

Supporting Information

Azobenzene-based (meth)acrylates: Controlled radical polymerization, photoresponsive solid-liquid phase transition behavior, and application to reworkable adhesives

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Preparation of 10-[4-(4-hexylphenylazo)phenoxy]decyl (meth)acrylate

Potassium carbonate (2.5 g, 18 mmol), potassium iodide (0.22 g, 1.3 mmol), 4-hydroxy-4'-hexylazobenzene (5.0 g, 17.7 mmol), and 10-bromo-1-decanol (4.2 g, 17.7 mmol) were added to a dried DMF (90 mL) under argon atmosphere. After stirring at 90 °C for 20 h, the mixture was diluted with dichloromethane, washed with deionized water, and dried over magnesium sulfate. The product was used for the next reaction without further purification. Acryloyl chloride (0.80 g, 8.8 mmol) was added to a dry THF solution (25 mL) of 4-(10-hydroxydecyloxy)-4'-hexylazobenzene (1.9 g, 4.4 mmol) and triethylamine (1.8 g, 17 mmol) at 0 °C. After stirring for 4 h at room temperature, the solution was concentrated, diluted with dichloromethane, washed with 2 M hydrochloric acid solution twice, and dried over magnesium sulfate. The acrylate monomer was purified with silica gel column chromatography using the mixed solvent of hexane and dichloromethane (from 1:2 to 1:1 by vol.). The eluent was concentrated and the residue was recrystallized from the mixed solvent of hexane and ethanol to yield the pure monomer (1.8 g, 82%). Corresponding methacrylate monomer was similarly synthesized by using methacryloyl chloride instead of acryloyl chloride.

10-[4-(4-hexylphenylazo)phenoxy]decyl acrylate

¹H NMR (CDCl₃, δ): 7.88 (2H, ArH, dd, J = 9.6 Hz, 5.6 Hz), 7.79 (2H, ArH, dd, J = 8.8 Hz, 4.4 Hz), 7.29 (2H, ArH, dd, J = 8.4 Hz, 4.0 Hz), 6.99 (2H, ArH, dd, J = 9.6 Hz, 5.6 Hz), 6.40 (1H, CH=CH₂, dd, J = 17.6 Hz, 1.4 Hz), 6.12 (1H, CH=CH₂, dd, J = 17.6 Hz, 10.4 Hz), 5.81 (1H, CH=CH₂, dd, J = 7.2 Hz, 1.2 Hz), 4.15 (2H, CH₂OCO, t, J = 6.8 Hz, 6.8 Hz), 4.03 (2H, ArOCH₂, t, J = 6.8 Hz, 6.8 Hz), 2.67 (2H, ArCH₂, t, J = 7.8 Hz, 7.8 Hz), 1.81 (2H, CH₂CH₂OCO,

tt), 1.66 (2H, CH₂CH₂Ar, tt), 1.54-1.25 (24H, CH₂, m), 0.86 (3H, CH₃, t, J = 7.0 Hz, 7.0 Hz). MALDI-TOF MS calcd for C₃₁H₄₄N₂O₃Na ([M+Na]) 515.32, found 515.33. Anal. Calcd. (wt%) : C 75.57, H 9.00, N 5.69. Found (wt%): C 75.70, 9.08, 5.73.

