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Poly(amide-ether) Thermoplastic Elastomers Based on Monodisperse Aromatic Amide Hard Segments as Shape-Memory and Moisture-Responsive Materials

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Supporting Information

ABSTRACT: A series of high-molecular-weight $(M_n \text{ up to } M_n)$ 29000) multiblock poly(N-methylbenzamide)-b-poly-(ethylene glycol) polymers [poly(MAB_{x-x}-b-PEG)], utilizing</sub>monodisperse telechelic aromatic N-methylbenzamide-based molecules (MAB_{x-x}) (molar mass distribution M_w/M_n = 1.02-1.04) with H₂N-PEG-NH₂, were successfully prepared via conventional solution polycondensation; their shapememory and moisture-responsive properties were thoroughly investigated. The resultant multiblock copolymers showed three thermal transitions: the glass transition (T_{g}) and melting $(T_{\rm m})$ of the PEG segment at -35 and 55 °C, respectively, and



T_g of the MAB_{x-x} segment at 215 °C. Hard opaque pale-yellow films were successfully prepared using the solution-cast method, and several films showed good shape-memory properties, i.e., a shape fixity of 91% and a shape recovery of 97%. These properties were only observed for multiblock copolymer films having both crystalline PEG (degrees of crystallinity from 34.8% to 43.7% were observed) and aggregated monodisperse MAB_{x-x} phases. The existence of this cocrystalline structure is critical</sub> for the retention of temporary shape at ambient temperature and the recovery of original shape above T_m for the PEG phase in the copolymer film. Upon soaking the film in water for 5 days, it swelled by ≈ 660 vol % (590 wt %) with a density change from 1.15 to 1.02 g/cm³. Furthermore, we demonstrated that the film exhibits moisture-responsive behavior within just 10 s upon exposing only one of its surfaces to humid air.

INTRODUCTION

Poly(ether-*b*-amide) multiblock copolymers $(PEBAs)^{1-7}$ are an important class of thermoplastic elastomers (TPEs) because their properties may be tuned using appropriate polyether soft segments (SSs) and crystalline aliphatic-amide hard segments (HSs). They are commonly applied as gas separation membranes,⁸⁻²⁰ reactive multiphase blends,^{21,22} thermoelectric generator components,²³ conductive materials,^{24,25} and shape-memory polymers (SMPs).²⁶ The properties of TPEs are strongly influenced by the molecular weight distribution (M_w/M_p) of the HS,²⁷⁻³⁶ but M_w/M_p cannot be usually controlled for aliphatic polyamides such as nylon-6,6 and nylon-6,10. Furthermore, amide-based HSs generally have hydrogen-bonding sites, making it difficult to prepare specifically desired (particularly longer) HSs because of their poor solubility.

We have recently reported a rapid and efficient synthetic strategy for preparing monodisperse $(M_w/M_n = 1.03 - 1.05)$ non-hydrogen-bonding N-methylaminobenzoic acid (MAB)based oligomeric HSs (MAB_{$x-x^{j}$} where x is the repeating number of the building block across the core molecule terephthalic acid) using the common condensation reagent SOCl₂. These MAB-based HSs were used to fabricate novel linear³⁷⁻³⁹ and hyperbranched⁴⁰ TPE materials via copolymerization with amorphous poly(propylene glycol) (PPG). These copolymers showed higher storage moduli (up to 4.84 GPa) with clearer phase segregation between the HS and SS phases compared to those of copolymers comprising broad- $M_{\rm w}/M_{\rm n}$ HSs. However, thermal transition temperatures of the

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HS domains were observed from 40 to 60 °C, which are much lower than the expected value of 200 °C observed in the homopolymer poly(MAB). This is due to the incomplete phase segregation of the HS and SS domains. Consequently, to realize clearer phase segregation, we prepared multiblock copolymers based on MAB_{*x*-*x*} with PEG as a crystalline SS, eventually identifying a phase with SMP characteristics.

SMPs have been widely studied, leading to the development and industrial application of materials with unique memory/ recovery behaviors that can be induced by a wide variety of external stimuli, including heat,⁴¹ light,⁴² humidity,⁴³ and magnetic field.⁴⁴ Furthermore, the use of hydrophilic PEG segments has presented the possibility of using such materials for biomedical applications, such as drug-delivery systems, contact lenses, catheters, and wound dressings. Because the PEG domain is hydrophilic, moisture-responsive SMPs that exploit hydration and dehydration mechanisms can be designed.^{45–47}

Accordingly, we herein report the synthesis of monodisperse MAB-based poly(MAB_{x-x}-b-PEG) multiblock copolymers and their thermal, mechanical, SMP, and moisture-sensitive properties. The mechanism of their SMP behavior was fully investigated using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), polarized optical microscopy (POM), atomic force microscopy (AFM), and dynamic mechanical analysis (DMA).

EXPERIMENTAL SECTION

Materials. MAB was purchased from Wako Pure Chemical Industries Ltd. and purified via sublimation. Poly(MAB) was prepared via the polycondensation of MAB in the presence of telephthalic acid in NMP at 100 °C for 1 h according to a previously reported procedure.⁴⁸ Triphenyl phosphite (TPP) was purchased from Tokyo Chemical Industry Co. Ltd. and distilled under reduced pressure for polycondensation. Telechelic PEGs comprising NH₂ groups (H₂N-PEG-NH₂) with $M_n = 3350$ (PEG3k), 8000 (PEG8k), and 10000 (PEG10k) $(M_w/M_n \approx 1.5)$ were prepared via the reported procedure for commercially available telechelic PEGs having OH groups at the terminals (Sigma-Aldrich Co., LLC.).⁴⁹ N-Methylpyrrolidone (NMP) was purchased from Kanto Chemical Co. Inc. and dried over calcium hydride (CaH₂) and distilled under reduced pressure. Triethylamine (TEA) from Wako Pure Chemical Industries Ltd. was dried over KOH and distilled under a N2 atmosphere. Thionyl chloride (Tokyo Chemical Industry Co. Ltd.) was distilled prior to use. Diphenyl (2,3dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) was prepared according to the literature.⁵⁰ All other reagents and solvents were used without further purification.

