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Preparation of Supramolecular Extenders with Precise Chain Lengths via Iterative Synthesis and Their Applications in Polyurethane Elastomers

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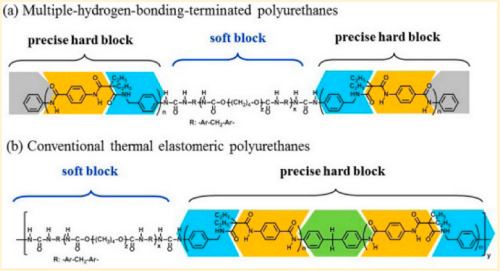
Supporting Information

ABSTRACT: In this study, we synthesized a dual-functional building intermediate, 4-(3,3-diethyl-2,4-dioxoazetidin-1-yl)benzoyl chloride (DEDA-BC), from readily available starting materials, including 4-isocyanatobenzoyl chloride and *p*-tolyl isocyanate. In its iterative syntheses of hard segments, we first treated the highly reactive acid chloride of DEDA-BC with the monoamine (aniline) or the diamine (4,4′-methylenedianiline, 4,4′-MDA) to form first-generation azetidien-2,4-dione intermediates. We then reacted these derivatives with 4-aminobenzylamine at the more-selective azetidine-2,4-dione group of DEDA-BC to form the first-generation of benzyl amine extenders. Using this alternating method, we obtained high yields of supramolecular extenders of various chain lengths (n = 1−3) in a systematic manner, without the need for tedious purification steps, under catalyst-free conditions. The mono- and diamine extenders with numbers of repeating units ranging from one to three were synthesized precisely through this new iterative synthetic approach. The molar mass increases between each generation were 365 g mol^{-1} for the monoamine series and 730 g mol^{-1} for the diamine series. The three generations of supramolecular extenders possessed the distinctive characteristics of multiple hydrogen bonding moieties and narrow molecular weight distributions. Their gelation phenomena in THF revealed that these amine extenders underwent supramolecular assembly, through intermolecular hydrogen bonding, to form organogels. We used these well-defined extenders with various chain lengths in the preparation of polyurethane (PU) elastomers. Small-angle X-ray scattering revealed well-defined microdomains in the morphologies of the PU elastomers presenting multiply hydrogen-bonded terminal groups. The tensile and thermal properties of the prepared PUs were dependent on the effects of the content of hard segments, the chain length, and the strength of hydrogen bonding.



INTRODUCTION

The self-assembly of macromolecules into microphase patterns is an interesting topic because relatively low molecular weight supramolecular arrays are capable of spontaneously forming ordered nanostructures.[1,2] The versatility of supramolecular assemblies offers the possibility to build a diverse range of chemical architectures from amphiphiles,[1] linear block copolymers,[3] and dendritic systems.[4] The incorporation of multiple hydrogen bonding units can improve a polymer's properties, including its melt rheology, phase separation behavior, and thermal stability during melt processing.[5] Van der Schuur et al.[6] were the first to establish chain-extended polyurethane (PU) elastomers rich in hydrogen-bonded amide and amine units. They found that increasing the length of the amide chain extender improved the thermal stability and tensile properties of the PU. The Hayes group reported a series of thermo-responsive microphase-separated supramolecular PUs[7−11] in which the degree of microphase separation, depending on the nature of the terminal functional groups, was affected by the extent and pattern of hydrogen bonding. In general, thermo-reversible PU elastomers consisting of alternating soft and rigid (e.g., urethane, urea) segments are classified as thermoplastic PUs. The hard domains act as thermo-reversible physical cross-links, providing the characteristic thermoplastic and elastomeric behavior of the polymer. External thermal stimuli can alter the thermodynamic equilibrium, offering a route toward functional supramolecular networks that can be exploited to attain the thermo-reversible microphase-separated morphologies responsible for the characteristic viscoelastic mechanical properties of PUs. These supramolecular PUs may enable the production of new thermoplastic elastomers, adhesives, and tunable polymeric materials.

Much research[6,12−14] has revealed that the molecular weight polydispersity (PD) and the length of the hard segments both

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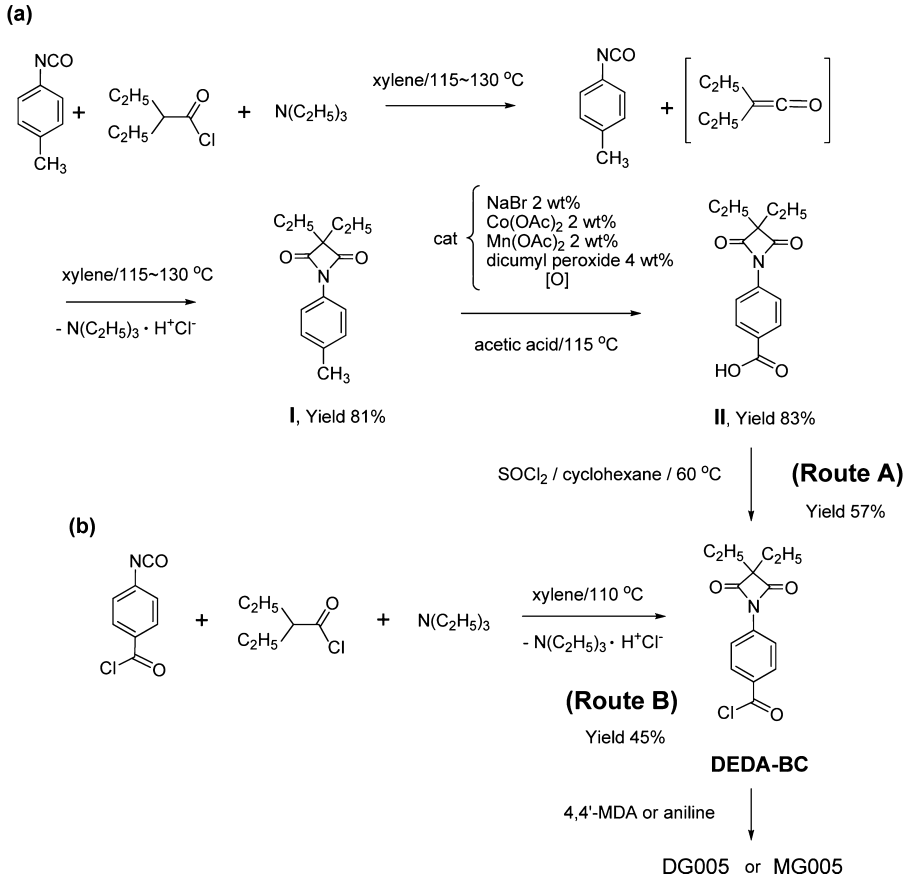
Scheme 1. Two Synthetic Routes Toward DEDA-BC, from (a) *p*-Tolyl Isocyanate (Route A) and (b) 4-Isocyanatobenzoyl Chloride (Route B)



play significant roles in affecting the material properties of PUs, due to the formation of different morphologies in the bulk state. Reports of hard-segment intermediates with uniform chain lengths are rare because of a lack of precise and efficient methodologies for their synthesis. Harrell[15] synthesized monodisperse hard segments with uniform chain length, but these compounds did not possess any hydrogen bonding sites or rigid structures; nevertheless, narrowing the size distribution of the hard segments did increase the modulus and tensile strength of the PU. Harthcock and co-workers[16] used a cumbersome process, based on gel permeation chromatography, to isolate individual extenders, of uniform chain length, from a random mixture of products from the reaction of 1,4-butanediol with 4,4′-methylene-*p*-diphenyl diisocyanate (MDI) blocks; the critical hard-segment size required to initiate phase separation was an MDI unit extended at least with two butanediol moieties. Recently, Sijbesma et al.[17] used a protection/deprotection approach to prepare segmented poly(ether urea)s with hard segments of uniform chain length, but these systems consisted mainly of aliphatic backbones; that is, they differed vastly from the majority of PUs prepared herein from aromatic diisocyanate and malonamide/(urethane urea) systems. Nakaname and co-workers[18,19] also found that the physical properties of materials reached their optimal performance when the weight ratio of the hard and soft segments was at a specific optimal ratio; beyond this ratio, the properties of PU elastomers do not necessarily rise as their hard-segment contents increase.