10-[4-(4-hexylphenylazo)phenoxy]decyl methacrylate

¹H NMR (CDCl₃, δ): 7.88 (2H, ArH, dd, J = 9.2 Hz, 4.8 Hz), 7.79 (2H, ArH, dd, J = 8.8 Hz, 4.0 Hz), 7.29 (2H, ArH, dd, J = 8.8 Hz, 5.2 Hz), 6.99 (2H, ArH, dd, J = 9.6 Hz, 5.6 Hz), 6.10 (1H, CH₂=C), 5.55 (1H, CH₂=C), 4.14 (2H, CH₂OCO, t, J = 6.8 Hz, 6.8 Hz), 4.03 (2H, ArOCH₂, t, J = 6.8 Hz, 6.8 Hz), 2.67 (2H, ArCH₂, t, J = 7.8 Hz, 7.8 Hz), 1.95 (3H, C=C-CH₃). 1.81 (2H, CH₂CH₂OCO, tt), 1.66 (2H, CH₂CH₂Ar, tt), 1.54-1.25 (24H, CH₂, m), 0.89 (3H, CH₃, t, J = 7.0 Hz, 7.0 Hz). MALDI-TOF MS calcd for C₃₂H₄₆N₂O₃Na ([M+Na]) 529.72, found 529.36. Anal. Calcd. (wt%) : C 75.85, H 9.15, N 5.53. Found (wt%): C 75.41, 9.08, 5.65.

ATRP of 10-[4-(4-hexylphenylazo)phenoxy]decyl methacrylate (Example of PM1)

7.82 mg (0.0790 mmol) of Cu(I)Cl, 301 mg (0.595 mmol) of **AzM** monomer, 18.2 mg (0.0790 mmol) of HMTETA, 39.5 μmol of EBiB (0.982 M anisole solution), 1.2 mL of dry anisole were mixed under argon in a pre-dried 30 mL Schlenk tube. The reaction mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum. After stirring the mixture for 15 min at room temperature, the Schlenk tube was placed in the oil bath preheated at 80 °C for 20 h. Aliquot was taken for ¹H NMR measurement, and the conversion was determined on the basis of

the intensity of the peak at 2.67 ppm corresponding to the methylene protons (2H) of hexyl group linked to the phenyl ring and that of at 5.81 ppm corresponding to the proton (1H) of the vinyl group. The solution was passed through an activated neutral alumina column. The resulting solution was concentrated, followed by precipitation into methanol twice and hexane. The yellow polymer was freeze-dried from its benzene solution (0.23 g, 77% yield). $M_{n,\text{GPC-LS}} = 12800 \text{ g mol}^{-1}$, $M_w/M_{n,\text{GPC-LS}} = 1.24$.