Synthesis of 4,4'-Dicarboxylphenylterephthalamide (AB_{1-1}). This building block was prepared directly from terephthaloyl chloride (1.016 g, 5.000 mmol) by stirring 4-aminobenzoic acid (1.392 g, 10.15 mmol) in NMP (10 mL) at 25 °C for 1 h.⁵¹ The reaction mixture was then poured into water, and the precipitate was collected by filtration. The product was washed with tetrahydrofuran (THF) and dried at 100 °C for 8 h under reduced pressure to provide the title compound as a white powder in 79.0% yield. ¹H NMR (400 MHz, DMSO- d_{6} , ppm): δ 7.96 (s, 8H, Ar–H), 8.13 (s, 4H, Ar–H), 10.70 (s, 2H, N–H), and 12.78 (s, 2H, COO–H).

Synthesis of MAB_{1-1} . Terephthaloyl chloride (1.016 g, 5.000 mmol) and NMP (5 mL) under nitrogen were added into a 30 mL three-necked flask equipped with a three-way stopcock; MAB (1.392 g, 10.200 mmol) was then added to the solution, and the reaction was kept at 25 °C for 2 h. The reaction solution was poured into water, and the precipitate was collected by filtration. The product was recrystallized from water/methanol to afford the title compound as a white powder in 93.0% yield. ¹H NMR (400 MHz, DMSO- d_{60} ppm): δ 7.13 (s, 4H, Ar-H), 7.18, 7.20 (d, 4H, Ar-H), 7.76, 7.79 (d, 4H, Ar-H).

Synthesis of Monodisperse HS MAB_{x-x} and $Broad-M_w/M_n$ HS $brMAB_{5-5}$. These building blocks were prepared according to our previously reported method.³⁷

Synthesis of H_2 N-PEG-NH₂. These were prepared according to a previously reported procedure.⁴⁹ Briefly, into a solution of HO-PEG-OH ($M_n = 8000, 4.00 \text{ g}, 0.50 \text{ mmol}$) in CH₂Cl₂ (45 mL) were added triethylamine (1.198 g, 11.84 mmol) followed by methane sulfonyl chloride (0.3448 g, 3.010 mmol) via syringe at 25 °C. After 18 h, the solution was poured into diethyl ether (200 mL), and the precipitate was collected. The obtained white powder was placed in an autoclave and reacted with NH_{3aq} (25 wt %, 25 mL) at 130 °C for 18 h. The reaction mixture was then transferred to a separation flask, and the product was extracted three times with CH₂Cl₂ and washed with water. The organic layer was concentrated and poured into diethyl ether. The resultant precipitate was collected and dried at 40 °C for 12 h to afford the 2.43 g of title compound in 60.7% yield (Figure 3s).

PEG3k. White powder, yield: 49%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 2.68, 2.69, 2.71 (t, 1H, NH–*H*), 3.50 (s, 308H, CH–*H*).

PEG8k. White powder, yield: 61%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 2.86, 2.87, 2.88 (s, 1H, NH–H), 3.50 (s, 744H, CH–H).

PEG10k. White powder, yield: 73%. ¹H NMR (400 MHz, DMSO- d_{6} , ppm): δ 2.81, 2.82, 2.83 (s, 1H, NH–H), 3.50 (s, 903H, CH–H).

Multiblock Copolymerization. Typical procedure for poly-(MAB₅₋₅-b-PEG8k): into a 30 mL two-necked flask equipped with a three-way stopcock were added MAB₅₋₅ (0.1498 g, 0.100 mmol), H₂N-PEG-NH₂ (0.800 g, 0.100 mmol), NMP (1.00 mL), and triethylamine (0.0240 g, 0.240 mmol). The flask was heated to 70 °C, and DBOP (0.0922 g, 0.240 mmol) was added to initiate the polymerization. After 6 h, the viscous solution was poured into diethyl ether, and the precipitate was collected. This was dissolved with CHCl₃ at 45 °C and reprecipitated in hexane. The product was dried at 45 °C for 8 h under reduced pressure to afford the title compound in 64% yield.

Poly(*AB*₁₋₁-*b*-*PEG3k*). Brown compound, yield: 66%. ¹H NMR (400 MHz, DMSO- d_{6_7} ppm): δ 3.50 (s, CH₂−*H*), 7.01−7.51 (m, Ar−*H*), 7.89−8.48 (m, Ar−*H*). ¹³C NMR (100 MHz, DMSO- d_{6_7} ppm): δ 70.20, 120.17, 120.42, 120.45, 120.76, 122.87, 125.20, 128.49, 129.53, 130.32, 130.96, 150.42, 151.13, 153.90, 170.11. Elemental analysis (C_{173.28}H_{318.56}N₄O_{78.6})_n: calculated C: 55.99, H: 8.64 (%), N: 1.57; found C: 54.92, H: 8.77, N: 1.34 (%).

Poly(*AB*₁₋₁-*b*-*PEG8k*). Brown compound, yield: 64%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 3.50 (s, CH₂−*H*), 6.97−7.51 (m, Ar−*H*), 7.88−8.11 (m, Ar−*H*). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ 70.20, 120.25, 120.45, 122.87, 128.49, 129.42, 130.32. Elemental analysis (C_{384,4}H_{740.8}N₄O₁₈₄)_{*n*}: calculated C: 55.18, H: 8.92 (%), N: 0.66; found C: 54.55, H: 8.48, N: 0.63 (%).

