Supporting information for

One-way and two-way shape memory effects of a high-strain *cis*-1,4 polybutadiene-polyethylene copolymer based dynamic network via self-complementary quadruple hydrogen bonding

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Fig. S1 Normalized stress relaxation for UHPB at various temperatures ranging from 30 to 100 °C. The stress relaxation experiment was performed on rectangular specimen ($25 \times 4 \times 1 \text{ mm}^3$) by using a TA-Q800 DMA apparatus. The sample was initially preloaded with 1×10^{-3} N force and then equilibrated for 15 min at the required temperature. The sample was stretched to a constant strain of 1%, and then the stress decay was monitored over time.



Fig. S2 Compression molding of UHPB.



Fig. S3 DSC cooling and heating thermograms (5 °C min⁻¹) for UHPB (100%). The nomenclature

UHPB (100%) refers to UHPB with hydrogenation degree of 100%.



Fig. S4 (a) Consecutive dual-shape memory cycles of UHPB-2 containing 4.1 mol% of UPy moieties. (b) Representativestress-strain curve of UHPB-2.



Fig. S5 Quadruple-shape memory behavior of UHPB. The quantitative shape memory properties were: $R_f(0\rightarrow 1) = 47.4\%$; $R_f(1\rightarrow 2) = 66.6\%$; $R_f(2\rightarrow 3) = 74.2\%$; $R_r(3\rightarrow 2) = 54.1\%$; $R_r(2\rightarrow 1) = 95.3\%$; $R_r(3\rightarrow 0) = 97.3\%$.



Fig. S6 (a) Consecutive two-way shape memory cycles of UHPB. (b) The strain changes of elongation upon cooling (EUC) and contraction upon heating (CUH) in ten cycles. (c) The actuation reversibility, $R_{ac} = (CUH/EUC) \times 100\%$, in ten cycles.



Fig. S7 1D-WAXD patterns of the unstretched and stretched UHPB. Samples were prepared by compression molding.



Fig. S8 High-strain dual-shape memory behavior of UHPB. The quantitative shape memory properties were: R_{f} : 93.8%, R_{f} : 89.0%.



Fig. S9 Representative stress-strain curves of the UHPB and UHPB (100%).