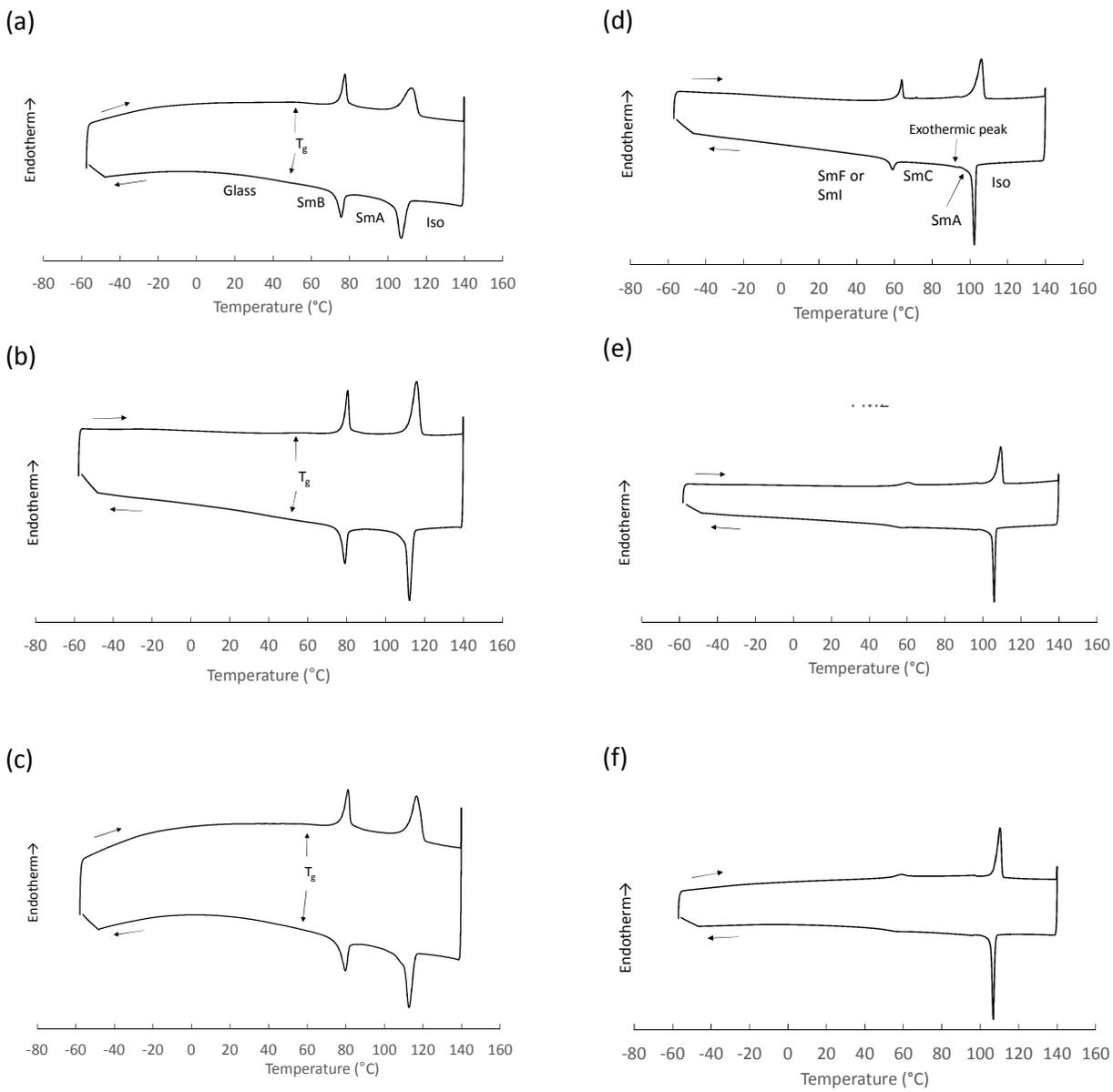
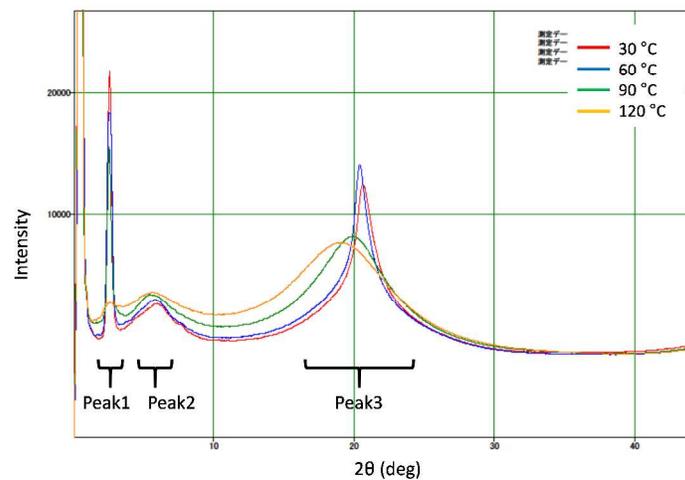
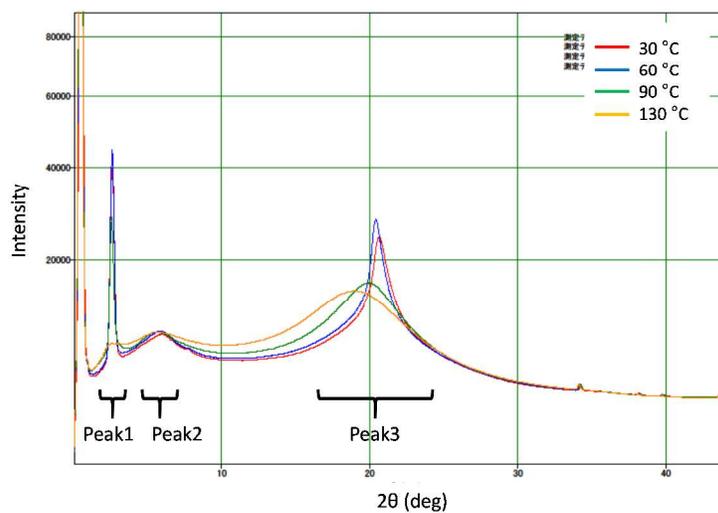


Figure S1. DSC thermograms of (a) PA4, (b)PA5, (c) PA6, (d) PM1, (e) PM2, and (f) PM3 (second scan at 10 °C/min).