*Poly(MAB*₁₋₁-*b*-*PEG3k)*. Brown compound, yield: 59%. ¹H NMR (400 MHz, DMSO- $d_{6^{\prime}}$ ppm): δ 3.50 (s, CH₂−H), 7.00−7.49 (m, Ar−H), 7.68−7.78 (m, Ar−H). ¹³C NMR (100 MHz, DMSO- $d_{6^{\prime}}$ ppm): δ 38.10, 70.20, 120.17, 120.41, 120.45, 120.76, 122.87, 128.49, 129.53, 130.32. Elemental analysis (C_{175.28}H_{322.56}N₄O_{78.6})_n: calculated C: 56.22, H: 8.68 (%), N: 1.49; found C: 55.66, H: 8.65, N: 1.55 (%).

*Poly(MAB*₁₋₁-*b*-*PEG8k)*. Brown compound, yield: 43%. ¹H NMR (400 MHz, DMSO- d_6 , ppm): δ 3.50 (s, CH₂-H), 6.97-7.39 (m, Ar-H), 7.68-7.78 (m, Ar-H). ¹³C NMR (100 MHz, DMSO- d_6 , ppm): δ 38.10, 70.36, 120.44, 122.83, 127.11, 128.35, 129.63, 136.38, 137.82. Elemental analysis (C_{386.4}H_{744.8}N₄O₁₈₄)_n: calculated C: 55.28, H: 8.94 (%), N: 0.67; found C: 54.87, H: 8.72, N: 0.68 (%).

*Poly(MAB*₅₋₅-*b*-*PEG3k)*. Brown compound, yield: 66%. ¹H NMR (400 MHz, DMSO- d_{6} , ppm): δ 3.50 (s, CH₂−H), 6.83−7.23 (m, Ar−H), 7.69−7.71 (m, Ar−H). ¹³C NMR (100 MHz, DMSO- d_{6} , ppm): δ 38.08, 69.18, 70.11, 120.53, 126.48, 128.62, 129.61, 134.08, 145.79, 168.91. Elemental analysis (C_{239.28}H_{378.56}N₁₂O_{86.6})_n: calculated C: 59.75, H: 7.93 (%), N: 3.49; found C: 58.99, H: 7.53, N: 3.04 (%).

Poly(MAB₅₋₅-b-PEG8k). Brown compound, yield: 64%. ¹H NMR (400 MHz, DMSO- d_{6} , ppm): δ 3.49 (s, CH₂-H), 6.88–7.23 (m, Ar-H), 7.67–7.79 (m, Ar-H). ¹³C NMR (100 MHz, DMSO- d_{6} , ppm): δ 37.88, 69.35, 70.33, 120.28, 123.07, 126.44, 128.01, 128.46, 129.50, 130.93, 132.01, 134.01, 137.43, 145.83, 147.77, 149.00, 154.08, 165.65, 166.87, 168.79, 169.68. Elemental analysis

Scheme 1. Synthesis of Various HS-Type Molecules



 $(C_{450.4}H_{800.8}N_{12}O_{192})_n$: calculated C: 57.18, H: 8.53 (%), N: 1.77; found C: 56.53, H: 8.36, N: 1.58 (%).

*Poly(MAB*₅₋₅-*b-PEG10k).* Brown compound, yield: 59%. ¹H NMR (400 MHz, DMSO- d_6 , ppm): δ 3.49 (s, CH₂-H), 6.89–7.23 (m, Ar-H), 7.68 (m, Ar-H). ¹³C NMR (100 MHz, DMSO- d_6 , ppm): δ 37.80, 69.32, 70.35, 120.33, 122.00, 126.30, 128.00, 129.34, 134.20, 145.83, 147.51, 162.14, 169.08. Elemental analysis (C₅₄₁₂H_{982.4}N₁₂O₂₃₈)_n: calculated C: 56.72, H: 8.64 (%), N: 1.46; found C: 56.73, H: 8.48, N: 1.19 (%).

*Poly(brMAB*₅₋₅-*b*-*PEG8k)*. Brown compound, yield: 43%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 3.50 (s, CH₂−*H*), 6.83−7.23 (m, Ar−*H*), 7.69−7.71 (m, Ar−*H*). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ 38.10, 60.71, 70.35, 72.94, 77.80, 119.84, 123.50, 126.71, 128.40, 129.71, 134.42, 145.79, 165.40, 168.92. Elemental analysis $(C_{450.4}H_{800.8}N_{12}O_{192})_n$: calculated C: 57.18, H: 8.53 (%), N: 1.77; found C: 56.56, H: 8.37, N: 1.55 (%).

*Poly(MAB*₁₀₋₁₀-*b*-*PEG3k)*. Brown compound, yield: 73%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 3.46 (s, CH₂−*H*), 6.83−7.22 (m, Ar−*H*), 7.69−7.71 (m, Ar−*H*). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ 38.15, 69.14, 70.32, 120.40, 122.43, 126.48, 128.22, 129.42, 129.61, 130.56, 134.08, 145.80, 165.75, 167.14, 168.95. Elemental analysis (C_{319.28}H_{448.56}N₂₂O_{96.6})_{*n*}: calculated C: 62.44, H: 7.36 (%), N: 5.02; found C: 61.28, H: 7.05, N: 4.69 (%).

*Poly(MAB*₁₀₋₁₀-*b*-*PEG8k)*. Brown compound, yield: 70%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 3.50 (s, CH₂−*H*), 6.86−7.22 (m, Ar−*H*), 7.69−7.71 (m, Ar−*H*). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ 38.39, 69.24, 70.12, 120.30, 122.21, 123.94, 126.48, 128.08, 129.37, 129.55, 130.76, 134.27, 145.76, 168.95. Elemental analysis $(C_{530.4}H_{870.8}N_{12}O_{202})_n$: calculated C: 59.03, H: 8.13 (%), N: 2.86; found C: 58.59 H: 8.00, N: 2.60 (%).