Recently, we used the building block 4-isocyanato-4′-(3,3-dimethyl-2,4-dioxoacetidino)diphenylmethane (IDD), which exhibits selective reactivity, to synthesize a series of polyurea/malonamide dendritic structures without the need for protection/deprotection chemistry.[20] The presence of strong noncovalent interactions, particularly hydrogen bonds, in the side-chain and end-capped dendritic PU elastomers improved their mechanical properties significantly, especially with respect to the shape memory effect.[21−23] Iterative synthesis based on two alternative addition reactions of the dual-functional intermediate IDD allowed us to introduce three generations of supramolecular extenders, with uniform chain lengths, into thermo-reversible PUs.[24] We prepared supramolecular pseudo-triblock PUs having a hard segment content of approximately 41% by attaching extenders of uniform chain length to both ends of NCO-terminated prepolymers. The increases in the number of hydrogen bonding sites and aromatic units of the chain extenders with narrow molecular weight distributions resulted in more physical cross-linking in the hard segment domains. The pseudotriblock system[24] appeared to enhance the mechanical properties of the elastomers more effectively than did an approach using dendritic extenders.[22,23] In addition, we employed the dual-functional IDD building blocks to prepare a series of specific polymer intermediates that we applied as dendritic intercalating agents for clays,[25−27] silicate-anchored macroinitiators,[28] multiply hydrogen-bonding epoxy reactive modifiers,[29] and polymalonamide elastomers.[30]

In this present study, we synthesized a new dual-functional building intermediate, 4-(3,3-diethyl-2,4-dioxoazetidin-1-yl)-

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benzoyl chloride (DEDA-BC), from readily available starting materials, including 4-isocyanatobenzoyl chloride and *p*-tolyl isocyanate. The synthesized DEDA-BC possesses selective reactivity, featuring both an azetidine-2,4-dione group and a highly active acid chloride group in the same molecule. An acid chloride is more reactive than an isocyanate, converting an amino group into a stable amide within seconds. Moreover, we prepared DEDA-BC directly from 4-isocyanatobenzoyl chloride by diethyl ketene cycloaddition. Alternatively, an efficient synthetic scheme (see Scheme 1a) based on *p*-tolyl isocyanate in three steps involving cycloaddition, oxidation and chlorination has also been developed. The intermediate DEDA-BC is superior to IDD for the systematic preparation, through iterative synthesis, of well-defined amine extenders allowing multiple hydrogen bonding supramolecular interactions (so-called "supramolecular extenders").[24] The iterative processes investigated in this study allow rapid and efficient syntheses without the need for complicated separations. The resulting supramolecular amine extenders increase the number of hydrogen bonding sites and the molecular length while narrowing the molecular weight distribution (i.e., monodispersion). Indeed, we synthesized both mono- and di-functional amine extenders using an iterative strategy (Figure 1) and then

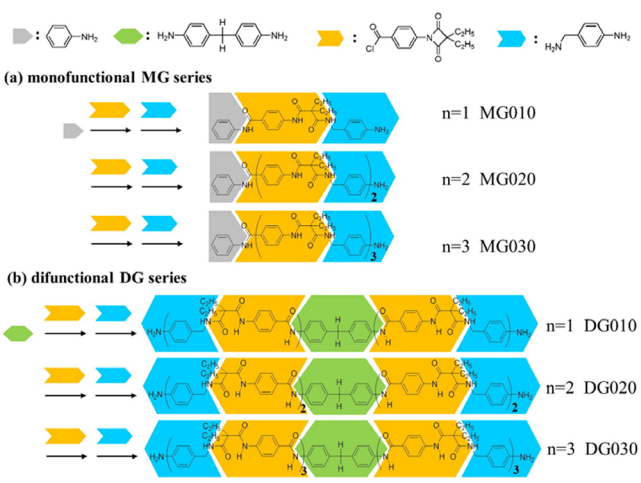

Figure 1. Iterative syntheses of the MHB (a) monofunctional MG series and (b) difunctional DG series of extenders.

embedded them into PUs featuring precisely sized hard segments (Figure S1, Supporting Information). We used the well-defined monoamine extenders as end-capping agents to react with the isocyanate-terminated prepolymers, forming supramolecular "pseudo-triblock" A–B–A PU systems. The design of these PUs terminated with multiple hydrogen bonding sites, abbreviated herein as "MHB PUs" (Figure S1a, Supporting Information), has been adopted in previous studies.[7−11,24] On the other hand, we also prepared conventional thermal elastomeric PUs by extending the isocyanate-terminated prepolymer using diamine extenders (Figure S1b, Supporting Information). Structurally, these designed extenders exhibited large numbers of rigid amide units and aromatic rings, potentially making them more incompatible with the polyether soft segments of resulting PUs. On the basis of experimental results obtained from thermal analyses, morphological studies, and tensile measurements, herein we describe the effects of the supramolecular extenders on the hydrogen bonding–induced phase separation and mechanical properties of PU elastomers. Through efficient and iterative syntheses, we have established the structure–property relationships of elastomeric PUs in terms of the impacts of different hard segments, with precise chain lengths, on phase separation, physical properties, and domain sizes.

EXPERIMENTAL SECTION

Materials. 4-Isocyanatobenzoyl chloride, 2-ethylbutyryl chloride, triethylamine, and aniline were obtained from Acros Organics; 4-aminobenzylamine was obtained from Aldrich. Liquid reagents were further purified through distillation prior to use. The polyether diol PTMO 2000, with an average of approximately 27 repeating tetramethylene ether groups, was obtained commercially from DuPont (Terathane); it had an average molecular weight of 2058 g mol^{-1}, calculated based on the hydroxyl number of 54.5 mg of KOH g^{-1} (as determined by ASTM D4274 and ASTM E222); it was dried under vacuum at 80 °C for 6 h prior to use.

Measurements. NMR spectra were recorded using Varian Unity Inova-600 and Gemini-200 FT-NMR depending on sample's solubility. Thermal analyses of the polymers were performed under a N_2 atmosphere through differential scanning calorimeter (DSC) using a Seiko SII Model SSC/5200 operated at heating and cooling rates of 10 °C min^{-1}, holding for 5 and 3 min at +180 and −100 °C, respectively. Thermogravimetric analysis (TGA) was performed using a Seiko SII Model SSC/5200 operated at a heating rate of 10 °C min^{-1}. Fourier transform infrared (FTIR) spectra were recorded over the range from 4000 to 400 cm^{-1} using a Perkin-Elmer Spectrum One FTIR spectrometer. Melting points (mp) of the samples were measured using a Fargo MP-2D melting point apparatus operated at a heating rate of 3 °C min^{-1}. Gel permeation chromatography (GPC) of the polymer materials and supramolecular extenders was performed using either Shodex GPC KD-800 (802, 803, and 806M) columns and *N*,*N*-dimethylformamide (DMF) as the mobile phase or Viscotek viscoGEL (I-MBLMW-3078 and I-MBHMW-3078) columns and *N*-methyl-2-pyrrolidine (NMP) as the mobile phase. The samples were analyzed using a Shodex RI-101 GPC operated at a flow rate of 1.0 mL min^{-1} with polystyrene calibration over the molecular weight range from 682 to 1 670 000 g mol^{-1}. Elemental CHN analysis was performed using an Elementar vario EL III system. Fast atom bombardment (FAB) and electron ionization (EI) mass spectra were recorded using a Finnigan/Thermo Quest MAT 95XL apparatus. The mechanical behavior of the materials was measured at room temperature using a universal testing machine (HT-8504; Hung Ta Instruments, Taiwan) operated at a crosshead speed of 50 mm min^{-1}. Dumbbell-shaped film samples were prepared having a gauge section of 20 mm (L) × 5 mm (W) × 0.4–0.5 mm (H). Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WXRD) data were recorded using Rigaku D/MAX-2500 and D/MAX-2200PC instruments equipped with a rotating anode X-ray tube, with CuK radiation (wavelength: 1.54 Å), operated at 40 kV and 30 mA.

Notation. 4-(3,3-Diethyl-2,4-dioxoazetidin-1-yl)benzoyl chloride is abbreviated herein as "DEDA-BC." The monoamine extenders and their azetidine-2,4-dione intermediates are assigned as "MG0*n*0" and "MG0(n−1)5," respectively, where n represents the number of repeating units of the extender; for example, the extender featuring just one repeating unit is MG010, while its corresponding azetidine-2,4-dione intermediate is MG005. Similarly, the difunctional amine extenders and their intermediates are assigned as "DG0*n*0" and "DG0(n−1)5," respectively, where n represents the number of repeating units of the extender; for example, the extender featuring just one repeating unit is DG010 and its corresponding intermediate is DG005. The "pseudo-triblock" systems for the MHB PUs were prepared by attaching MG-series monoamine extenders to both ends of the NCO-terminated prepolymers; they comprise the "M-series" PUs. Correspondingly, the thermal elastomeric PUs consisting of DG-series diamine extenders are designated as "D-series" PUs. Furthermore, 1,4-butanediol was employed in control experiments for the D-series PUs.

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DEDA-BC. Two synthetic routes of DEDA-BC molecule were employed, either directly from 4-isocyanatobenzoyl chloride (Scheme 1b; route B) or indirectly from *p*-tolyl isocyanate (Scheme 1a; route A). Pure crystalline DEDA-BC was directly synthesized from 4-isocyanatobenzoyl chloride with diethyl ketene via ketene/isocyanate cycloaddition (route B).[30] A solution of Et_3N (10.1 g, 100 mmol) in dry xylene (40 mL) was added dropwise to a solution of 4-isocyanatobenzoyl chloride (5.00 g, 27.5 mmol) and 2-ethylbutyryl chloride (7.50 g, 55.7 mmol) in dry xylene (50 mL) at 110 °C under dry N_2 over a period of 1 h. The resulting mixture was then heated under reflux for another 2 h. After cooling to room temperature, the precipitated salts were filtered off and the clear filtrate and washings were concentrated under vacuum. Fine crystals (3.5 g, 45%; mp 107−108 °C) were obtained after recrystallization of the residue from dry cyclohexane (50 mL). Finally, a solution of DEDA-BC (2.48×10^{-7} M) in cyclohexane was prepared for subsequent experiments. FTIR (cm^{-1}, cyclohexane): 1769 (C═O of acyl chloride), 1748 and 1870 (C═O of azetidine-2,4-dione). ^1H NMR (200 MHz, $CDCl_3$, δ): 1.04 (t, 6H, CH_3), 1.84 (q, 4H, CH_2), 8.02 and 8.17 (AA′XX′, 4H, ArH). EIMS: calcd, m/z 279.07; found, 279.2.

