

Supporting Information

A Rapid Recoverable Shape Memory Polymer with Topologically Well-controlled Poly(ethyl methacrylate) Structures

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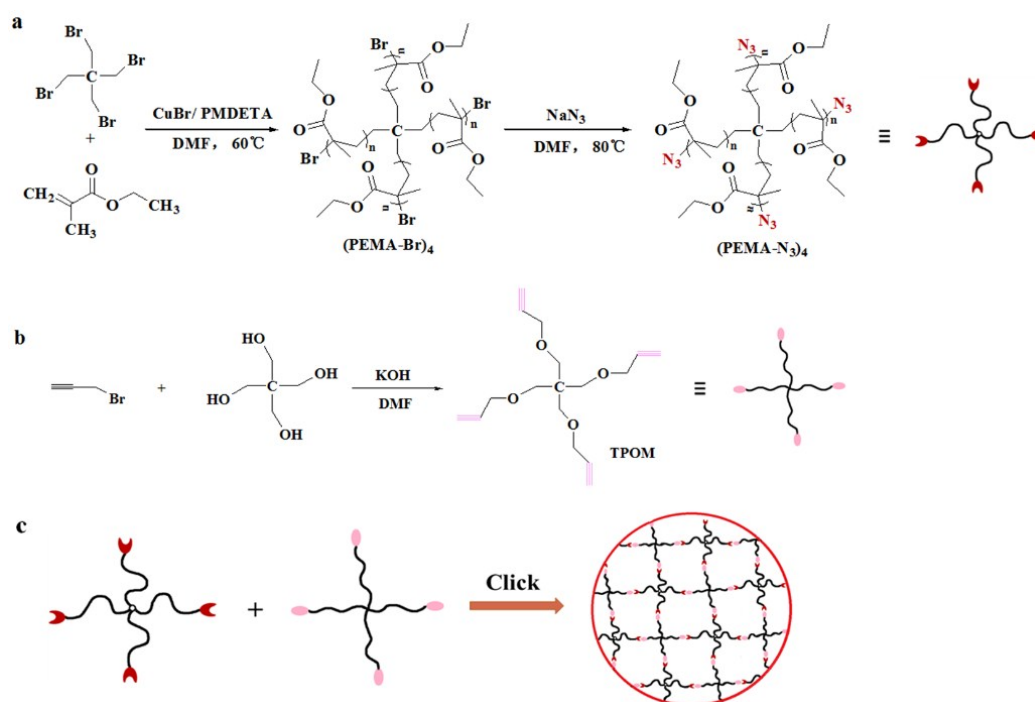


Figure S1. The specific synthesis route of well-controlled shape memory polymer (PEMA)₄-TPOM by ATRP and CuAAC reaction

