

Electronic Supplementary Information

Heat Managing Organic Materials: Phase Change Materials with High Thermal Conductivity and Shape Stability

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Materials

Triethylene glycol (Sigma-Aldrich), methacryloyl chloride (Sigma-Aldrich), tetrakis(triphenylphosphine) palladium(0) (Pd(PPh₃)₄, Sigma-Aldrich), triethylamine (TEA, Sigma-Aldrich), hydrochloric acid (HCl, 37%, Sigma-Aldrich), 6-bromonaphthalen-2-ol (TCI), 4-hydroxyphenylboronic acid (TCI), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (Sigma-Aldrich), p-toluenesulfonyl chloride (TCI), 2,2'-azobis(isobutyronitrile) (AIBN, TCI), polyethylene glycol methyl ether acrylate (HO, Alfa Aesar), silicone (SH0189, Xinus), potassium carbonate (K₂CO₃, Showa), 2-butanone (butanone, Showa), chloroform (CHCl₃, Showa), sodium sulfate (Na₂SO₄, Showa), sodium chloride (NaCl, Showa), sodium carbonate (Na₂CO₃, Showa), and silica gel (63-200 μm, Merck) were used as received. Tetrahydrofuran (THF, Showa), toluene (Showa), butanone (Showa), ethyl acetate (EA, Samchun Chemical), n-hexane (Hex, Samchun Chemical), ethanol (EtOH, Showa), and dichloromethane (DCM, Showa) were purified before use.

Characterization

Chemical structures of TM1 and their intermediates were investigated using proton (¹H) and carbon-13 (¹³C) nuclear magnetic resonance (NMR, JNM-EX400, JEOL). Chemical shifts were quoted as parts per million (ppm) using tetramethylsilane (TMS) as a reference. The molecular weight of TM1 was confirmed by a gas chromatography/mass spectrometer (GC-MS/MS, Xevo TQ-S, Waters) equipped with an APCI ionization source. The molecular structure of TM1 was investigated by two-dimensional (2D) wide-angle x-ray diffraction (WAXD) (D8 Discover 3kW, Bruker). The diffraction peaks were calibrated using a silicon crystal standard at $2\theta = 28.466^\circ$. The phase transition behaviors of TM1 and AHGs were confirmed using differential scanning calorimetry (DSC, DSC 4000, Perkin Elmer) and a polarized optical microscope (POM, ECLIPSE LV100 POL, Nikon) equipped with a temperature controller (FP 90, Mettler Toledo). The structural characterization of AHGx was conducted using a Fourier transform infrared spectroscopy (FT-IR, Frontier, Perkin Elmer) scanning in a range of 500-4000 cm⁻¹ using the ATR method in a transmission mode. The mechanical property of AHG3 was investigated by a universal testing machine (UTM, Quasar 2.5, GALDABINI). The thermal stability of AHGx was confirmed using a thermogravimetric analysis (TGA) instrument (SDT Q600, Waters). The heating rate was kept at 10 °C min⁻¹ as the temperature rose from 100 °C to 600 °C in a nitrogen atmosphere. Morphological observations of AHGx were conducted using field emission scanning electron microscopy (FE-SEM, SUPRA40VP, Carl Zeiss). Thermal conductivities of AHGx were measured at room temperature using the transient plane source (TPS) technique (TPS 500S, HotDisk). Temporal heat storage-release properties of the AHGx were observed using an infrared (IR) camera (FLIR C3, FLIR).

Sample Preparations

Preparation of TM-HO mixtures. AHGx was obtained by the polymerization of a homogenous mixture of TMs and HO. A series of AHGs were prepared with TM1 and HO, in which the molar ratios of TM1 to HO were $x : 10 - x$ ($x = 0, 2, 3, 5, \text{ and } 10$). 1 wt% crosslinker (TM2) and 0.1 wt% initiator (AIBN) were added to the TM1-HO mixture, which was dissolved in CHCl₃ and then dried in a vacuum.

