SUPPORTING INFORMATION

Polyurethane by Ionic Liquid Crosslink; A New Class of Super Shape-Memory

Like Polymer

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Fig S1: ¹H NMR spectrum of PCL-diol.



Fig S2: GPC traces of (a) PCL-diol ($M_n = 1360$, D = 1.17) (b) Isocyanate terminated prepolymer ($M_n = 2150$, D = 1.39), and (c) PU-BDO ($M_n = 29847$, D = 1.72)



Fig S3: DSC thermograms of PCL-diol. obtained at heating and cooling rate of 10 °C/min.



Scheme S1: Synthesis of non-ionic cross-linked polyurethane (PU-TMP).



Scheme S2: Synthesis of linear polyurethane (PU-BDO).

| Sample | V_e (cm ³) | V _r | $C_d \times 10^4 \text{ (mol/cm}^3)$ |
|--------|--------------------------|----------------|--------------------------------------|
| PU-IL | 0.4172 | 0.2765 | 2.43 |
| PU-TMP | 0.3982 | 0.2792 | 2.51 |

Table S1: Crosslink density of PU-IL and PU-TMP.

*(V_e = equilibrium volume of swollen sample, V_r = volume fraction of the crosslinked polymer in the swollen sample and C_d = rosslink density).



Fig S4: FTIR spectrum of MDI.



Fig S5: DSC heating (a) and cooling (b) thermograms of PU-BDO, PU-IL, and PU-TMP in the temperature range -80 °C to 200 °C (heating and cooling rate = 10 °C/min).



Fig S6: DSC heating thermogram of PU-TMP after fixing to temporary shape ($T_g = -29$ °C, $T_m = 28.8$ °C, $\Delta H_m^a = 2.1$ J/g, $\Delta H_m^b = 3.08$ J/g and $X_c = 2.3\%$).



Fig S7: Plots of tan δ vs. temperature for PU-BDO, PU-IL, and PU-TMP (heating rate 10 K/min).

The stress-strain plot (Figure S7) for all SMPUs was obtained by stretching the samples to 100% elongation at two different temperature (20 °C and 50 °C), and the respective modulus values were reported in Table S2. The trend in the tensile modulus (modulus at 100% elongation) of PU-BDO, PU-TMP, and PU-IL is completely different at 20 °C and 50 °C. At 20 °C the modulus of PU-BDO > PU-IL > PU-TMP, whereas at 50 °C modulus of PU-TMP > BDO > PU-IL. Thus the trend in modulus obtained from DMA analysis is in complete agreement with the tensile analysis.



Fig S8: Typical stress-strain plots of the PU BDO, PU-IL, and PU-TMP at (a) 20 °C and (b) 50 °C.

Table S2: Tensile modulus of PU-BDO, PU-IL and PU-TMP at room temperature and at 50 °C.

| Sample | Modulus at 100% strain (MPa) | 100% strain (MPa) Modulus at 100% strain (MPa) | |
|--------|------------------------------|--|-------------|
| | at room temp. | at 50 °C | modulus (%) |
| PU-BDO | 6.26 | 2.99 | 52.23 |
| PU-IL | 5.80 | 2.60 | 55.17 |
| PU-TMP | 4.15 | 3.50 | 15.66 |



Fig S9: Cyclic tensile testing machine attached with thermal chamber.

Table S3: Water absorption by PU-BDO, PU-IL and PU-TMP at 50 °C.

| Sample | Water absorption (%) | | |
|---------------|----------------------|----------------|--|
| | Normal water | Salt water | |
| PU-BDO | 1.2±0.06 | 1.0±0.03 | |
| PU-IL | 2.0 ± 0.09 | 2.8 ± 0.08 | |
| PU-TMP | $0.9{\pm}0.04$ | $0.7{\pm}0.02$ | |