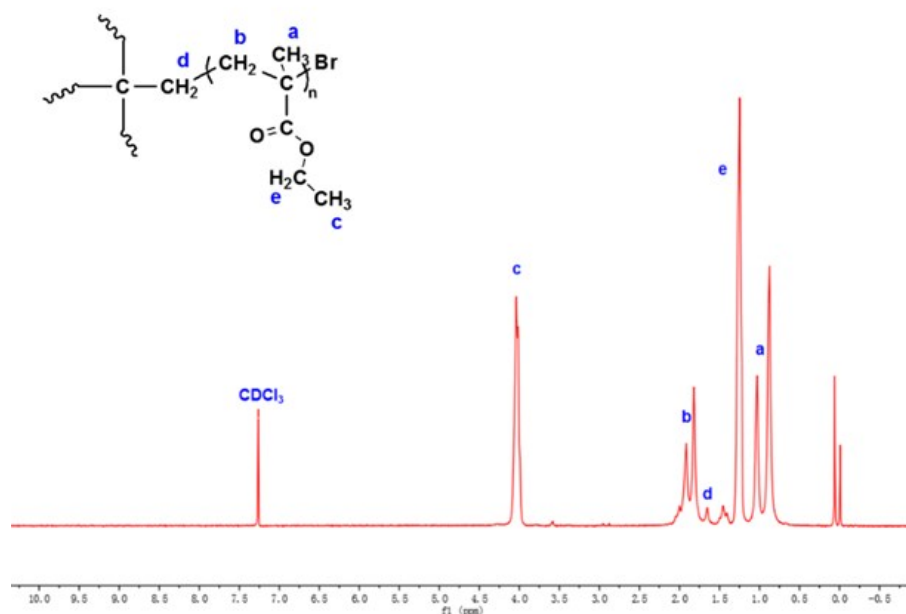


Figure S2. The ¹H-NMR of tetra-arm (PEMA-Br)₄

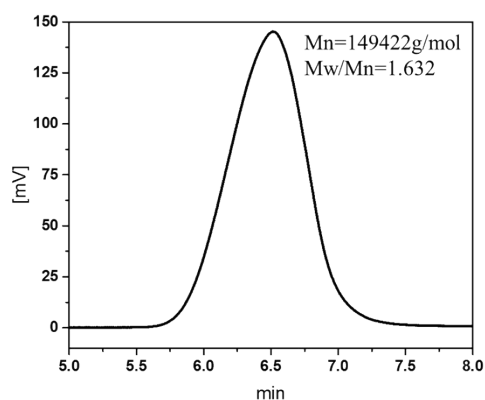


Figure S3. The GPC trace of well-controlled tetra-arm (PEMA-Br)₄ polymer monomer

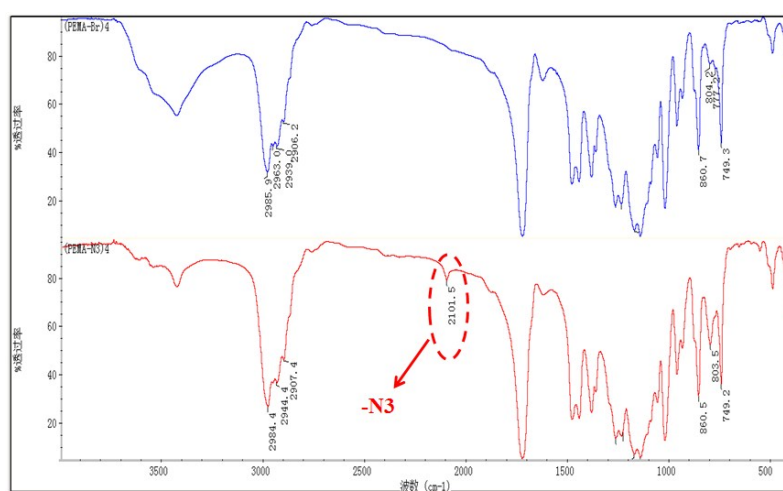


Figure S4. Compared with the FT-IR spectra of four arm (PEMA-Br)₄ before and after modification