Fabrication of AHGx samples. Homogeneous TMs-HO mixtures were cast in a silicone mold with a diameter of 1 cm and a depth of 0.5 cm at 70 °C. A vacuum was applied to eliminate air voids and the samples were polymerized at 130 °C for 36 h in a nitrogen atmosphere. After polymerization, the crosslinked polymer samples were detached from the silicone mold. All AHGx samples were obtained using the same method.

Synthesis

The TM2 and its intermediates were synthesized as reported in our previous work³⁶.

2-bromo-6-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphthalene (1): 6-bromonaphthalen-2-ol (0.018 mol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (0.018 mol), and K_2CO_3 (0.037 mol) were added into 50 ml of butanone. The mixture was stirred at 70 °C for 3 days. After completion of the reaction, the solvent was evaporated in vacuo and the residue was extracted with $CHCl_3$ and water. The organic layer was dried with Na_2SO_4 and the product 1 was obtained by column chromatography on silica gel, eluting with EA:Hex = 1:2 (5 g, Yield: 72%). 1H NMR (400 MHz, $CDCl_3$): δ = 3.36 (s, 3 H), 3.53 (t, 2 H), 3.64 (t, 2 H), 3.67 (t, 2 H), 3.76 (t, 2 H), 3.91 (t, 2 H), 4.22 (t, 2 H), 7.08 (d, 1 H), 7.18 (m, 1 H), 7.48 (d, 1 H), 7.56 (d, 1 H), 7.56 (d, 1 H), 7.63 (s, 1 H), 7.63 (s, 1 H), and 7.88 (s, 1 H) ppm.

4-(6-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphthalen-2-yl)phenol (2): 4-Hydroxyphenylboronic acid (0.036 mol) was added into a solution of 1 (0.024 mol) in 20 ml of toluene and 10 ml of EtOH. $Pd(PPh_3)_4$ (0.0012 mol) and a solution of Na_2CO_3 (0.048 mol) in 24 ml of water was added into the reaction mixture, then the mixture was stirred at 90 °C for 3 days. After completion of the reaction, the solvent was evaporated in vacuo and the residue was extracted with $CHCl_3$ and water. The organic layer was dried with Na_2SO_4 and product 2 was obtained by column chromatography on silica gel, eluting with EA:Hex = 1:1 (6.18 g, Yield: 67%). 1H NMR (400 MHz, $DMSO-d_6$): δ = 3.23 (s, 3 H), 3.43 (m, 2 H), 3.55 (m, 4 H), 3.62 (m, 2 H), 3.82 (t, 2 H), 4.22 (t, 2 H), 6.88 (d, 2 H), 7.18 (m, 1 H), 7.33 (d, 1 H), 7.59 (d, 2 H), 7.72 (d, 1 H), 7.85 (q, 2 H), 8.02 (s, 1 H), and 9.56 (s, 1 H) ppm.

2-(2-(2-(4-(6-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphthalen-2-yl)phenoxy)ethoxy)ethoxy)ethan-1-ol (3): TEA (0.31 mol) was added drop-wise into a mixture of p-toluenesulfonyl chloride (0.15 mol) and triethylene glycol (0.77 mol) in 400 ml of DCM. The reaction mixture was stirred at room temperature for 12 hours. After the reaction, the mixture was extracted with DCM and 1N HCl solution. The organic layer was dried with Na_2SO_4 and the product was obtained by column chromatography on silica gel, eluting with EA:Hex = 2:1 (40 g, Yield: 85%). 1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 2.68 (s, 1 H), 3.53 (m, 4 H), 3.62 (m, 4 H), 3.68 (m, 2 H), 4.18 (m, 2 H), 7.35 (d, 2 H), and 7.80 (d, 2 H) ppm.