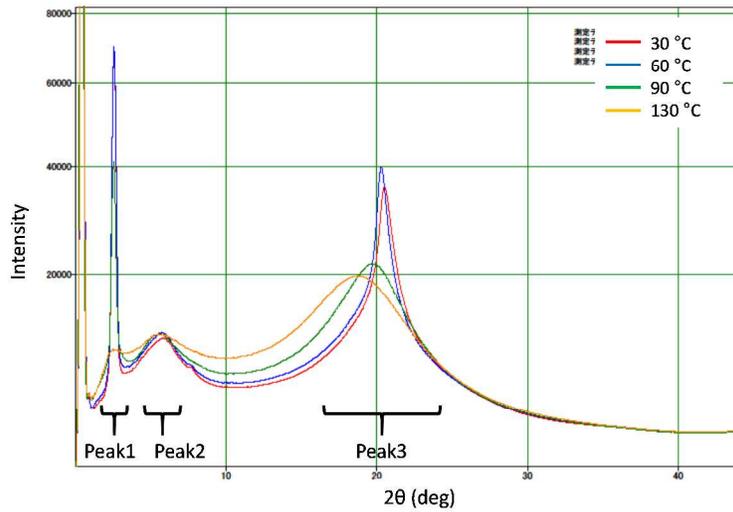
Temp (°C)	2 θ (°)			d (Å)		
	peak1	peak2	peak3	peak1	peak2	peak3
30	2.57	5.96	20.6	34.3	14.8	4.30
60	2.59	5.88	20.4	34.1	15.0	4.35
90	2.58	5.58	19.9	34.3	15.8	4.46
120	2.49	5.65	19.0	35.5	15.6	4.68

Figure S2. XRD patterns of PA4 at 30 °C (red), 60 °C (blue), 90 °C (green), and 120 °C (yellow), and the peak list of diffraction angle 2θ and lattice spacing d .



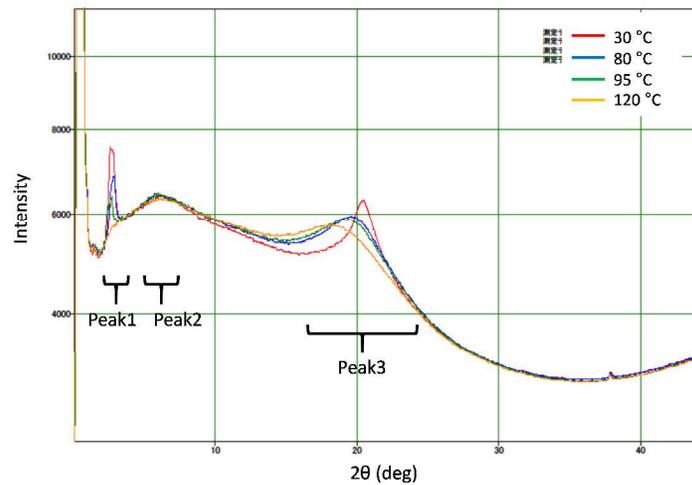
Temp (°C)	2 θ (°)			d (Å)		
	peak1	peak2	peak3	peak1	peak2	peak3
30	2.60	5.92	20.3	34.0	14.9	4.31
60	2.61	5.90	20.4	33.8	15.0	4.34
90	2.60	5.73	19.9	34.0	15.4	4.46
130	2.49	5.74	19.0	35.5	15.4	4.67

Figure S3. XRD patterns of PA5 at 30 °C (red), 60 °C (blue), 90 °C (green), and 130 °C (yellow), and the peak list of diffraction angle 2θ and lattice spacing d .