*Poly(MAB*₁₀₋₁₀-*b-PEG10k)*. Brown compound, yield: 74%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 3.47 (s, CH₂-*H*), 6.71–7.36 (m, Ar–*H*), 7.68 (m, Ar–*H*). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ 38.15, 69.24, 70.12, 120.41, 122.67, 126.5, 127.0, 128.10, 129.40, 129.53, 130.66, 134.00. Elemental analysis $(C_{621.2}H_{1052.4}N_{22}O_{248})_n$: calculated C: 58.33, H: 8.29 (%), N: 2.41; found C: 57.83, H: 8.26, N: 2.58 (%).

Poly(MAB).⁴⁸ FT-IR [KBr (cm⁻¹)]: 3399 (N–H), 3280–3100 (amine and guanamine hydrogen bonding), 3052 (aromatic C–H), 1579 (aromatic C=C), 1477 (triazine C=N), 1415, 806 (aromatic C–H), 1194 (aromatic C–N). ¹H NMR (400 MHz, DMSO- d_{6} , ppm): δ 6.67–8.04 (Ar–H), 8.22, 9.24 (–NH–).

Film Fabrication. All films were prepared using the solution casting method. Polymer samples were dissolved in dry NMP at 25 wt %, and

the solution was cast on a glass substrate. The cast film was dried at 30, 50, 70, 90, and 110 $^{\circ}C$ for 2 h each and at 120 $^{\circ}C$ for 48 h under reduced pressure.

Measurements. NMR spectroscopy was performed on a Bruker AC-400P spectrometer at 400 MHz for ¹H and 100 MHz for ¹³C measurements. Deuterated dimethyl sulfoxide (DMSO-d₆) was used as the solvent with tetramethylsilane as the internal reference. The $M_{\rm ref}$ $M_{\rm w}$ and $M_{\rm w}/M_{\rm n}$ values were determined using a Tosoh HLC-8220 gel permeation chromatograph (GPC) equipped with refractive index as well as UV detectors and a consecutive polystyrene gel column (TSK-GEL α -M ×2) at 40 °C and eluted with NMP containing 0.01 mol/L LiBr at a flow rate of 1.0 mL/min. DSC was performed on a HITACHI X-DSC7000 system at a heating rate of 20 °C/min under nitrogen. DMA was performed on a HITACHI DMS7100 at a heating rate of 2 °C/min under nitrogen. Polymer films were cut into pieces with dimensions of $20 \times 9 \times 0.12 \text{ mm}^3$, and a load was applied to the films with a strain amplitude of 5 μ m and a frequency of 1 Hz. The modes of the polymers in the crystalline phase were examined by WAXD measurements using a Rigaku R-axis Rapid diffractometer equipped with a graphite monochromator using Cu K α radiation at 45 kV and 200 mA. Tapping mode AFM measurements were performed with a NanoNavi S-image SPM system (Hitachi High-Tech Sci. Co., Tokyo, Japan) using a cantilever with a force constant of ~ 15 N m⁻¹ and a resonance frequency of 120 kHz. The scan size and tip velocity of the AFM measurements were 10 μm^2 and 200 nm/ s, respectively. Tensile properties of the films were measured on an AGS-X (SHIMADZU) at an extension rate of 10 mm/min. The thermoresponsive SMP effect was investigated using a DMS7100 as follows: a rectangular film (length L_0) was set in the chamber, which was heated at 90 $^{\circ}\text{C}$, followed by cooling to 50 $^{\circ}\text{C}$, at which point the film was elongated by 70% ($L_{\rm m}$). The chamber was cooled to -20 °C, and the stress was released. This strain was denoted as $L_{\rm Ret}$. The chamber was heated to 90 °C again, and the final strain (L_{Res}) was measured. This tensile test was performed twice to determine the shape-memory fixity ratio (R_f) and recovery ratio (R_r) using eqs 1 and 2 (presented in Table 3).

RESULTS AND DISCUSSION

Polymer Synthesis. By use of our previously reported rapid and efficient synthetic method, a series of non-hydrogenbonding HSs MAB_{x-x} (x = 1, 5, and 10), along with short HSs such as AB_{1-1} and $brMAB_{5-5}$ (broad- M_w/M_n of 1.6), were prepared in moderate yields (Scheme 1), and their structures

Scheme 2. Synthesis of PEBAs via Direct Solution Polycondensation



Figure 1. ¹H NMR spectra of (a) H₂N-PEG-NH₂ (PEG8k) and (b) PEBA poly(MAB₅₋₅-b-PEG8k).

Table	1.	Synthesis	of	PEBAs
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segment								
run	hard	soft	yield (%)	$M_{\rm n}^{\ a}$ (Da)	$M_{\rm n}^{\ b}$ (Da)	$M_{\rm w}/M_{\rm n}^{\ b}$	composition ^c MAB:PEG	film
1	AB_{1-1}	PEG3k	52	3720n	8800	1.8	1.00:1.25	brittle
2	AB_{1-1}	PEG8k	59	8370 <i>n</i>	15000	2.0	1.00:1.04	brittle
3	MAB_{1-1}	PEG3k	69	3750n	19000	2.1	1.00:0.84	brittle
4	MAB_{1-1}	PEG8k	76	8400 <i>n</i>	29100	2.0	1.00:1.08	brittle
5	MAB ₅₋₅	PEG3k	66	4810 <i>n</i>	22500	1.8	1.00:0.82	flexible
6	MAB ₅₋₅	PEG8k	64	9500n	29300	2.1	1.00:0.92	flexible
7	MAB ₅₋₅	PEG10k	59	11460 <i>n</i>	27400	1.9	1.00:0.78	flexible
8	brMAB ₅₋₅	PEG8k	43	9500n	22500	1.9	1.00:0.92	brittle
9	MAB ₁₀₋₁₀	PEG3k	73	6140 <i>n</i>	11700	2.2	1.00:1.00	brittle
10	MAB ₁₀₋₁₀	PEG8k	70	10800 <i>n</i>	22100	1.8	1.00:0.97	flexible
11	MAB ₁₀₋₁₀	PEG10k	74	12800n	29200	1.9	1.00:094	flexible
^a Calculated	d $M_{\rm n}$ of the poly	mer repeating u	nit. ^b Determin	ed by GPC (N	MP containing	0.01 M LiBr,	PSt standard). ^c Determined ł	y ¹ H NMR.

were characterized via ¹H NMR analysis (Figure 1s). Copolymerization of these monomers with H₂N-PEG-NH₂ ($M_n = 3K$, 8K, and 10K, $M_w/M_n \approx 1.5$) monomers was performed using the well-known phosphine-based condensation reagent DBOP in NMP at 70 °C for 6 h to afford the corresponding multiblock copolymers (PEBAs) (Scheme 2).