2-(2-(2-(4-(6-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphthalen-2-yl)phenoxy)ethoxy)ethoxy)ethan-1-ol (4): K_2CO_3 (0.032 mol) was added into a mixture of 2 (0.0078 mol) and 3 (0.012 mol) in 50 ml of butanone. The reaction mixture was stirred at 70 °C for 2 days. After reaction, the solvent was evaporated in vacuo and the residue was extracted with $CHCl_3$ and water. The organic layer was dried with Na_2SO_4 and the product 4 was obtained by column chromatography on silica gel, eluting with EA (2.14 g, Yield: 53%). 1H NMR (400 MHz, $DMSO-d_6$): δ = 3.21 (s, 3 H), 3.54 (m, 16 H), 3.78 (t, 2 H), 3.82 (t, 2 H), 4.15 (t, 2 H), 4.23 (t, 2 H), 4.45 (s, 1 H), 7.05 (d, 2 H), 7.18 (m, 1 H), 7.32 (d, 1 H), 7.68 (d, 2 H), 7.75 (d, 1 H), 7.86 (q, 2 H), and 8.06 (s, 1 H) ppm.

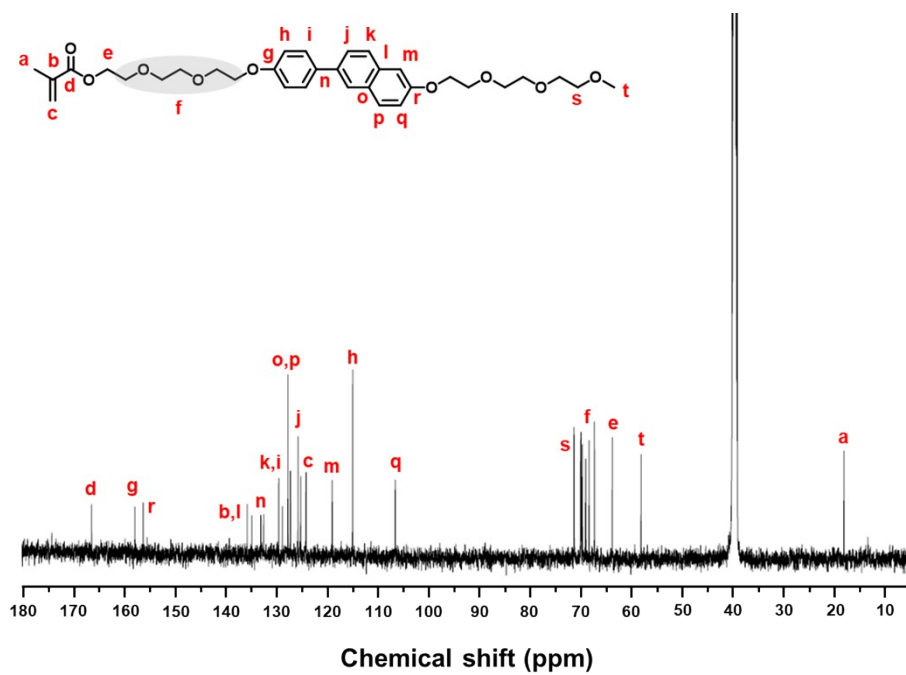


Fig. S3 ¹³C NMR spectrum of TM1.