Temp (°C)	2θ (°)			d (Å)		
	peak1	peak2	peak3	peak1	peak2	peak3
30	2.58	5.88	20.5	34.2	15.0	4.33
60	2.57	5.72	20.3	34.4	15.4	4.37
90	2.58	5.60	19.8	34.3	15.8	4.48
130	2.38	5.56	18.8	37.1	15.9	4.72

Figure S4. XRD patterns of PA6 at 30 °C (red), 60 °C (blue), 90 °C (green), and 130 °C (yellow), and the peak list of diffraction angle 2θ and lattice spacing d.



Temp (°C)	2θ (°)			d (Å)		
	peak1	peak2	peak3	peak1	peak2	peak3
30	2.66	6.33	20.4	33.2	14.0	4.36
80	2.79	5.85	19.8	31.7	15.1	4.49
95	2.63	5.82	19.4	33.5	15.2	4.57
120		6.11	18.6		14.5	4.77

Figure S5. XRD patterns of PM1 at 30 °C (red), 80 °C (blue), 95 °C (green), and 120 °C (yellow), and the peak list of diffraction angle 2θ and lattice spacing d.

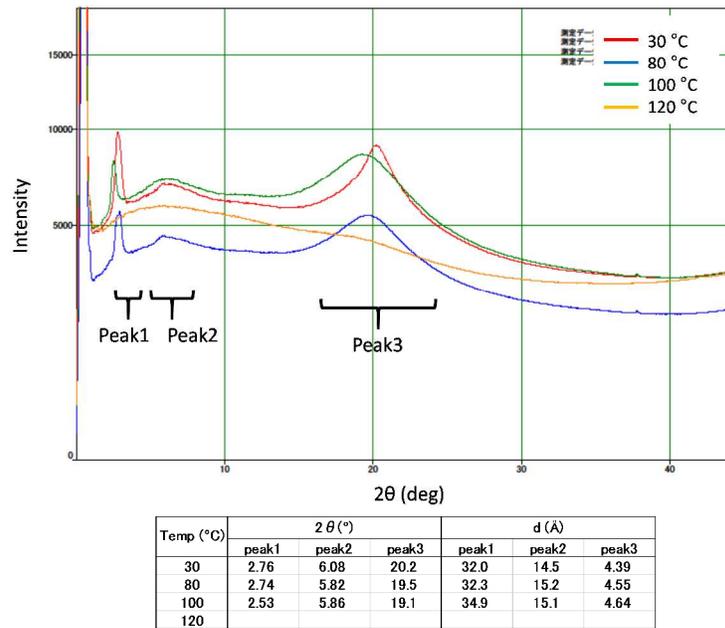


Figure S6. XRD patterns of PM2 at 30 °C (red), 80 °C (blue), 100 °C (green), and 120 °C (yellow), and the peak list of diffraction angle 2θ and lattice spacing d .

