

Supporting Information

SI 1 Synthesis of trisazide of tris (4-hydroxyphenyl) triglycidylether methane and propargylation of quinol and novolac oligomer.



SI2a



SI2b

Characterization of propargyl novolac (B₃): FTIR (KBr, cm⁻¹): 3288 (propargyl –CH), 2100 (propargyl), 3424 (-OH). Proton NMR (ppm, CDCl₃): δ = 7.18 (m, Ar), 6.94 (m, Ar), 4.6-4.9 (-OCH₂), 3.45 (propargyl –CH). Extent of propargylation was estimated from hydroxyl value of the resin after reaction. OH _{initial} = 500 mg KOH/g; OH _{after functionalization} = 62 mg KOH/g. Extent of propargylation = 85 %. Molecular weight of oligomer ~ 600 g/mol (inherent viscosity =0.04 dL/g).

SI2c

SI 2 a) FTIR spectra of A_3 and B_2 monomers b) Proton NMR spectra of A_3 and B_2 monomers c) Characterization of propargyl novolac (B_3)

SI 3 Calculation of swell ratio (Q) of SMPs

$Q = 1 + (\rho_1 / \rho_2) [(W_d / W_s) - 1]$

Where Q= swell ratio W_d = Weight of dry sample W_s =Weight of swollen sample ρ_1 =Specific density of the swelling medium (= 0.86 g/cm³ for toluene) ρ_2 =Specific density of the polymer (taken as 1.20 g/cm³)

SI 4 Calculation of cross-link density of SMPs

According to theory of rubber elasticity, cross-link density of moderately cross-linked polymers can be calculated using the equation

X density = G/RT

X density = Cross-link density in moles/m³ G = Rubbery modulus (at $T_{trigger}+20^{\circ}C$) R= Universal gas constant (8.314 cm³ MPa K⁻¹ mol⁻¹) T= (T trigger +20 °C) in Kelvin scale



SI 5 FTIR traces imply the completion of click polymerization after the temperature treatment of $A_3B_2B_3$. (Click polymerization at 135 °C)



SI 6 a) AFM image indicates absence of second phase or phase separation in $A_3B_2B_3$ shape memory polymer (wrinkles on the surface (formed during curing) are seen) b) SEM image shows no phase separation in $A_3B_2B_3$.



SI 7 Differential scanning calorimetry manifests the cross-linking of $A_3B_2B_3$ system in two steps (both steps are overlapped) imply cohabitance of two kinds of click polymerizations (10 °C/min.).

SI 8 Dual trigger temperatures in A₃B₂B₃73 and A₃B₂B₃37 SMPs (from DMA, frequency=1 Hz).

SI 9 Recovery strength of SMPs as a function of temperature (derived from DMA)

SI 10a) Dynamical mechanical analysis of A_3B_2 and A_3B_3 polymers at different applied frequencies (1Hz and 10 Hz)b) FTIR spectra showing hydrogen bonding of triazole groups with octafluoro1,6- hexane diol in A_3B_2 and A_3B_3 cross-linked polymers.

SI 11 Calculation of water absorption ratio of SMPs

$$Q = [(W_s / W_d) - 1] \ge 100$$

Q = Water absorption (weight %)

- W_s Weight of the swollen sample
- W_d-Weight of the dry sample

SI 12 Thermogravimetric profiles of A_3B_2 , A_3B_3 and $A_3B_2B_3$ cross-linked polymers (N₂, 10 °C/min.)