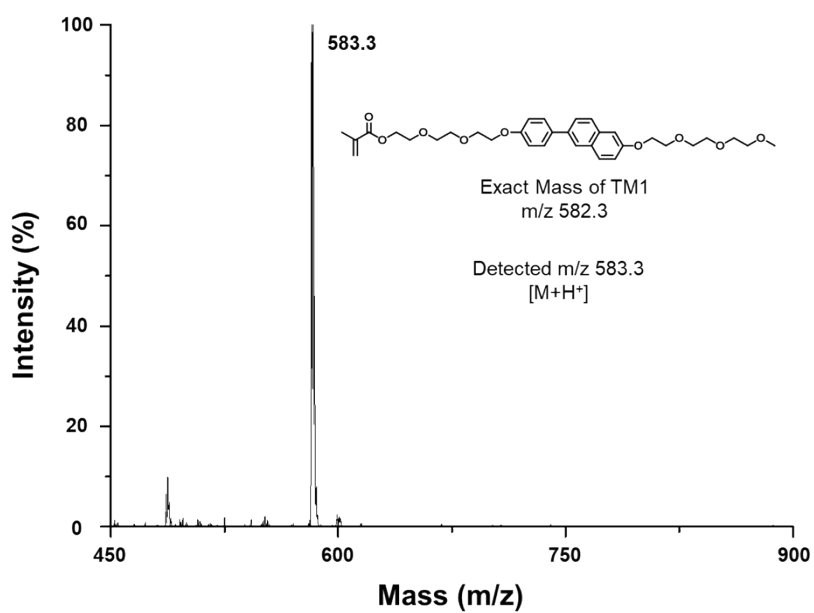


Fig. S4 Mass spectrum of TM1.

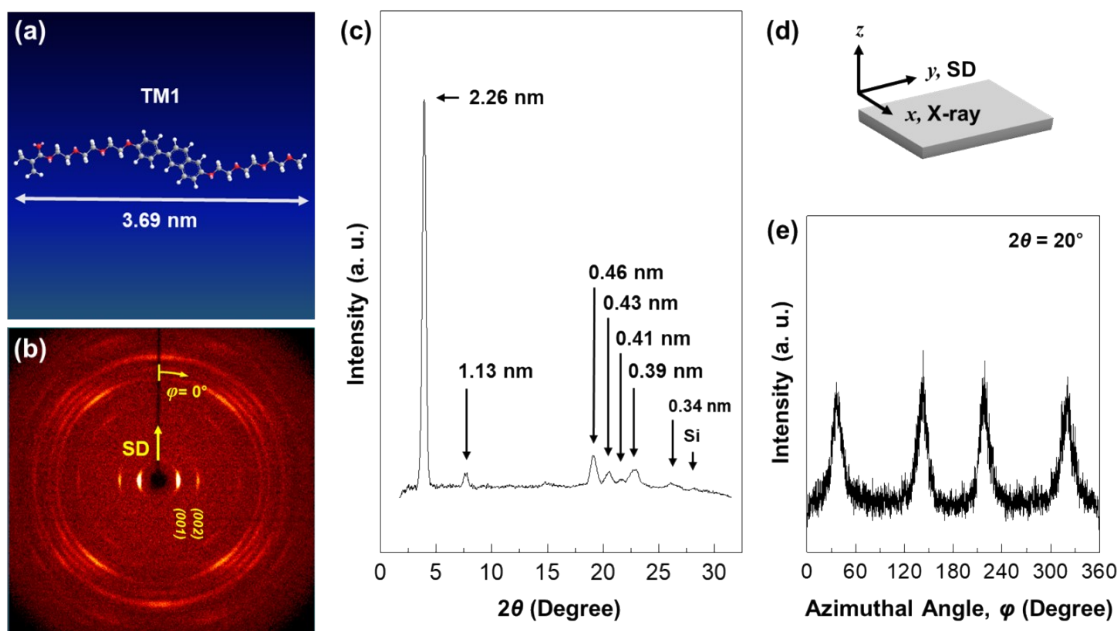


Fig. S5 (a) Illustration of the energy-minimized TM1 molecule. (b) 2D WAXD pattern and (c) 1D WAXD spectrum of a sheared TM1 sample at room temperature. (d) Schematic illustration of the oriented TM1 specimen. (e) Azimuthal scan between $2\theta = 19^\circ$ and $2\theta = 21^\circ$.

