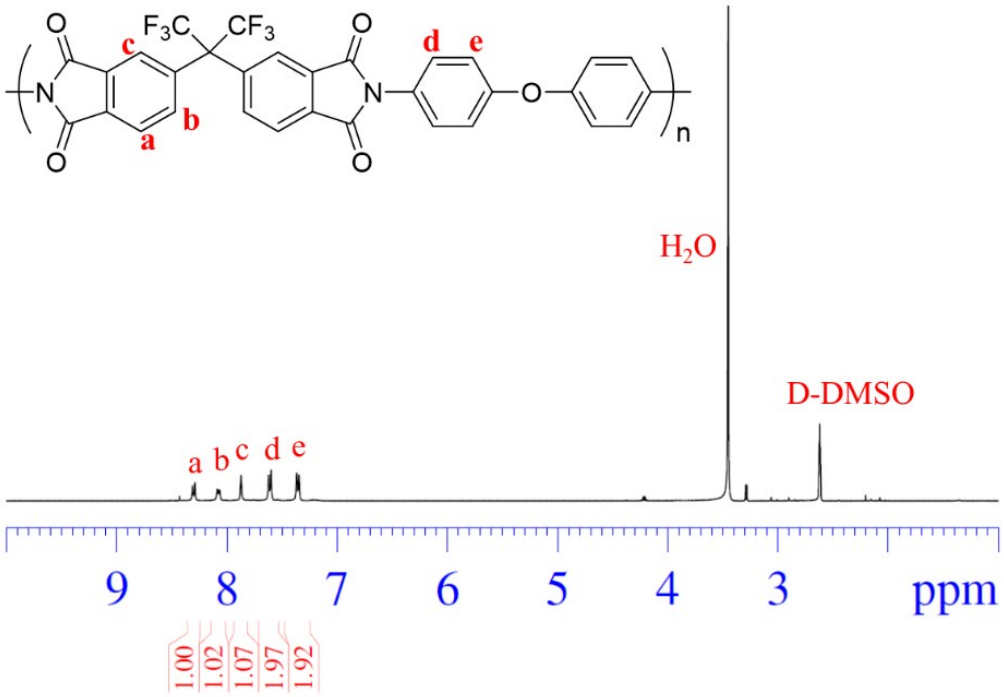

Figure S6. ^{1}H NMR spectrum of 6FDA-ODA PI.

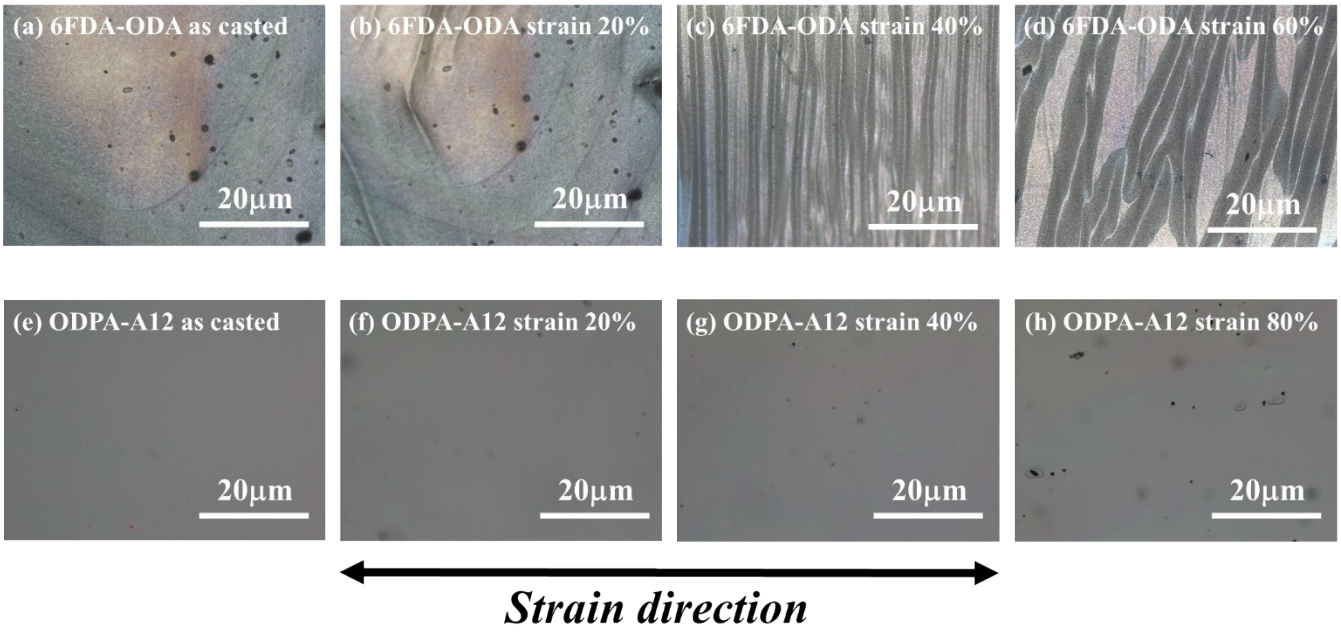

Figure S7. The OM images of the (a) as-cast, (b) 20% strain, (c) 40% strain, and (d) 60% strain 6FDA-ODA films and (e) as-cast, (f) 20% strain, (g) 40% strain, (h) 80% strain ODPA-A12 films on the PDMS substrate.

References

1. G. R. Husk, P. E. Cassidy and K. L. Gebert, *Macromolecules*, 1988, **21**, 1234-1238.