As shown in the GPC traces of MAB₅₋₅ ($M_n = 1100$, $M_w/M_n = 1.03$), H₂N-PEG-NH₂ (PEG8k, $M_n = 8120$, $M_w/M_n = 1.52$), and the block copolymer poly(MAB₅₋₅-b-PEG8k) ($M_n = 29300$, $M_w/M_n = 2.10$) (Figure 2s), the unimodal peak of the

block copolymer is shifted to a higher molecular weight and has the moderate M_w/M_n of 2.1. Figure 1 shows the ¹H NMR spectra of H₂N-PEG-NH₂ (PEG8k) and the block polymer poly(MAB₅₋₅-*b*-PEG8k). The triplet signal labeled *a* (Figure 1a) observed at 2.65 ppm is assignable to the α protons of the terminal amino groups of PEG8k and is completely absent from the spectrum of the block copolymer. A new signal labeled *a* (Figure 1b) is observed at 3.30 ppm, which is assignable to the α protons of the amide groups. When the integration of signal *f* (Figure 1b) at 7.70 ppm (corresponding

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Poly(AB ₁₋₁ -	Poly(MAB ₁₋₁ -	Poly(MAB ₁₋₁ -	Poly(MAB ₅₋₅ -	Poly(MAB ₅₋₅ -
<i>b</i> -PEG8k)	<i>b</i> -PEG3k)	<i>b</i> -PEG8k)	<i>b</i> -PEG3k)	<i>b</i> -PEG8k)
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Poly(MAB ₅₋₅ -	Poly(MAB ₁₀₋₁₀ -	Poly(MAB ₁₀₋₁₀ -	Poly(MAB ₁₀₋₁₀ -	Poly(<i>br</i> MAB ₅₋₅
<i>b</i> -PEG10k)	<i>b</i> -PEG3k)	<i>b</i> -PEG8k)	<i>b</i> -PEG10k)	<i>b</i> -PEG8k)

Figure 2. Digital camera images of PEBA films cast from NMP solutions.





to the terephthaloyl group) is set to 4.0, the integration of the aromatic protons at 7.00 ppm is calculated to be \approx 40.0. Thus, the integration of the methylene protons *b* and *c* for PEG8k observed at 3.35 ppm can be calculated to be 801, which is comparable to the value of 797 observed in Figure 1a. These results clearly confirm the satisfactory formation of the multiblock copolymer with the expected structure.

Table 1 summarizes the results of block copolymerization with PEG. When the polymerization is conducted with AB_{1-1}

and PEG3k in NMP, the transparent homogeneous solution becomes turbid with time probably due to the strong molecular interactions between polymer chains. The lower molecular weight of the resulting polymer can be explained by this poor solubility in NMP. The HS to SS ratios calculated from the ¹H NMR results are 1:1.25 to 1:0.78. Except for poly(AB_{1-1} -*b*-PEG3k) and poly(AB_{1-1} -*b*-PEG8k), the other polymers in Table 1 exhibit good solubility and the precipitates become too fine to be collected perfectly. Therefore, the

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Table 2. Thermal Properties of PEBAs

run	PEBA	$M_{\rm n}^{\ a}$	$T_{\rm m}(SS)^{b}$	$T_{g}(HS)^{b}$	$\Delta H(\text{PEG})^{c}$ (J/g)	χ^d (%)	SMP ^e
1	poly(AB ₁₋₁ - <i>b</i> -PEG3k)	8800	45		71.2	36.2	n
2	$poly(AB_{1-1}-b-PEG8k)$	15000	55	202	141	71.6	n
3	poly(MAB ₁₋₁ - <i>b</i> -PEG3k)	19000	44		96	48.8	n
4	poly(MAB ₁₋₁ - <i>b</i> -PEG8k)	29100	57		130	66.1	n
5	poly(MAB ₅₋₅ -b-PEG3k)	22500	33	218	30.3	15.4	n
6	poly(MAB ₅₋₅ -b-PEG8k)	29300	52	232	82.4	41.2	у
7	poly(MAB ₅₋₅ -b-PEG10k)	27400	55	215	86.0	43.7	у
8	poly(<i>br</i> MAB ₅₋₅ - <i>b</i> -PEG8k)	22500	54		118	60.0	n
9	poly(MAB ₁₀₋₁₀ - <i>b</i> -PEG3k)	11700	39	213	16.3	8.3	n
10	poly(MAB ₁₀₋₁₀ - <i>b</i> -PEG8k)	22100	53	213	68.5	34.8	у
11	poly(MAB ₁₀₋₁₀ - <i>b</i> -PEG10k)	29200	55	213	78.7	40.0	у

^{*a*}Determined by GPC (NMP containing 0.01 M LiBr, PSt standard). ^{*b*}Determined by DSC. ^{*c*}Heat of fusion of T_m . ^{*d*}Degree of crystallization determined by ΔH . ^{*e*}Shape-memory property.