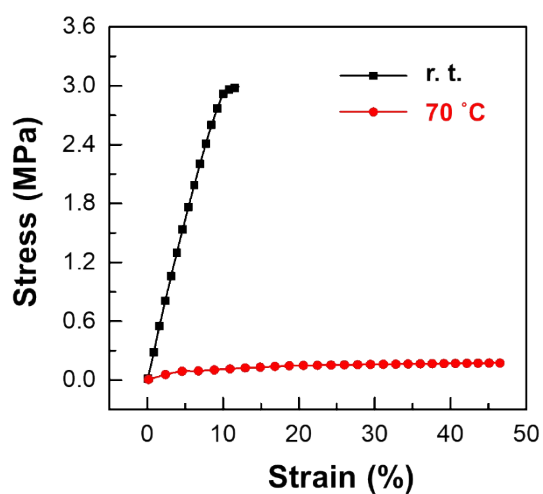


Fig. S6 Stress-strain curves of AHG3 at (a) room temperature and (b) 70 °C.

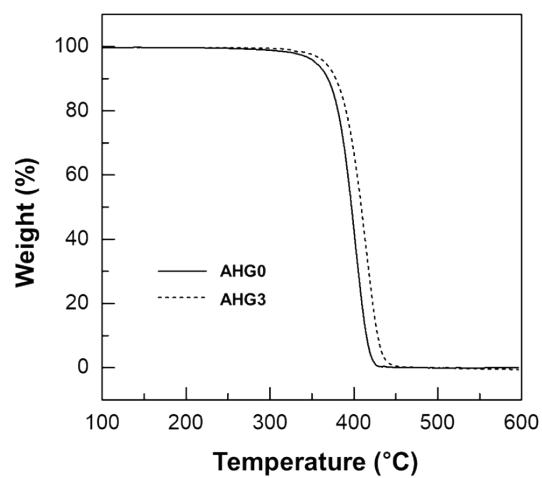


Fig. S7 TGA curves of AHG0 and AHG3.

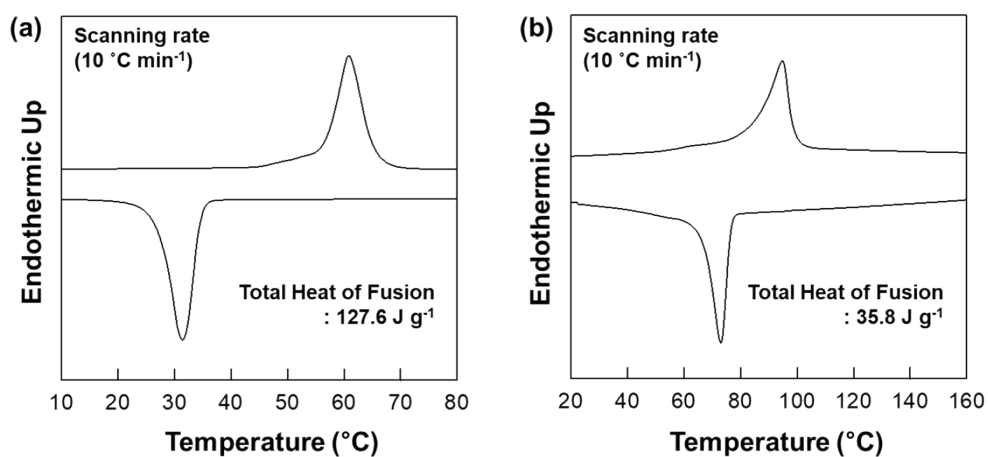


Fig. S8 DSC curves of (a) AHG0 and (b) AHG10.