4-(3,3-Diethyl-2,4-dioxozazetidin-1-yl)-*N*-phenylbenzamide [MG005]. The solution of DEDA-BC (2.48×10^{-7} M, 3.5 g, 12 mmol) in cyclohexane was added dropwise over 30 min to a solution of aniline (1.2 g, 13 mmol) and Et_3N (1.3 g, 13 mmol) in cyclohexane (50 mL) at room temperature under dry N_2. The precipitate was filtered off; evaporation of the solvent provided a powder that was partitioned between EtOAc and water (1:1, v/v). Concentration of the organic phase provided a slightly yellow powder, which was dissolved in THF (30 mL) and then added dropwise into cyclohexane (600 mL). After repetitive washing and drying in a vacuum oven at 60 °C, a white powder (4.1 g, 98%) was obtained. Mp: 163−167 °C. FT-IR (cm^{-1}): 3310 (−NH stretch of amides), 1869 and 1740 (stretching vibration of −C═O of azetidine-2,4-diones), 1650 (-C═O of amide groups). ^1H NMR (300 MHz, acetone-d_6, δ): 1.03 (t, 6H, CH_3), 1.87 (q, 4H, CH_2), 7.09 (t, 1H, ArH), 7.33 (t, 2H, ArH), 7.82 (2H, ArH), 7.92 (2H, ArH), 8.12 (2H, ArH), 9.61 (s, 1H, NH). Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 70.73; H, 5.90; N, 8.95. EIMS: calcd, m/z 336.15; found, 336.4. GPC (DMF): PD = 1.01; M_n = 1680 g mol^{-1}.

***N*^{1}-(4-Aminobenzyl)-2,2-diethyl-*N*^{3}-(4-(phenylcarbamoyl)-phenyl)malonamide [MG010].** A solution of 4-aminobenzylamine (380 mg, 3.1 mmol) in dry DMF (1 mL) was added slowly at room temperature to a solution of MG005 (1.0 g, 2.9 mmol) in dry DMF (6 mL) under dry N_2. After 1 h, all of the MG005 had been consumed [TLC; eluent = EtOAc/*n*-hexane, 3:2 (v/v)], so the mixture was poured into water (150 mL) and stirred for several minutes. The precipitate was purified through two cycles of dissolving in DMF and precipitating from water. Collection and drying under vacuum at 60 °C provided a white powder (1.2 g, 91%). Mp 212−218 °C. FT-IR(cm^{-1}): 3330 (−NH stretch of amides), 1652 (-C═O of amide groups). ^1H NMR (300 MHz, DMSO-d_6, δ): 0.68 (t, 6H, CH_3), 1.93 (q, 4H, CH_2), 4.17 (d, 2H, CH_2), 4.94 (s, 2H, NH_2), 6.45 (d, 2H, ArH), 6.92 (d, 2H, ArH), 7.05 (t, 1H, ArH), 7.31 (t, 2H, ArH), 7.76 (4H, ArH), 7.93 (2H, ArH), 8.44 (t, 1H, NH), 10.13(s, 1H, NH), 10.78 (s, 1H, NH). Anal. Calcd for $C_{27}H_{30}N_4O_3$: C, 70.72; H, 6.59; N, 12.22. Found: C, 70.81; H, 6.57; N, 12.58. EIMS: calcd, m/z 458.23; found, 458.6. GPC (DMF): PD = 1.01; M_n = 4020 g mol^{-1}.

MG015. The solution of DEDA-BC (2.48×10^{-7} M; 3.5 g or 12 mmol) in cyclohexane was added dropwise at room temperature to a solution of MG010 (5.0 g, 11 mmol) and Et_3N (1.2 g, 12 mmol) in dry THF (90 mL) under dry N_2 over 30 min. The precipitate was filtered off and the solvents evaporated. The residue was partitioned between EtOAc and brine and then the organic phase was washed sequentially with 0.5 N $NaOH_{(aq)}$ and 0.5 N $HCl_{(aq)}$. Evaporation of the solvent provided a powder that was dissolved in DMF (30 mL) and poured into H_2O (1.200 L). The precipitate was collected to provide a fine powder (7.3 g, 96%). Mp: 258−263 °C. FT-IR (cm^{-1}): 3330 (−NH stretch of amides), 1870 and 1742 (stretching vibration of −C═O of azetidine-2,4-diones), 1650 (−C═O of amide groups). ^1H NMR (300 MHz, DMSO-d_6, δ): 0.70 (t, 6H, CH_3), 0.95 (t, 6H, CH_3), 1.82 (q, 4H, CH_2), 1.94 (q, 4H, CH_2), 4.32 (d, CH_2), 7.05 (t, 1H, ArH), 7.25−7.36 (m, 4H, ArH), 7.66−7.86 (m, 8H, ArH), 7.94 (2H, ArH), 8.07 (2H, ArH), 8.60 (t, 1H, NH), 10.14 (s, 1H, NH), 10.29 (s, 1H, NH), 10.60 (s, 1H, NH). Anal. Calcd for $C_{41}H_{43}N_5O_6$: C, 70.17; H, 6.18; N, 9.98. Found: C, 69.57; H, 6.29; N, 9.98. FABMS: calcd, m/z 701.32; found, 702.4. GPC (DMF): PD = 1.01; M_n = 6480 g mol^{-1}.

MG020. A solution of 4-aminobenzylamine (0.38 g, 3.1 mmol) in dry DMF (1 mL) was added slowly at room temperature to a solution of MG015 (2.0 g, 2.8 mmol) in dry DMF (12 mL) under dry N_2. After 1.5 h, all of the MG015 had been consumed [TLC; eluent: EtOAc/*n*-hexane, 3:1 (v/v)]. The mixture was poured into water (300 mL) and stirred for several minutes. The precipitate was purified through two cycles of dissolving in DMF and precipitating from water. Collection of the precipitate and drying under vacuum at 60 °C provided a white powder (2.2 g, 94%). Mp 100−110 °C. FT-IR (cm^{-1}): 3332 (−NH stretch of amides), 1654 (−C═O of amide groups). ^1H NMR (400 MHz, DMSO-d_6, δ): 0.67 (m, 12H, CH_3), 1.91 (m, 8H, CH_2), 4.16 (d, 2H, CH_2), 4.31 (d, 2H, CH_2), 4.92 (s, 2H, NH_2), 6.44 (d, 2H, ArH), 6.93 (d, 2H, ArH), 7.04 (t, 1H, ArH), 7.23−7.34 (m, 4H, ArH), 7.66−7.86 (m, 8H, ArH), 7.91 (t, 4H, ArH), 8.44 (t, 1H, NH), 8.58 (t, 1H, NH), 10.09 (s, 1H, NH), 10.12 (s, 1H, NH), 10.59 (s, 1H, NH), 10.76 (s, 1H, NH). Anal. Calcd for $C_{48}H_{53}N_7O_6$: C, 69.97; H, 6.48; N, 11.90. Found: C, 68.75; H, 6.78; N, 11.65. FABMS: calcd, m/z 823.41; found, 825. MALDI−TOF−MS: m/z 846.5 $[M + Na]^+$, 853.6 $[M + Na + Li]^+$. GPC (DMF): PD = 1.02; M_n = 4140 g mol^{-1}.

MG025 and **MG030** were prepared using similar procedures, but with dry DMF instead of THF to improve the solubility.

MG025. Yield = 77%. Mp: 273−277 °C. FT-IR (cm^{-1}): 3315 (−NH stretch of amides), 1870 and 1737 (stretching vibration of −C═O of azetidine-2,4- diones), 1654 (−C═O of amide groups). ^1H NMR (600 MHz, DMSO-d_6, δ): 0.73 (tt, 12H, CH_3), 0.97 (t, 6H, CH_3), 1.84 (q, 4H, CH_2), 1.96 (qq, 8H, CH_2), 4.34 (d, 4H, CH_2), 7.07 (t, 1H, ArH), 7.26 (t, 4H, ArH), 7.33 (t, 2H, ArH), 7.68−8.10 (m, 20H, ArH), 8.59 (q, 2H, NH), 10.10 (s, 1H, NH), 10.12 (s, 1H, NH), 10.27 (s, 1H, NH), 10.61 (s, 1H, NH), 10.62 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6, δ): 8.87, 8.92, 22.74, 27.26, 42.17, 58.62, 71.35, 118.72, 119.40, 120.20, 120.33, 123.47, 127.50, 127.56, 128.40, 128.43, 128.54, 129.14, 129.43, 129.47, 132.92, 134.66, 135.03, 135.33, 137.61, 137.91, 139.25, 141.59, 164.29, 164.69, 164.79, 171.26, 171.61, 172.56. Anal. Calcd for $C_{62}H_{66}N_8O_9$: C, 69.77; H, 6.23; N, 10.50. Found: C, 69.34; H, 6.24; N, 10.37. FABMS: calcd, m/z 1066.50; found, 1067. GPC (DMF): PD = 1.02; M_n = 6560 g mol^{-1}.