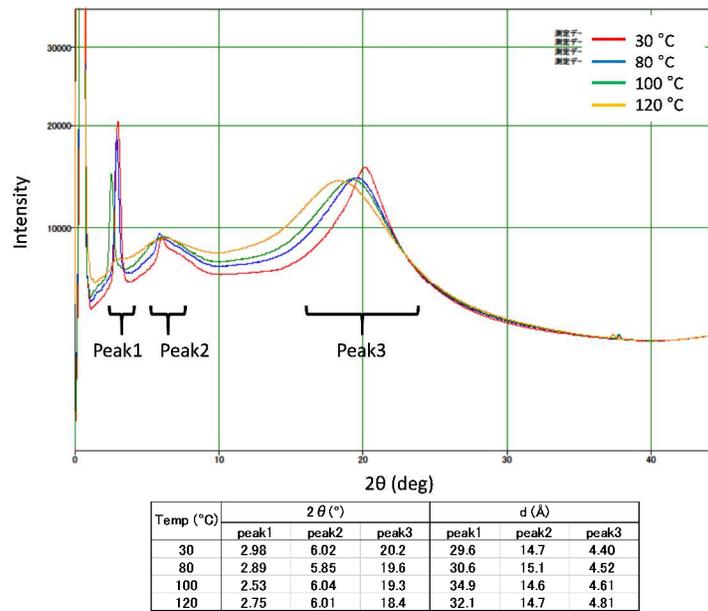


Figure S7. XRD patterns of PM3 at 30 °C (red), 80 °C (blue), 100 °C (green), and 120 °C (yellow), and the peak list of diffraction angle 2θ and lattice spacing d .

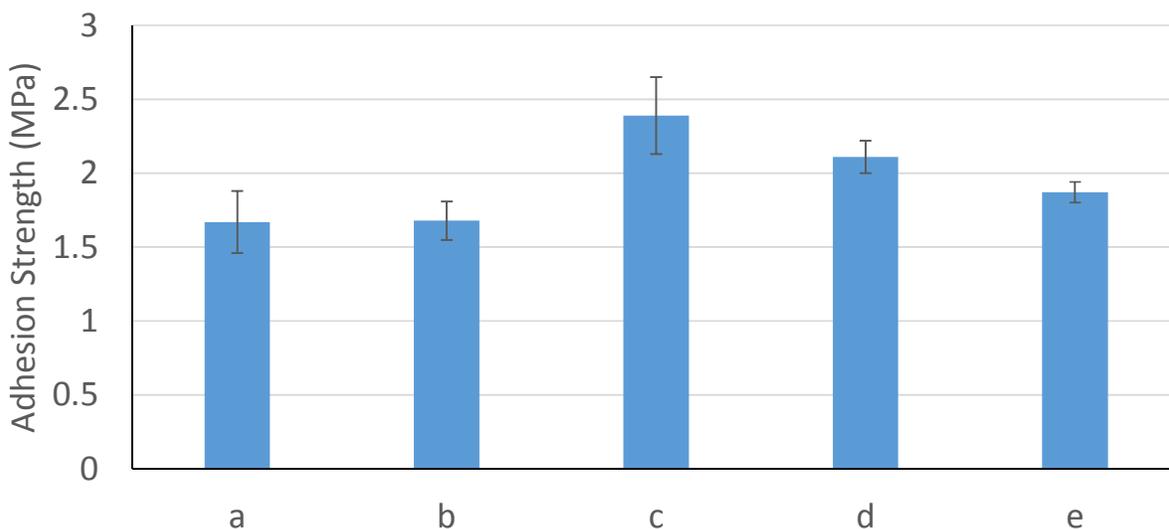


Figure S8. Adhesion strength of PA4: (a) thermally bonded specimen cooling from 150 °C to 25 °C within 5 min, (b) thermally bonded specimen cooling from 150 °C to 25 °C at a rate of 1 °C min⁻¹, (c) photochemically bonded specimen [thermally bonded specimen sequentially irradiated with UV (365 nm, 50 mW cm⁻², 5 min) and green (520 nm, 40 mW cm⁻², 5 min) lights], (d) thermally bonded specimen (cooling within 5 min) irradiated with purple light at 25 °C (405 nm, 25 mW cm⁻², 1 h), and (e) thermally bonded specimen (cooling within 5 min) irradiated with green light at 25 °C (520 nm, 40 mW cm⁻², 1 h)

The values are larger than those listed in Figure 10 in the manuscript, since new glass substrate (TEMPAX glass) and tensile testing machine (Shimadzu Autograph AGS-10 kN, 500 N load cell SLBL-500N, and a holding apparatus SCG-1kNA) were used. The values can be compared within this experiment.

¹H NMR measurements showed that sample a and b contained ~0 % cis-azobenzene fraction, while c, d, and e contained ~5 %, ~5 %, ~2 % of cis-azobenzene, respectively.