Figure 4. SMP characteristics of PEBA films. (a) poly(MAB₅₋₅-b-PEG3k), (b) poly(MAB₅₋₅-b-PEG8k), and (c) poly(MAB₅₋₅-b-PEG10k).

isolated yields range from 43% to 74%. The oligomeric fraction could not be completely collected. Thus, the measured composition of the block copolymer is not always 1:1, as expected. The solubilities in ordinal organic solvents and water were assessed. The polymers (Table 1, runs 3–11) are highly soluble in DMF, *N*,*N*-dimethylacetamide (DMAc), MeOH, CHCl₃, and CH₂Cl₂ and moderately soluble in NMP and DMSO. We expected that the polymers might be soluble in water due to the hydrophilic PEG segment and form micelle in the media. However, they are totally insoluble in water. To obtain a homogeneous solution, a high concentration of 10 M HCl is required as the solvent. However, they are insoluble in THF, acetone, ethanol, ethyl acetate, toluene, and diethyl ether. Although the PEBA samples are insoluble in distilled water, they became too swollen to be retrieved.

Polymer films were prepared by solvent-casting a 25 wt % NMP solution onto a glass substrate. As shown in Figure 2, the films appear light yellow to dark brown. They are opaque, except for the poly(AB_{1-1} -*b*-PEG3k) and poly(MAB_{1-1} -*b*-PEG3k) samples. The poly(MAB_{5-5} -*b*-PEG3k), poly(MAB_{10-10} -*b*-PEG3k), poly(MAB_{10-10} -*b*-PEG8k), and poly(MAB_{10-10} -*b*-PEG10k) films exhibit hard plastic characteristics at room temperature and soft rubbery behavior at 80 °C. Poly(MAB_{5-5} -*b*-PEG3k) shows rubbery behavior both at room temperature and at 80 °C. The other films, including the high- M_w/M_n -HS-based PEBA poly-

($brMAB_{5-5}$ -b-PEG8k), show hard plastic behavior at 20 °C but are easily destroyed upon folding. Furthermore, these films are almost melted at 80 °C and do not maintain their shape.

Thermal Properties. Figure 3 shows the DSC profiles (second scan, 20 $^{\circ}C/min$, N₂) of the PEBA samples at from between 0-100 °C and 150-250 °C. The endothermic peak corresponding to the $T_{\rm m}$ of the PEG segment is observed around 55 °C. The shorter PEG3k-segment-containing polymers show lower $T_{\rm m}$ values with lower heats of fusion (ΔH) from 33 and 45 °C due to the lower degree of crystallization (χ). Conversely, the poly(MAB₅₋₅-*b*-PEG) and $poly(MAB_{10-10}-b-PEG)$ samples show thermal transitions around 220 °C, which are assignable to the T_g of the HS. These values seem to be independent of the length of PEG segment. Our previously reported block copolymer,³⁷ poly-(MAB₅₋₅-*b*-PPG) (amorphous–crystalline PEBA), presents its HS $T_{\rm g}$ between 50 and 90 °C, far lower than the expected value of 170 °C. Furthermore, this lower T_g was detected only by DMA measurements; thus, the phase segregation is not sufficient in the poly(MAB₅₋₅-b-PPG) film. Conversely, the crystalline-crystalline PEBA copolymer exhibits more definitive segregation in the films.

The thermal properties of the prepared PEBA samples are summarized in Table 2. Because of the hydrogen bonding at the terminal of the PEG segment, the $T_{\rm g}$ s for the HS of poly(MAB₅₋₅-*b*-PEG) and poly(MAB₁₀₋₁₀-*b*-PEG) are ob-



Figure 5. Representative example of two sequential shape-memory cycles for poly(MAB₅₋₅-b-PEG8k).



	L_0^{a} (%)	L_m^{b} (%)	L_{Ret}^{c} (%)	L_{Res}^{d} (%)	R_f (%)	R_r (%)		
cycle 1	0	73.9	67.5	2.5	91	97	R_f (%) = $\frac{L_{\text{Ret}} - L_0}{L_m - L_0} \times 100$	(1)
cycle 2	0.5	91.0	82.9	4.1	91	96	$R_r (\%) = \frac{L_m - L_{\text{Res}}}{L_m - L_0} \times 100$	(2)

 ${}^{a}L_{0}$ is the original length. ${}^{b}L_{m}$ is the deformed length. ${}^{c}L_{Ret}$ is retained length. ${}^{d}L_{Res}$ is the length after recovery.



Figure 6. POM images (left) and WAXD profiles (right) of PEBA samples.

served around 215 °C, which are higher than the $T_{\rm g}$ s observed for MAB₅₋₅ (170 °C) and MAB₁₀₋₁₀ (180 °C). The value of ΔH for the PEG segment was determined via DSC measurements, and the χ values were calculated using the reported $\Delta H_{\rm m}^0$ of 196.8 J/g.⁵² The χ values of the PEG segments in the PEBA samples are from 8.3% to 71.6%, depending on the structural combination of HS and SS. Basically, the PEG3k-based block copolymer samples exhibit low χ values and no SMP properties. Thermally induced SMP behavior can be attributed to the coexistence of a rigid HS crystalline phase and SS domains. Above the $T_{\rm m}$ of the PEG segment, the melted PEG phase allows deformation of the film, whereas the crystalline HS phase memorizes the original shape. On cooling to room temperature, the film loses its flexibility and becomes rigid, giving a temporary shape that is subject to internal stress. The films exhibiting SMP properties have χ values from 34.8% to 43.7%. The samples having lower χ values for the PEG segment cannot fix the temporary shape against the internal stress, so these films relax, even at room temperature. Conversely, the samples having higher χ values cannot maintain the film properties above $T_{\rm m}$ due to the absence of the crystalline HS domain. Thus, moderate χ values are required to maintain the temporary shape at room temperature and the film shape above $T_{\rm m}$.

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Figure 7. AFM images of PEBA films (scale bar is 500 nm).