MG030. Yield = 92%. Mp: 151−158 °C. FT-IR (cm^{-1}): 3325 (−NH stretch of amides), 1653 (-C═O of amide groups). ^1H NMR (600 MHz, DMSO-d_6, δ, Figure S2a, Supporting Information): 0.71 (m, 18H, CH_3), 1.92 (m, 12H, CH_2), 4.19 (d, 2H, CH_2), 4.34 (d, 4H, CH_2), 4.92 (s, 2H, NH_2), 6.47 (dd, 2H, ArH), 6.94 (d, 2H, ArH), 7.07 (t, 1H, ArH), 7.26 (d, 4H, ArH), 7.33 (t, 2H, ArH), 7.69 (dd, 4H, ArH), 7.76−7.97 (m, 14H, ArH), 8.44 (t, 1H, NH), 8.59 (m, 1H, NH), 10.10 (s, 1H, NH), 10.12 (s, 1H, NH), 10.62 (s, 1H, NH), 10.64 (s, 1H, NH), 10.79 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6, δ): 8.93, 8.99, 27.25, 27.33, 27.71, 42.19, 42.23, 58.48, 58.62, 113.64, 119.34, 119.41, 120.21, 120.34, 123.47, 126.38, 127.50, 128.21, 128.42, 128.54, 129.43, 129.47, 134.66, 137.91, 139.25, 141.52, 141.57, 141.59, 147.43, 164.69, 164.80, 171.27, 171.36, 172.45, 172.56, 172.58. Anal. Calcd for $C_{69}H_{76}N_{10}O_9$: C, 69.68; H, 6.44; N, 11.78. Found: C, 68.11; H, 7.44; N, 11.49. FABMS: calcd, m/z 1188.58; found, 1189. MALDI−TOF−MS: m/z 1211.6 $[M + Na]^+$ (Figure S3a, Supporting Information). GPC (DMF): PD = 1.02; M_n = 8580 g mol^{-1}.

3,3-Diethyl-1-*p*-tolylazetidine-2,4-dione (Compound I). Another synthesis of DEDA-BC molecule based on p-tolyl isocyanate in three steps involving cycloaddition, oxidation and chlorination has been prepared as follows (Scheme 1a; route A). A solution of Et_3N (60.8 g, 600 mmol in dry xylene (150 mL) was added dropwise over 4 h to a solution of *p*-tolyl isocyanate (20.0 g, 150 mmol) and 2-ethylbutyryl chloride (40.4 g, 300 mmol) in xylene (170 mL) at 115 °C. The resulting mixture was then heated at 120 °C for another 49 h, at which point FTIR spectroscopy revealed the complete disappearance of the signal for the CNO groups (2270 cm^{-1}). The reaction mixture was cooled to −10 °C and filtered to remove the precipitated

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salt. The clear filtrate and washings were concentrated under vacuum. Distillation under high vacuum at 78−80 °C provided 3,3-diethyl-1-*p*-tolylazetidine-2,4-dione (28.16 g, 81%). FTIR (cm^{-1}): 1851 and 1742 (symmetric and asymmetric stretching of azetidine-2,4-dione C═O units). ^{1}H NMR (200 MHz, δ, DMSO-d_6): 0.92 (t, 6H, CH_3), 1.79 (q, 4H, CH_2), 2.31 (s, 3H, $ArCH_3$), 7.27 and 7.56 (AA′XX′, 4H, ArH). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 8.34, 20.70, 39.50, 71.11, 119.30, 129.88, 130.51, 136.63, 171.80. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.19; H, 7.31; N, 5.61. EIMS: calcd, *m*/*z* 231.13; found, 231.1.

4-(3,3-Diethyl-2,4-dioxoazetidin-1-yl)benzoic Acid (Compound II). The autoxidation[30] of 3,3-diethyl-1-*p*-tolylazetidine-2,4-dione was conducted in a three-neck, round-bottom, Pyrex reaction flask equipped with a magnetic stirrer bar, a gas dispersion fritted disk, a snake-shaped condenser, and a thermometer under an atmosphere of dry O_2. 3,3-Diethyl-1-*p*-tolylazetidine-2,4-dione (10.0 g, 43 mmol) was mixed with NaBr, $Co(OAc)_2$, and $Mn(OAc)_2$ (200 mg, 2 wt % each) and dicumyl peroxide (400 mg, 4 wt %) in AcOH (110 mL). O_2 was introduced into the solution through a fritted disk. The solution was stirred at 115 °C. After 8 h, 3,3-diethyl-1-*p*-tolylazetidine-2,4-dione had been consumed completely [TLC; EtOAc/*n*-hexane, 1:4 (v/v)] and FTIR spectroscopy revealed the appearance of new absorptions at 1730 and 2700−3700 cm^{-1} (CO_2H). The mixture was poured into water (800 mL) and then the solid was collected and dried to provide 4-(3,3-diethyl-2,4-dioxoazetidin-1-yl)benzoic acid (9.94 g, 88%). Mp: 144−145 °C. FTIR (cm^{-1}): 1730 and 2700−3700 (C═O and O−H groups of carboxylic acid), 1851 and 1742 (symmetric and asymmetric stretching of azetidine-2,4-dione C═O groups). ^{1}H NMR (200 MHz, δ, DMSO-d_6): 0.92 (t, 6H, CH_3), 1.79 (q, 4H, CH_2), 7.82 and 8.04 (AA′XX′, 4H, ArH), 13.18 (broad s, 1H, COOH). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 8.81, 39.50, 71.36, 118.79.3, 128.65, 130.92, 136.56, 167.95, 171.54. Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.00; H, 5.28; N, 5.05. EIMS: calcd, *m*/*z* 261.1; found, 261.1.

DG005. $SOCl_2$ (22.7 g, 191 mmol) was added to a suspension of 4-(3,3-diethyl-2,4-dioxoazetidin-1-yl)benzoic acid (5.00 g, 19.1 mmol) in cyclohexane (40 mL) at 60 °C under N_2. After 2 h, a homogeneous solution had formed, with all of the starting material having been consumed [TLC; EtOAc/*n*-hexane, 1:4 (v/v)]. Evaporation of the solvents provided a solid (5.36 g), which was dissolved in dry methyl ethyl ketone (50 mL). A solution of 4,4′-methylenedianiline (4,4′-MDA) (1.94 g, 9.8 mmol) and Et_3N (3.88 g, 38.3 mmol) in dry methyl ethyl ketone (40 mL) was added slowly into the former solution at 0 °C over 10 min. The precipitated salts were filtered off and the solvent evaporated. The residue (5.73 g) was purified with EtOH (80 mL) to remove impurities. Drying at 60 °C under vacuum provided DG005 (5.50 g, 83%). Mp: 162−163 °C. FT-IR (cm^{-1}): 3310 (−NH stretch of amides), 1869 and 1740 (stretching vibration of −C═O of azetidine-2,4-diones), 1650 (-C═O of amide groups). ^{1}H NMR (200 MHz, DMSO-d_6, δ): 0.95 (t, 12H, CH_3), 1.82 (q, 8H, CH_2), 3.89 (s, 2H, $ArCH_2Ar$), 7.19 (d, 4H, ArH), 7.67 (4H, ArH), 7.84 (4H, ArH), 8.07 (4H, ArH), 10.26 (s, 2H, NH). Anal. Calcd for $C_{41}H_{40}N_4O_6$: C, 71.91; H, 5.89; N, 8.18. Found: C, 71.77; H, 5.83; N, 7.92. EIMS: calcd, *m*/*z* 684.3; found, 684.5. GPC (NMP): PD = 1.06; M_n = 920 g mol^{-1}.

DG010. 4-Aminobenzylamine (2.16 g, 17.7 mmol) was added into a solution of G005 (5.5 g, 8 mmol) in dry DMF (40 mL) at room temperature (20−25 °C) under N_2. After 30 min, DG005 had been consumed [TLC; EtOAc/*n*-hexane, 2:3 (v/v)]. The solution was poured slowly into water (900 mL) and then the precipitate was filtered off and dried at 80 °C under vacuum to give G010 (6.87 g, 92%). Mp: 203−204 °C. FT-IR(cm^{-1}): 3330 (−NH stretch of amides), 1652 (−C═O of amide groups). ^{1}H NMR (200 MHz, DMSO-d_6, δ): 0.67 (t, 12H, CH_3), 1.93 (q, 8H, CH_2), 3.88 (s, 2H, $ArCH_2Ar$), 4.17 (d, 4H, CH_2), 4.92 (s, 4H, NH_2), 6.45 (d, 4H, ArH), 6.92 (d, 4H, ArH), 7.17 (d, 4H, ArH), 7.67 (4H, ArH), 7.74 (4H, ArH), 7.92 (4H, ArH), 8.45 (t, 2H, NH), 10.09 (s, 2H, NH), 10.77 (s, 2H, NH). Anal. Calcd for $C_{55}H_{60}N_8O_6$: C, 71.10; H, 6.51; N, 12.06. Found: C, 71.06; H, 5.96; N, 11.93. EIMS: calcd, *m*/*z* 928.5; found, 929. GPC (NMP): PD = 1.10; M_n = 2070 g mol^{-1}.