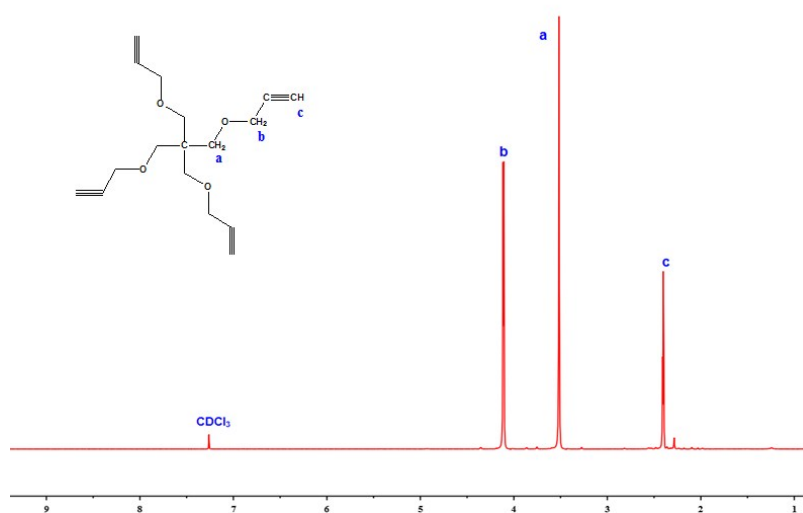


Figure S5. The ¹H NMR spectrum of TPOM

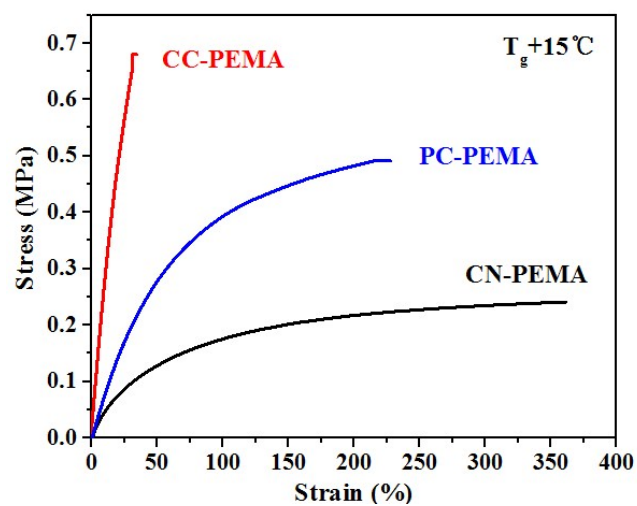


Figure S6. Tensile stress-strain curves obtained by DMA for CN-PEMA, CC-PEMA and PC-PEMA samples

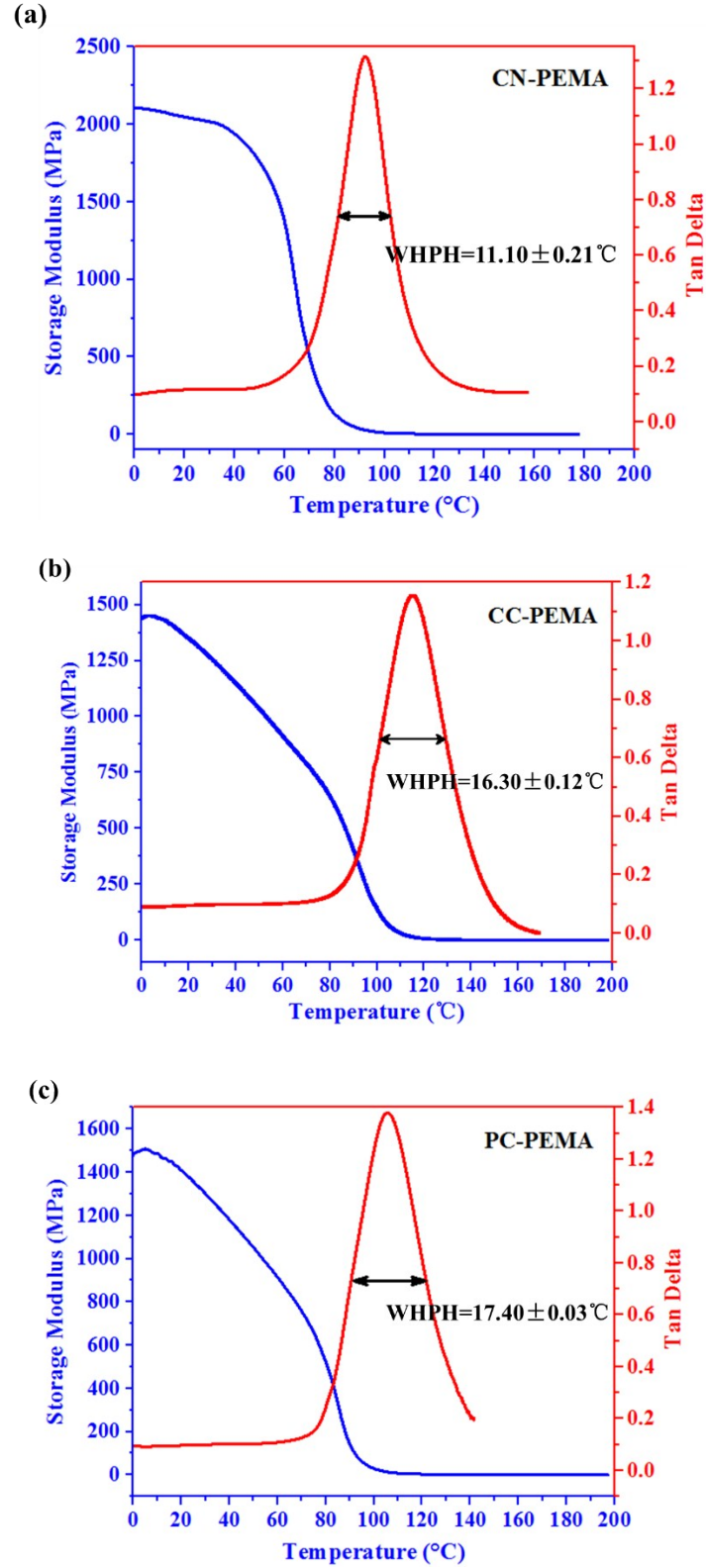


Figure S7. The storage modulus (E') and loss angle ($\tan \delta$) for (a) CN-PEMA, (b) CC-PEMA and (c) PC-PEMA