Figure 8. DMA profiles of the relation between (a) E' and temperature as well as (c) tan δ and temperature for PEBA films having SMP property and (b) those of the relation between E' and temperature as well as (d) tan δ and temperature for PEBA films that do not show SMP character.

SMP Properties. SMP properties were expected for our block copolymers since they have two segregated crystalline domains in the films, as confirmed by the DSC results. Figure 4 shows the results of SMP testing for poly(MAB₅₋₅-*b*-PEG3k),

poly(MAB₅₋₅-*b*-PEG8k), and poly(MAB₅₋₅-*b*-PEG10k) films. The films were wrapped around a glass rod at 80 $^{\circ}$ C to form helix-shaped ribbons. They were then cooled to room temperature, and the rod was removed. Because the poly-

(MAB₅₋₅-*b*-PEG3k) film exhibits rubbery behavior both at room temperature and at 80 °C, the helical shape is not maintained, even after cooling to room temperature. However, the curved film recovers its flat shape when heated to 80 °C. Conversely, the poly(MAB₅₋₅-*b*-PEG8k) and poly(MAB₅₋₅-*b*-PEG10k) films show excellent SMP properties, with a stable temporary fixed shape and perfect recovery of the original flat shape. In tensile testing, the film (1.1 cm × 0.3 cm × 100 μ m) can be elongated by up to 400% at 80 °C, and the temporary shape is almost perfectly maintained upon cooling (Figure 4s). The original shape is quickly recovered (within 3 s) when the film is reheated to 80 °C.

To study the shape-memory behavior in more detail, stressstrain-temperature curves were obtained using DMA. A quantitative demonstration of temperature memory properties with the deformation temperature at 90 °C and a strain value of 70% was performed for two cycles (Figure 5). From these results, the values of $R_{\rm f}$ and $R_{\rm r}$ were calculated using eqs 1 and 2 and are summarized in Table 3. The excellent values of $R_{\rm f}$ = 91% and $R_{\rm r}$ = 97% demonstrate the potential of the temperature memory functionality of the PEBA films.

WAXD and POM Studies. Several PEBA films prepared herein show excellent SMP properties. To more fully understand the criteria required for these properties, we performed WAXD analysis. Figure 6 shows the POM images of PEBA samples at 25, 80, and 250 °C along with the corresponding WAXD profiles. In the profile of poly-(MAB₅₋₅-b-PEG3k) (no SMP properties), diffraction peaks are observed at 18° and 21° , which are assignable to MAB₅₋₅ HS, and at 20° and 24° , which are assignable to PEG SS. This low diffraction intensity for the PEG segment is also supported by the DSC measurements, where the χ value was 15.4% (Table 2, run 5). Under POM observation, an anisotropic structure is observed at 25 and 80 °C, but the observed structure at 25 °C is quite different from that of PEG8k. In the WAXD profile of poly(brMAB₅₋₅-b-PEG8k) (no SMP properties), only strong PEG peaks are observed ($\chi = 60\%$). Conversely, diffraction peaks corresponding to both HS and SS domains are observed in the WAXD measurement for SMP samples, i.e., $poly(MAB_{5-5}-b-PEG8k)$ ($\chi = 41.2\%$) and poly(MAB₅₋₅-*b*-PEG10k) (χ = 43.7%). In the POM images observed for these samples, two types of clear anisotropic structures are assignable to PEG and MAB₅₋₅ segments at 25 and 80 °C. Thus, to realize SMP properties, the two polymer segments should have crystalline structures with moderate γ values.

AFM Study. AFM analysis was performed to ascertain the surface morphologies of the films. Figure 7 depicts the AFM images of the block copolymer films. For poly($brMAB_{5-5}$ -b-PEG8k) ($\chi = 60\%$), fibril morphology corresponding to PEG spherulites is observed. This type of morphology is also clearly observed for the SMP samples poly(MAB₅₋₅-b-PEG8k) ($\chi = 41.2\%$) and poly(MAB₅₋₅-b-PEG10k) ($\chi = 43.7\%$) but not for poly(MAB₅₋₅-b-PEG3k) ($\chi = 15.4\%$).

DMA Study. The DMA profiles of SMP and non-SMP films are shown in Figure 8. Most non-SMP samples break at ~50 °C probably because of a lack of aggregation in the HS domain. In other words, the amide sequences AB_{1-1} and MAB_{1-1} are too short to form a stable phase. The $brMAB_{5-5}$ segment is also ineffective for endowing SMP properties probably because of the weaker aggregation due to its broad M_w/M_n . When the PEG segment is too short, such as in PEG3k, the properties of the block copolymer film are mainly

dictated by the MAB₅₋₅ segment. Thus, the E' value of the film starts to rapidly decrease around -30 °C (Figure 8b). As shown in Figure 8c, the SMP samples clearly show two peaks at -35 and 60 °C for T_g and T_m of PEG domain, respectively, whereas the peaks for non-SMP samples shown in Figure 8d are complicated and dissimilar. Again, it cannot hold its shape upon heating and cooling due to the lack of the contribution from the PEG domain in the $poly(MAB_{5-5}-b-PEG3k)$ film. In our previous study, the poly(MAB₅₋₅-*b*-PPG4k) films showed relaxations at -70 °C for T_g of the PPG segment and 50 °C for that of the MAB₅₋₅ segment.³⁷ The T_g for poly(MAB) is ≈ 200 °C; thus, T_g observed for the poly(MAB₅₋₅-*b*-PPG4k) film is significantly lower than the expected value. In contrast, the poly(MAB₅₋₅-*b*-PEG8k), poly(MAB₅₋₅-*b*-PEG10k), poly-(MAB₁₀₋₁₀-b-PEG8k), and poly(MAB₁₀₋₁₀-b-PEG10k) films in this study exhibit T_g values of ≈ 215 °C, which clearly indicates the almost perfectly phased segregated structures in the films.