DG015. $SOCl_2$ (9.11 g, 76.6 mmol) was added to a suspension of 4-(3,3-diethyl-2,4-dioxoazetidin-1-yl)benzoic acid (2.00 g, 7.70 mmol) in cyclohexane (15 mL) at 60 °C under N_2. After 2 h, a homogeneous solution had formed, with all of the starting material having disappeared [TLC; EtOAc/*n*-hexane, 1:4 (v/v)]. The solvents were evaporated to provide a solid product (2.14 g), which was collected and dissolved in dry methyl ethyl ketone (35 mL). A solution of DG010 (2.77 g, 3.00 mmol) and Et_3N (1.55 g, 15.3 mmol) in dry methyl ethyl ketone (40 mL) was added slowly (overnight) into the former solution at 0 °C. The precipitated salts were filtered off and the solvent evaporated; the residue (4.31 g) was added into EtOH (200 mL) to remove impurities. The solid was collected and dried at 60 °C under vacuum for 6 h to provide DG015 (3.83 g, 91%). Mp 184−185 °C. FT-IR (cm^{-1}): 3330 (−NH stretch of amides), 1870 and 1742 (stretching vibration of −C═O of azetidine-2,4-diones), 1650 (−C═O of amide groups). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 0.73 (t, 12H, CH_3), 0.98 (t, 12H, CH_3), 1.84 (q, 8H, CH_2), 1.99 (q, CH_2), 3.88 (s, 2H, $ArCH_2Ar$), 4.34 (d, 4H, CH_2), 7.20 (d, 4H, ArH), 7.28 (d, 4H, ArH), 7.67 (4H, ArH), 7.70 (4H, ArH), 7.79 (4H, ArH), 7.86 (4H, ArH), 7.96 (4H, ArH), 8.10 (4H, ArH), 8.60 (t, 2H, NH), 10.08 (s, 2H, NHCO), 10.27 (s, 2H, ArNH), 10.58 (s, 2H, NHCO). Anal. Calcd for $C_{83}H_{86}N_{10}O_{12}$: C, 70.42; H, 6.12; N, 9.89. Found: C, 70.05; H, 5.63; N, 9.98. EIMS: calcd, *m*/*z* 1414.5; found, 1415. GPC (NMP): PD = 1.11; M_n = 2490 g mol^{-1}.

More information on preparation and characterizations for difunctional extenders from **DG020** to **DG030** were presented in the Supporting Information.

MHB PUs. MHB PUs were prepared from NCO prepolymers that had been end-capped with monoamine extenders (MG series) at both ends. PUs of the same molar ratio were prepared from the same batch of prepolymers to obtain consistent molecular weights. A general procedure for preparing NCO prepolymers is described below. The reaction was conducted under a dry N_2 atmosphere in a three-neck, round-bottom flask equipped with a magnetic stirrer, a snake-shaped condenser, and a thermometer. The NCO prepolymer (20 wt % THF solution) was prepared by reacting 4,4′-MDI (9.7 g, 39 mmol) with PTMO 2000 (40 g, 19 mmol) in the presence of di-*n*-butyltin dilaurate (T-12) at 60 °C for 2 h. The reactions were monitored for the disappearance of the diol OH groups (3333 cm^{-1}). In each case, a stoichiometric amount of extenders dissolved in DMF (5 mL) was added into the NCO prepolymer solution (9.3 g) and vigorously stirred at room temperature for at least 30 min to ensure complete consumption of the isocyanate. The resulting solution was cooled and then poured into a Teflon mold to form polymer films for testing. NCO prepolymers that had been capped with stoichiometric amounts of aniline were prepared for comparison. Table 1 lists the molar ratios used in each case, with detailed reaction conditions.

Table 1. Compositions of MHB PUs with MG Series Extenders as End-Capping Agents

		4,4′-MDI/PTMO/MG		
PU	extender	molar ratio	feed (g)	hard-segment content (%)
M1	aniline	2/1/2	0.36/1.5/0.136	25
M2		3/2/2	0.27/1.5/0.068	18
M3		4/3/2	0.24/1.5/0.045	16
M4	MG010	2/1/2	0.36/1.5/0.668	41
M5		3/2/2	0.27/1.5/0.334	29
M6		4/3/2	0.24/1.5/0.223	24
M7	MG020	2/1/2	0.36/1.5/1.20	51
M8		3/2/2	0.27/1.5/0.60	37
M9		4/3/2	0.24/1.5/0.40	30
M10	MG030	2/1/2	0.36/1.5/1.73	58
M11		3/2/2	0.27/1.5/0.866	43
M12		4/3/2	0.24/1.5/0.578	35

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Elastomeric PUs. Thermal elastomeric PUs were prepared from NCO prepolymers that had been extended with diamine extenders (DG series). A general procedure for preparing the NCO prepolymers is described below. The reaction was conducted under dry N_2 in a three-neck, round-bottom flask equipped with a mechanical stirrer, a snake-shaped condenser, and a thermometer. The NCO prepolymer (20 wt % in toluene) was prepared by reacting 4,4′-MDI (12.97 g) with PTMO 2000 (70.01 g) in the presence of T-12 in dry toluene (34.48 g) at 80 °C for 2.5 h. The reaction was monitored for the disappearance of the diol OH groups. The isocyanate-equivalent weights of the NCO prepolymers (2441.86) was determined through isocyanate titration. A calculated amount of 1,4-butanediol, DG010, DG020, or DG030 dissolved in DMAc (10 g) was added into the prepolymer mixture at 80 °C. When rod-climbing occurred, the mechanical stirring was stopped and postcuring was performed at 100 °C for 3 h. PUs having the same molar ratio were prepared from the same batch of prepolymers to obtain consistent molecular weights.

To obtain a hard-segment content at 35 wt %, NCO prepolymers were prepared at four NCO/OH molar ratios and reacted with the DG extenders; Table 2 lists their recipes. The NCO prepolymers that had been reacted with stoichiometric amounts of 1,4-butanediol were prepared for comparison.

Table 2. Compositions of the Thermal Elastomeric PUs with DG Series Extenders

		4,4′-MDI/PTMO/extender (DG)		
PU	extender	molar ratio	feed (g)	hard-segment content (%)
D1	1,4-butanediol	1.52/1/0.44	3.70/20.00/0.53	17
D2	DG010		0.37/2.00/0.43	28
D3	DG020		0.37/2.00/0.77	35
D4	DG030		0.37/2.00/1.10	41
D5	1,4-butanediol	3.45/1/2.29	8.42/20.03/2.47	34
D6	DG010	1.81/1/0.72	0.45/2.06/0.66	35
D7	DG030	1.40/1/0.33	0.35/2.01/0.79	35

RESULTS AND DISCUSSION

Synthesis of the Building Block DEDA-BC. Pure crystalline DEDA-BC was synthesized from 4-isocyanatobenzoyl chloride and diethyl ketene, through a ketene/isocyanate cycloaddition, in 45% yield (Scheme 1b, route B). Because the acid chloride group was highly sensitive to moisture, a portion of the DEDA-BC molecules formed anhydride derivatives as soon as they had been prepared. The best procedure to avoid byproduct formation was for the crude, freshly prepared DEDA-BC to be dissolved in cyclohexane and reacted directly with aniline to form the amide derivative, named herein as MG005, in 98% yield.

In an alternative synthetic approach, we prepared DEDA-BC in three steps from readily available *p*-tolyl isocyanate (Scheme 1a, route A). In this alternative, but a longer synthesis, *p*-tolyl isocyanate was first converted into 3,3-diethyl-1-*p*-tolylazetidine-2,4-dione through cycloaddition of diethyl ketene. When compared with the reactivity of the isocyanate unit of 4-isocyanatobenzoyl chloride, that of *p*-tolyl isocyanate is much lower, due to the electron donating effect of the methyl group in the para-position. The yield of the cycloadduct could be enhanced to 81% by using xylene as the solvent and raising the reaction temperature to 130 °C. In the subsequent reaction, the autoxidation of the methyl group in 3,3-diethyl-1-*p*-tolylazetidine-2,4-dione was performed for 8 h at 115 °C in an AcOH solution under O_2 at atmospheric pressure, with $Co(OAc)_2$ and $Mn(OAc)_2$ as cocatalysts. The oxidation product, 4-(3,3-diethyl-2,4-dioxoazetidin-1-yl)benzoic acid, was readily isolated from the solution in 83% yield after recrystallization. This autoxidation procedure has been practiced in our group previously as a means of obtaining aromatic acids, ketones, and anhydrides.[30]

The carboxylic acid unit in 4-(3,3-diethyl-2,4-dioxoazetidin-1-yl)benzoic acid was further converted into an acid chloride moiety through treatment with $SOCl_2$ in cyclohexane under reflux for 2 h. After evaporation of the solvent and excess $SOCl_2$, we dissolved the crude DEDA-BC in dry methyl ethyl ketone to avoid contact with moisture from the air. The resulting solution containing DEDA-BC was added rapidly into an ice bath−cooled methyl ethyl ketone solution containing 4,4′-MDA and Et_3N, to form the amide derivative DG005. The yield of DG005 for the two-step reaction was generally high (>83%) after purification. In summary, the building block DEDA-BC synthesis through route A involved more steps than that through route B, but it provided a higher total yield (ca. 57%; cf. ca. 45%).