Table S1. The WHPH and reference of various acrylate-based SMPs

| Number | Polymer systems | WHPH(°C) | Reference |
|---|---|-----------|--------------|
| Copper(I)-catalyzed azide-alkyne cycloaddition network | | | |
| (a) | CN-PEMA-SMP | 11.3 | In this work |
| Conventional cross-linked networks | | | |
| (b) | CC-PEMA-SMP | 16.4 | In this work |
| (c) | PC-PEMA-SMP | 17.4 | In this work |
| AB copolymer networks | | | |
| (d) | MMA-co-PEGDMA | 22.5-26.3 | 29 |
| (e) | MMA-co-poly(ethylene glycol) dimethacrylate | 34-38 | 30 |
| (f) | PMMA-poly(ϵ -caprolactone) (40%) co-network | 33 | 31 |
| (g) | PMMA/poly(L-lactide) (50%) | 24 | 32 |
| Semi-IPNs | | | |
| (h) | PMMA/PEG (35%) semi-IPNs | 28-32 | 30 |
| (i) | Poly[MMA-co-(N-vinyl-2-pyrrolidone)]/PEG | 31 | 33 |
| (j) | PMMA/SPEG semi-IPNs | 31-55 | 23 |
| (k) | PMMA-PEG semi-IPN | 38.5 | 34 |

Table S2. Measured shape memory property parameters from six shape memory cycles for CN-PEMA sample with the deformation strain of over 30% after removing heat history

| Cycle | ϵ_n (%) | ϵ_m (%) | ϵ_u (%) | ϵ_p (%) | R_f (%) | R_r | V_r (% °C ⁻¹) |
|-------|------------------|------------------|------------------|------------------|-----------|-------|-----------------------------|
| 1st | 0.288 | 35.7 | 34.72 | 1.692 | 97.23 | 95.92 | 9.79 |
| 2nd | 1.692 | 36.18 | 35.22 | 3.03 | 97.22 | 96.01 | 10.84 |
| 3rd | 3.03 | 36.73 | 35.72 | 4.031 | 97.00 | 96.94 | 12.14 |
| 4th | 4.031 | 36.62 | 35.71 | 4.705 | 97.21 | 97.87 | 12.44 |
| 5th | 4.705 | 36.51 | 35.7 | 5.157 | 97.45 | 98.54 | 12.56 |
| 6th | 5.157 | 36.44 | 35.7 | 5.626 | 97.63 | 98.46 | 12.58 |

Table S3. Measured shape memory property parameters from three shape memory cycles for CC-PEMA sample with the deformation strain of over 30% after removing heat history

| Cycle | ϵ_n (%) | ϵ_m (%) | ϵ_u (%) | ϵ_p (%) | R_f (%) | R_r | V_r (% °C ⁻¹) |
|-------|------------------|------------------|------------------|------------------|-----------|-------|-----------------------------|
| 1st | 0.118 | 31.21 | 30.56 | 2.087 | 97.91 | 93.53 | 6.94 |
| 2nd | 2.087 | 32 | 31.23 | 2.893 | 97.43 | 97.23 | 7.23 |
| 3rd | 2.893 | 33.04 | 32.22 | 3.897 | 97.28 | 96.58 | 7.55 |

Table S4. Measured shape memory property parameters from three shape memory cycles for PC-PEMA sample with the deformation strain of over 30% after removing heat history

| Cycle | ϵ_n (%) | ϵ_m (%) | ϵ_u (%) | ϵ_p (%) | R_f (%) | R_r | V_r (% °C ⁻¹) |
|-------|------------------|------------------|------------------|------------------|-----------|-------|-----------------------------|
| 1st | 0.393 | 34.94 | 31.57 | 1.681 | 90.25 | 95.87 | 5.55 |
| 2nd | 1.681 | 34.65 | 31.58 | 2.972 | 90.69 | 95.68 | 5.62 |
| 3rd | 2.972 | 34.84 | 31.65 | 4.16 | 89.99 | 95.86 | 5.86 |