Mechanical Properties. Figure 9 shows the tensile test results for the block copolymer films. The SMP samples



Figure 9. Stress-strain curves for PEBA films.

poly(MAB₅₋₅-*b*-PEG8k) and poly(MAB₅₋₅-*b*-PEG10k) show typical plastic sample behavior with clear yield points and elongations of over 300%, whereas poly(*br*MAB₅₋₅-*b*-PEG8k) shows hard brittle characteristics because there is only a single PEG crystalline hard domain in the film. For poly(MAB₅₋₅-*b*-PEG3k), the film is very soft, even without heating, and it cannot maintain the film beyond only \approx 28% deformation. This can be explained by the low χ value (15.4%) of this PEG domain.

Table 4 summarizes the tensile testing results for the PEBA films. We expected that the SMP films would exhibit high elongation at high temperatures, such as 80 °C, which is beyond the melting point of the PEG segment. However, they break at similar elongation values to those observed at 25 °C. At this temperature, as expected, the rigidity and the yield strength of the films decreased. For the SMP films, the tensile moduli dramatically decrease to 1/7-1/10 of their original values and present S-type curves typical of TPE materials.

Swelling and Moisture-Responsive Properties. Because our films contain hydrophilic PEG domains, we expected that the SMP films would be moisture responsive. However, before testing the SMP films, we assessed the swelling behavior of the poly(MAB₅₋₅-*b*-PEG8k) film. The dried film ($\rho = 1.15$ g/cm³) was placed in a Petri dish at 20 °C with sufficient

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Table 4. Stress-Strain Curves of Multiblock Copolymers (MAB₅₋₅-*b*-PEG)

polymer	temp (°C)	σ_{TS}^{a} (MPa)	$ E_{b}^{b} $ (%)	(MPa)		
poly(MAB ₅₋₅ - <i>b</i> -PEG3k)	25	8.8	26.3	45.0		
poly(brMAB ₅₋₅ -PEG8k)	25	4.2	2.9	180.0		
poly(MAB ₅₋₅ -b-PEG8k)	25	9.7	312.0	218.0		
poly(MAB ₅₋₅ -b-PEG10k)	25	9.8	290.0	200.0		
poly(MAB ₅₋₅ -b-PEG3k)	80	2.2	21.9	18.3		
poly(<i>br</i> MAB ₅₋₅ -PEG8k)	80					
poly(MAB ₅₋₅ -b-PEG8k)	80	2.7	262.0	30.0		
poly(MAB ₅₋₅ -b-PEG10k)	80	1.7	174.0	20.0		
^{<i>a</i>} Tensile strength. ^{<i>b</i>} Elongation at break. ^{<i>c</i>} Young's modulus.						

deionized water to submerge the film. After 5 days, the film was carefully retrieved and carefully dabbed dry with a KimWipe. The volume and weight swelling ratios were calculated to be 659% and 587%, respectively. The ρ value of the swollen film was calculated to be 1.02 g/cm³. These results clearly demonstrate the moisture responsivity of the film. Thus, a 3 cm long rectangular film sample was prepared and secured with a clip as shown in Figure 10. Only one side, \sim 2 cm from the bottom, of this film was homogeneously exposed to moisture, and the film quickly started to bend. This deformation finishes within 1 min, and the film maintains its shape for a further hour. The polymer film began to bend from the narrow point near the grasped part although one side of the film had been homogeneously sprayed with water. This could explain the swelling of the sprayed part and the stress concentrated at the boundary between the crystalline upper part and swollen lower part. The film was placed in a drying oven at 100 °C for just 5 min, resulting in the film returning to its original shape. This moisture-responsive behavior can be explained simply as follows: the PEG domains on one side of the film absorb the sprayed water, and the film expands more on this side, resulting in its bent shape. The absorbed water is confined in the separated area by the MAB_{5-5} phases, and thus the film maintains its temporary shape under these stress conditions. When the film is placed in a drying oven, the absorbed water is quickly eliminated and once again the PEG domains form a crystalline structure, returning the overall shape back to its original form. Thus, this simple moisture responsivity can be explained in terms of the perfectly segregated hydrophilic PEG and hydrophobic MAB_{5-5} microdomains.

CONCLUSIONS

Monodisperse polyamide HSs based on *N*-methylbenzamide were utilized to construct novel PEBA materials with crystalline PEG as a soft segment. The resulting PEBA materials showed good thermoplastic elastomeric properties with $\sigma_{\rm TS}$, $E_{\rm yr}$ and $E_{\rm B}$ values of 1.7–9.8 MPa, 18.3–218 MPa, and up to 312%, respectively. The MAB_{5–5}-based PEBA showed good thermal SMP properties with $R_{\rm f}$ = 91% and $R_{\rm r}$ = 97% upon heating to 80 °C and cooling to room temperature. The PEBA material also showed moisture-responsive behavior, exhibiting stable bending deformation when one of its surfaces was exposed to water vapor. The material returned to its original shape within just 5 min in a drying oven at 100 °C.

Thus, our novel films show excellent potential for a wide range of biomedical and industrial applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b01817.



Figure 10. Swelling and moisture-responsive behavior of PEBA films.

SI 1: ¹H NMR spectra of MAB_{5-5} (up) and $brMAB_{5-5}$ (bottom) samples in CDCl₃; SI 2: GPC profiles of (a) MAB_{5-5} , (b) PEG8k, and (c) poly(MAB_{5-5} -*b*-PEG8k); SI 3: ¹H NMR spectra of HO-PEG-OH and NH₂-PEG-NH₂; SI 4: expanded ¹³C NMR spectrum of poly-(MAB_{10-10} -*b*-PEG3k) copolymer in DMSO-*d*₆; SI 5: shape-memory effect of poly(MAB_{5-5} -*b*-PEG8k) copolymer films (DOCX)

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Notes

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