Table 3. Characterization of the MG (Monoamine) and DG (Diamine) Series of Extenders

	yield (%)	melting point (°C)	$T_{m,onset}$[a] (°C)	ΔH_m (mJ mg^{-1})	T_g[b] (°C)	T_d (°C)	M_n[c] (g mol^{-1})	M_n[d] (g mol^{-1})	PD
Monoamine Extenders									
MG005	98	163−167	165	115.3	–	275	336	1680	1.01
MG010	91	212−218	216	148.3	71	338	458	4020	1.01
MG015	96	258−263	260	117.6	121	311	701	6480	1.01
MG020	94	100−111[e]	–	–	112	341	823	4140	1.02
MG025	77	273−277	259	98.4	150	326	1067	6560	1.02
MG030	92	151−158[e]	–	–	137	345	1189	8580	1.02
Diamine Extenders									
DG005	83	163−163	167	50.5	98	321	684	920	1.06
DG010	92	203−204[e]	–	–	89	336	929	2070	1.10
DG015	91	184−185	176	14.9	143	325	1415	2490	1.11
DG020	90	169−177[e]	–	–	135	353	1659	3830	1.12
DG025	84	207−209	184	17.8	156	331	2145	4250	1.12
DG030	91	181−182[e]	–	–	158	356	2389	5470	1.12

[a]DSC, first heating run. [b]DSC, second heating run. [c]Theoretical molecular weights. [d]GPC: MG005−MG030, DMF; DG005−DG030, NMP. [e]Obscured mp.

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Synthesis of MHB Monoamine Extenders with Precise Hard-Segments. We synthesized well-defined mono- and difunctional amine extenders, the MG and DG series, through iterative syntheses using DEDA-BC and 4-aminobenzylamine as the building blocks. The main difference was in the first step, where the monoamine extenders employed aniline as the starting material and the diamine extenders used 4,4′-MDA (Figure 1). In the iterative syntheses, the highly reactive acid chloride unit of DEDA-BC was first reacted with aniline or 4,4′-MDA to form the first generation of azetidien-2,4-dione intermediates, which were then reacted with 4-aminobenzylamine, at the more-selective azetidine-2,4-dione groups, to form the first generation of benzylamine extenders. With this alternating method, we systematically prepared supramolecular extenders with various chain lengths (n = 1−3) in high yields, without the need for tedious purification steps, and under catalyst-free conditions. Because all of the reactions were simple repetitive addition reactions, these syntheses were straightforward and efficient. Notably, this strategy could be performed without the need for protection and deprotection steps. We purified the extenders prepared using our iterative-synthesis strategy simply through precipitation or recrystallization, without resorting to column chromatography. We characterized all off the extenders and intermediates in terms of their melting points, their FTIR, NMR, and mass spectra, and their elementary analyses (see the Experimental Section and Supporting Data). For the purpose of illustration, we analyzed the chemical structure of the MG030 extender from its 600 MHz ^{1}H NMR spectrum (DMSO-d_6), which is presented in Figure S2a (Supporting Information) along with proton-by-proton assignments. Table 3 lists the yields and physical properties of these compounds. Theoretically, the molar mass increases between each generation would be 365 and 730 g mol^{-1} for the monoamine and diamine extender series, respectively.

We used GPC to confirm the consistent chain lengths of the amine extenders and the generations of azetidine-2,4-dione intermediates. The three monoamine extenders MG010−MG030 and their corresponding azetidine-2,4-dione intermediates MG005−MG025 all exhibited well-defined monodisperse structures in their GPC traces. The monodisperse peaks, each with a low PD of 1.01−1.02, indicated that these monoamine extenders possessed narrow molecular weight distributions (Figure 2a). In addition, the mass spectral data for the extenders matched their structural assignments. Therefore, we have successfully developed a basic strategy of iterative synthesis for the systematic preparation of monodisperse supramolecular extenders. It is important to note that similar retention times of MG010 and MG020 were observed in GPC results (Figure 2a). One possible explanation for this elution behavior is that two repeating units of MG020 might spontaneously fold up via strong intramolecular H-bonding interaction, resulting in same hydrodynamic volume shape when MG020 was dissolved in DMF.[24,30] Similar phenomenon was also observed for the monoamine extenders of MG015 and MG025 (Figure 2a). The key feature of our iterative synthesis lies in its dual-functional intermediates, possessing a highly reactive group and a highly selective group, that can allow the stepwise and alternating assembly of the molecular structure. The iterative synthesis is rapid and efficient, with simple purification of both the intermediates and final products, and little byproduct formation. Furthermore, we found that the building block DEDA-BC is superior to IDD, which we had used previously (PDs: 1.07−1.29)[24] for the systematic preparation of well-defined monoamine extenders through a similar iterative synthesis approach.

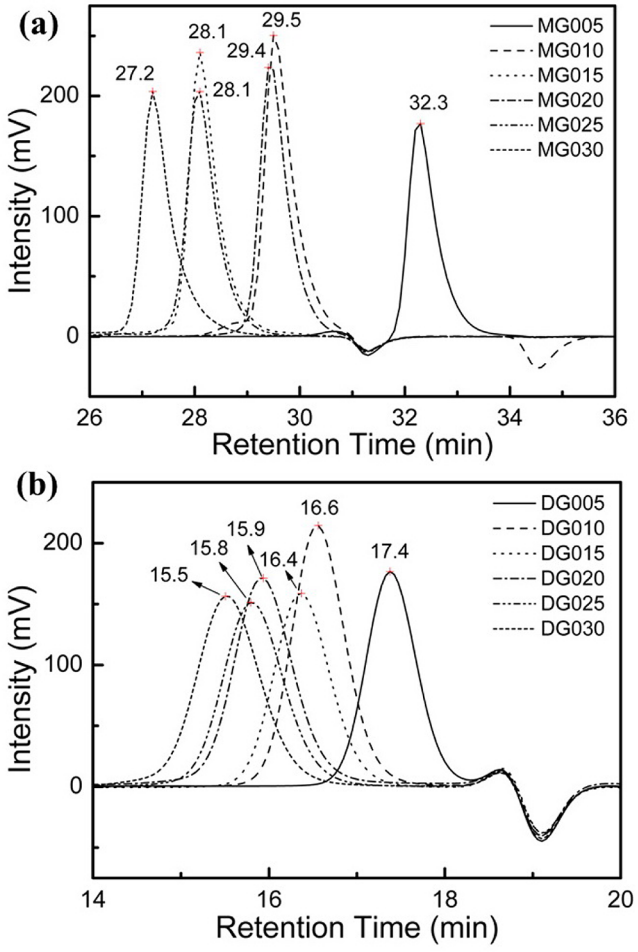

Figure 2. GPC traces of the prepared monoamine MG series of extenders and of the diamine extender DG030.

Properties of MHB Hard-Segment Monoamine Extenders. TGA data revealed that all of the prepared extenders and intermediates possess remarkable thermal stability. As listed in Table 3, the decomposition (5% weight loss) temperatures (T_d) of all of the intermediates were greater than 311 °C. The value of T_d of MG030, the longest monoamine extender, was 345 °C, the highest among the MG series. A clear trend existed in that the thermal stabilities of the monoamine extenders MG010−MG030 were greater than those of the corresponding azetidine-2,4-dione intermediates MG005−MG025. Furthermore, a similar trend existed among intermediates from the same series: the value of T_d increased upon increasing the chain length. These results suggest that the thermal properties of the extenders were enhanced significantly upon increasing the chain length of the hard segment, presumably through increased supramolecular interactions.

In Table 3, the melting points measured using DSC match perfectly with those observed from the melting point apparatus, except for those of MG020 and MG030. Interestingly, we could not observe clear melting points for MG020 and MG030 when using the melting point apparatus, consistent with the broad endothermal signals observed below 120 °C in their DSC traces. These unusual endothermal phenomena for MG020 and MG030 were presumably due to gradual dissociation of the

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inter- and intramolecular hydrogen bonds—resulting from the amine and amide groups along their respective long chains—in these temperature ranges.[31,32] In addition, the crystallinity and enthalpy observed through DSC analyses appeared to decrease upon increasing the chain length. As one might expect, longer molecular chains have greater difficulty at packing in an orderly and consistent manner, as would be the case for MG020 and MG030.