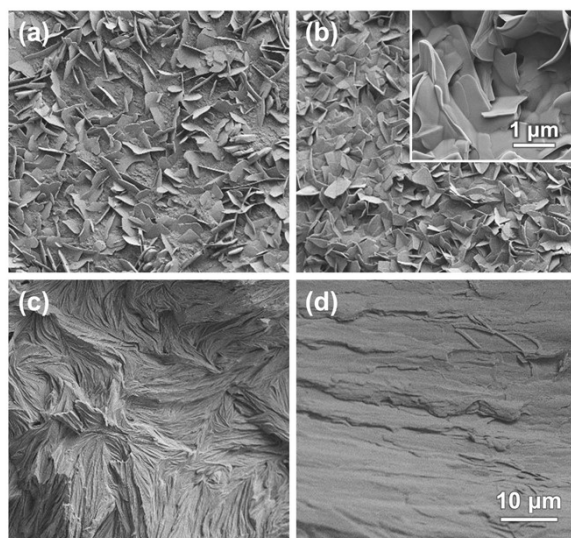


Fig. S9 Cross-sectional SEM images of (a) AHG10, (b) AHG5, (c) AHG3, and (d) AHG0.

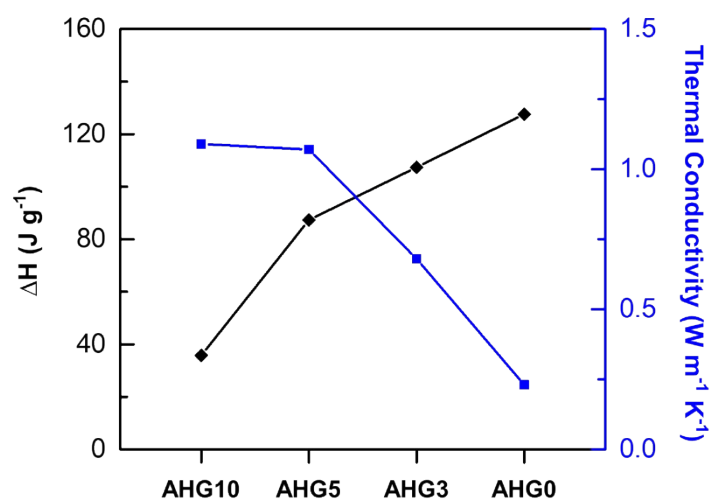


Fig. S10 Thermal conductivity and thermal energy storage density of AHGs.

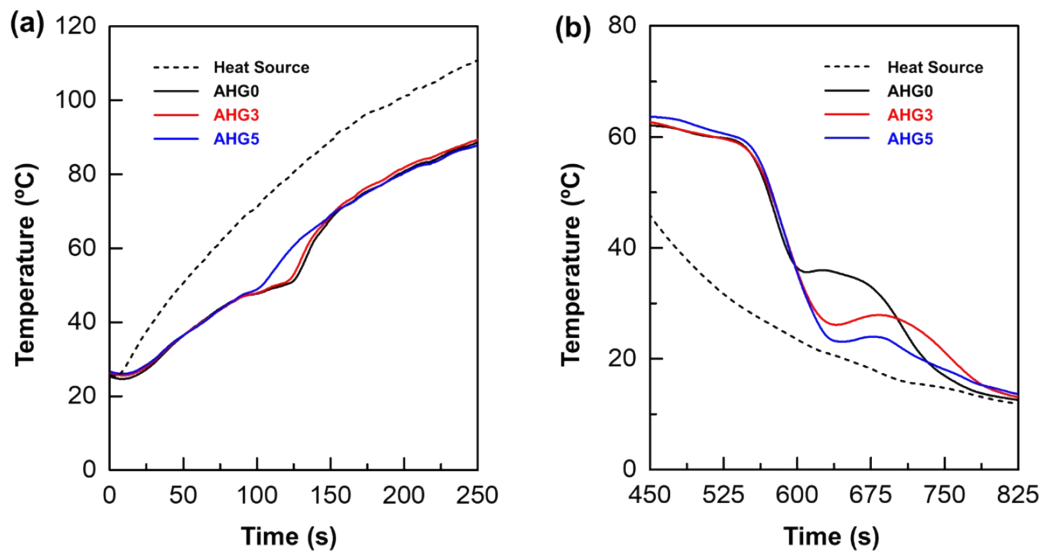


Fig. S11 Surface temperature changes of AHGs during (a) heating and (b) subsequent cooling.