Gelation of MHB Hard-Segment Monoamine Extenders. We employed WAXS to investigate the crystalline morphology of the prepared monoamine extenders and azetidine-2,4-dione intermediates. Figure 3 reveals no obvious

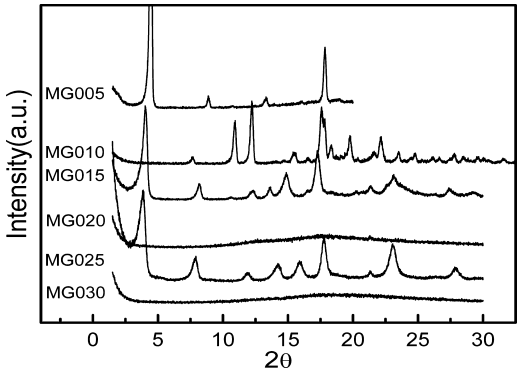

Figure 3. WAXS patterns of the MG series of extenders.

signals for MG020 and MG030 (amorphous), consistent with the data collected from the DSC and melting point analyses. In contrast, clear WAXS patterns existed for all of the other monoamine extenders and azetidine-2,4-dione intermediates. Similar to our findings in a previous study,[24] these low-molecular-weight extenders displayed distinct glass transitions during their second scans (Table 3). The glass transition behavior of these extenders appeared to resemble those of long-chain polymers, suggesting that the prepared extenders possessed supramolecular performance. Thus, we can consider the monoamine extenders to be "pseudo-polymers." The variations in the glass transition temperature might also have been due to different degrees of hydrogen bonding, which would have differed from the short amine chain in MG010 to the long amine chains in MG020 and MG030.

To obtain evidence for the association capability of the prepared monoamine extenders through their MHB sites, we performed a simple gelation test using THF as the solvent. Here, we dissolved the monoamine extenders and azetidine-2,4-dione intermediates in THF at room temperature and adjusted the concentration to less than 15 wt %. The gelation behavior of the extenders MG020 and MG030 in THF was particularly noteworthy. The solution of MG030 in THF at a dilute concentration of 3 wt % gelled after 60 min (inset to Figure 4, right-hand image), whereas it took just 10 min to gel at a concentration of 6.4 wt %. Gelation also occurred, after 2 days, for the solution of MG020 in THF at 5.9 wt %. The gelation ability increased upon increasing the chain length. The gels presumably formed as a result of trapping of the solvent in the 3D hydrogen-bonded networks formed by the amine extenders. The gelation phenomena, which could be switched through variations in temperature, appeared to be related to structural effects, particularly to the number of the hydrogen bonding sites resulting from the presence of amide and malonamide groups in the main chains. The numbers of such hydrogen

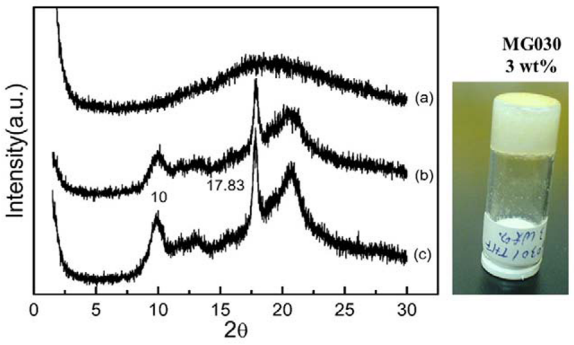

Figure 4. Photographs of the organogels and WAXS patterns of the MG030 extender (a) before and (b, c) after gelation at (b) 3 and (c) 6.4 wt %.

bonding sites in MG010, MG020, and MG030 were 6, 12, and 18, respectively. Increasing the degree of hydrogen bonding would presumably have a major effect on the gelation capabilities of these species. Because there are also many aromatic rings in these molecular chains, the secondary effects of $\pi-\pi$ stacking should also be taken into account, albeit as a minor factor.

We used WXRD spectroscopy to further characterize the self-assembled structures formed by the powders obtained after slow evaporation of THF gels (Figure 4). Dramatic differences appeared in the WXRD patterns before and after gelation. We observed crystalline patterns for the MG030 gel powder, indicating that the gelation procedure enhanced the self-organization of MG030 to form ordered structures. Similar results have been reported previously for hydrogen bond–rich urea, amide, and carboxylic acid derivatives; their XRD patterns also provided evidence for regular 2D molecular packing in the organogel state.[33−36] The DSC first-heating endothermal signals of the organogel powders were narrower than those of their original samples, becoming two glass transitions in their second-heating curves. This finding confirms that well-ordered structures had assembled after gelation. We suspect that time- and concentration-dependent structural arrangements formed after gelation of the amorphous monoamine extenders.

Preparation of MHB-Terminated PUs. We prepared the targeted MHB PU samples by attaching monoamine extenders with precise chain lengths to both ends of the NCO prepolymers. Table 1 lists their resulting formulations; Table 4 provides their characterization data. All the members of the PU M series had close molecular weights, in the range 24000–43000 g mol^{-1}; because they were produced from prepolymers with the same molecular weight, their different physical properties could have resulted only from differences in the lengths of their hard segments. Because these hard segments had precise chain lengths, but different numbers of polar amide sites, their polarities and degrees of noncovalent interactions would differ among the series and from those of the soft segments, which consisted of long-chain polyethers. Thus, the PU M-series constructed from hard and soft segments could essentially be considered as psudo-segmented PU elastomers, except that their molecular weights and some amide-linkages were not equal to those of traditional PUs. The PUs M1–M6, end-capped with aniline and MG010, were tacky-liquid polymers; similar to their low molecular weight preopolymers, they did not form films and we did not examine their thermal and mechanical properties.[37] Notably, however, the incorpo-

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Table 4. Characterization of the Prepared MHB PUs (M Series)[a]

PU	tensile strength (MPa)	elongation (%)	T_{gS} (°C)	T_{gH} (°C)	T_m (°C)	ΔH_m (mJ mg^{-1})	T_d (°C)	M_n (g mol^{-1})	PD
M7	5	22	−72	–	14	10.5	302	24 350	1.29
M8	0.7	211	−71	–	17	29.8	318	29 230	1.26
M9	0.8	430	–	–	20	42.9	316	43 650	1.31
M10	11	88	−61	130	16	14.5	297	31 170	1.24
M11	9	418	−72	139	14	19.6	321	34 920	1.22
M12	16	851	–	157	20	42.1	318	38 600	1.29

[a]PUs M1−M6, as tacky liquids, did not form films and were not subjected to DSC analysis. Molecular weights and PDs: M1, 14,765 and 1.67; M2, 22,715 and 1.48; M3, 31,228 and 1.46; M4, 20,210 and 1.46; M5, 25,489 and 1.38; M6, 31,830 and 1.42.

ration of MG020 and MG030 hard-segment end groups had a dramatic effect on the physical properties of the bulk materials M7−M12, transforming the viscous PUs into elastomers that exhibited highly temperature-dependent characteristics.

Among the stress−strain curves (Figure 5), PU M12 displayed particularly soft and tough characteristics, with PU

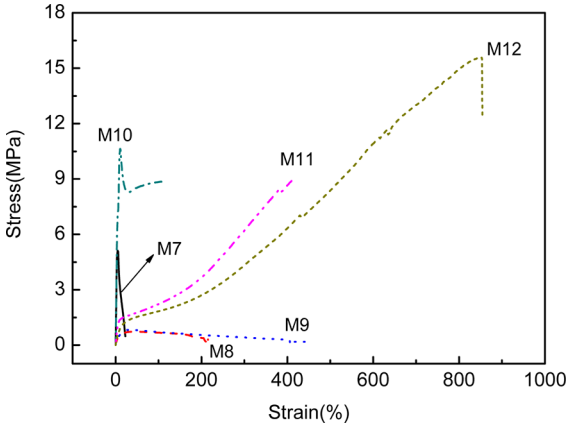

Figure 5. Stress−strain curves of the end-capped PUs M7−M12.

M10 exhibiting hard and strong characteristics (e.g., a Young's modulus of 1 MPa). The mechanical properties of PU M12 were clearly superior to those of other members of this series. The mechanical properties of the prepared PUs M10−M12 were also superior to those of PUs M7−M9. Thus, the mechanical properties of these PUs were greatly influenced by the composition, especially the length of the hard segment and the overall chain length. We attribute the superior performance of PU M12 to the increase in the total number of hydrogen bonding sites in the hard-segment portions of the monoamine extenders from 24 in PUs M7−M9 to 36 in PUs M10−M12. Furthermore, these hydrogen bonding sites formed physical interchain 3D networks within the supramolecular structures. Thus, the degree of physical cross-linking in PUs M10−M12 was also higher than that in PUs M7−M9. As a result, the hard segment having a molecular weight of 1188 g mol^{-1} (MG030, third generation) provided PUs with optimized mechanical properties. In a prior study, we found that the optimal composition, with respect to the phase-segregation morphology and mechanical strength, was that of a second-generation supramolecular extender (having a molecular weight of 1047 g mol^{-1}) coupled with an MDI/PTMO prepolymer having a molecular weight of 30,000 g mol^{-1}.[24] Recent reports have indicated that functionalization of the ends of PU oligomers with MHB groups can greatly enhance their physical properties.[5,8,21,24]

Thermal Properties and Thermoreversible Behavior of MHB-Terminated PUs. The TGA data of the MHB-terminated PUs (Table 4) revealed that they could be distinguished from conventional PUs in terms of their remarkable thermal stabilities. The values of T_d of the measured PUs were approximately 300 °C. The value of T_d of PU M11 (321 °C) was the highest in this series. In general, PUs are unstable at temperatures greater than 230 °C because of urethane bond decomposition and trans-urethane reaction, whereas amide-interchange reactions are rare at such temperatures. Thus, our amide-modified MHB PUs enhanced the thermal stability of the PUs. By introducing MHB-rich chain extenders, the value of ΔH_m of the PU decreased depending on decreasing the hard-segment content. With increasing generations and longer hard segments, the measured values of T_{gH} became clear. The values of T_{gH} increased from 130 to 157 °C

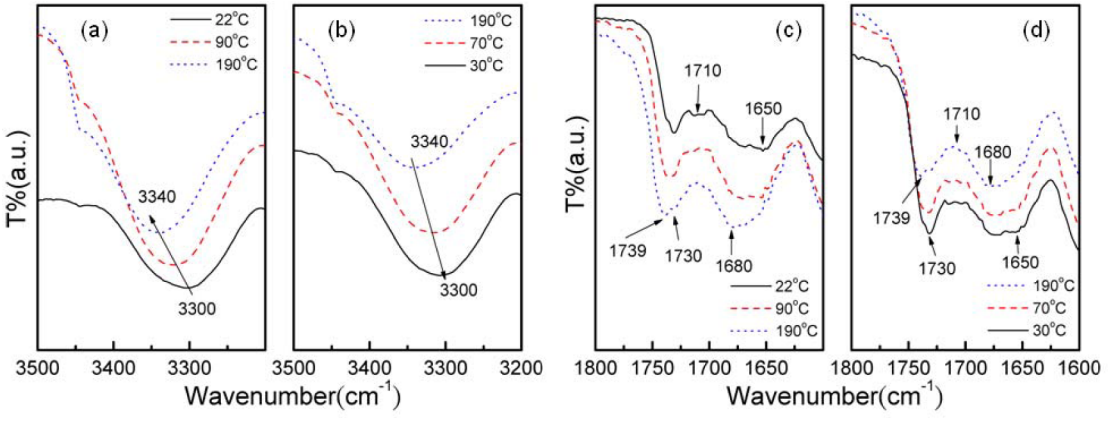

Figure 6. Variable-temperature FTIR spectra of the PU M12 after (a, c) heating and (b, d) cooling processes.

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(from M10 to M12) upon increasing the molecular weight from 31170 to 38600 g mol^{-1}. Thus, a longer MHB hard segment resulted in greater segregation of the phases of the hard and soft domains in the PUs.

We studied the thermo-reversibility behavior of the MHB PUs in terms of changes in the intensity and shifts in wavelength of the signals in their variable-temperature FTIR spectra. The signals for the N−H and C═O bonds of the malonamide and urethane groups underwent the most obvious changes upon changing the temperature. The formation and breaking of inter- and intrapolymer hydrogen bonds could be monitored during the thermal heating and cooling cycles. For example, upon increasing the sample temperature from room temperature to 190 °C, the characteristic signal for the N−H bonds, initially located at 3300 cm^{-1}, shifted gradually to 3340 cm^{-1} (see arrow in Figure 6a). Conversely, the signal at 3340 cm^{-1} for the N−H bonds at 190 °C gradually returned to 3300 cm^{-1} (Figure 6b) upon cooling of the sample to ambient temperature. Thus, extensive hydrogen bonding between polymer chains was evident at room temperature, but it gradually weakened upon elevating the temperature. Similarly, the characteristic absorptions of the C═O groups of the urethane and malonamide units in the prepared PUs also exhibited reversible phenomena, as indicated by the arrows in Figure 6, parts c and d. From the behavior of the signal at 1710 cm^{-1} for the hydrogen-bonded C═O groups, we hypothesize that physical cross-linking network of hydrogen bonds disappeared upon heating to approximately 90 °C, but it reappeared after cooling to below 70 °C. As evidenced from the variable-temperature FTIR spectra, our PUs displayed optimal mechanical and physical properties at ambient temperature because they featured a high density of physically cross-linked networks formed through hydrogen bonding.

Morphologies of MHB-Terminated PUs. To better differentiate the morphologies and performances of the PUs with respect to their monoamine extenders, we used SAXS to analyze their well-defined phase-segregated microdomains. The SAXS patterns in Figure 7 reveal that well-ordered hard domains existed in the prepared PUs. Using the equation

$$d = 2\pi/q$$

for lamellar structures as our basis, the average interdomain spacings in all of our prepared PUs were in the range 38−48 nm. These values appear to be related to the precise chain lengths of the hard segments used to prepare the end-capped PUs, and are consistent with our previous findings.[21,22,24] Incidentally, the intensities of the signals in SAXS patterns are often related to the degrees of ordering of the structures in the materials. Thus, the intensities of the signals for PUs M10−M12 were greater than those for PUs M8−M9, except for PU M7; again, this result implies that the hard segment having a molecular weight of 1188 g mol^{-1} had the critical length required for a well-ordered morphology in the prepared PUs. These results suggest that weak noncovalent interactions can be utilized to afford a range of self-assembled PU-based materials with various morphologies.

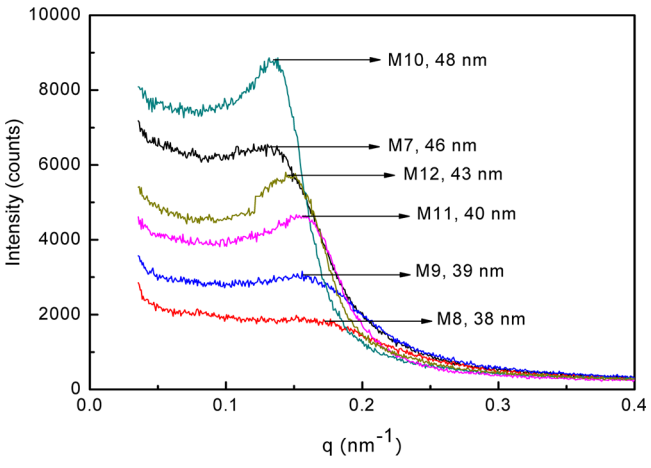

Figure 7. SAXS patterns of the end-capped PUs M7−M12 at room temperature.

Synthesis of Diamine Extenders With Precision Chain Length. We prepared extenders DG010−DG030 with difunctional groups, and their respective thermal elastomeric PUs, to address the more-practical aspects of PU formulation. The diamine extenders with precise chain lengths were also prepared from DEDA-BC and 4,4′-MDA as starting materials, again using an iterative approach. We used these diamine extenders to form thermal elastomeric PUs, for which we then determined structure−property relationships, especially those related to the chain length of the hard segments.

Using NMP as the eluting solvent, GPC analysis of the diamine extenders revealed a narrow molecular weight distribution, within the range 1.06−1.12 (Figure 2b). The molecular weight distributions of the diamine extenders were slightly broader than those for the corresponding monoamines, most likely because of the different eluents that we used and the large differences in molecular mass. Nevertheless, the precision and consistency of the chain lengths in the DG series was confirmed through elemental analysis and MALDI−TOF mass spectrometry. For instance, a signal appeared at m/z 2412 [M + Na]$^+$ in the MALDI−TOF mass spectrum of the extender DG030, close to the theoretical value of m/z 2389 (Figure S3b, Supporting Information).

Properties of Diamine Extenders with Precise Chain Lengths. In Table 3, both of monoamine MG and diamine DG series of extenders exhibit similar trends in their thermal stabilities: with increasing chain length, the decomposition temperatures increased. The value of T_d of DG030 (356 °C) was the highest among the DG series; it was also higher than that of the corresponding monoamine MG030 extender (345 °C). Thus, the thermal stability of the MG- and DG-series of extenders was dependent on their chain lengths as well as the number of malonamide and amide units, with DG030 having the highest molecular weight (2389 g mol^{-1}) and greatest number of hydrogen bonding sites (36). The DSC first-heating curves for DG010, DG020, and DG030 were similar to those of the corresponding monoamine extenders, with the endothermal peaks for DG005, DG015, and DG025 broadening upon increasing the chain length. As was the case with the M-series, we could not detect clear melting points for DG010, DG020, and DG030 in the melting point apparatus, whereas those of DG005 (167 °C), DG015 (177 °C), and DG025 (184 °C) exhibited an increasing trend. Because of the gradual dissociation of hydrogen bonds, the crystallinity and enthalpy, observed through DSC analyses, appeared to decrease upon increasing the chain length. The values of ΔH_m of the DG series were lower than those of the MG series. A comparison of the properties of the DG and MG series of extenders revealed that the magnitude of the generation-to-generation variation in the DG series was less dramatic than that in the MG series.

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Table 5. Characterization of the Prepared Thermal Elastomeric PUs (D Series)

PU	tensile strength (MPa)	elongation (%)	T_{gS} (°C)	T_{gH} (°C)	T_c (°C)	ΔH_c (mJ mg^{-1})	T_m (°C)	ΔH_m (mJ mg^{-1})	T_d (°C)	M_n (g mol^{-1})	PD
D1[a]	–	–	−66	–	–	–	18	17.2	279	24 860	2.11
D2	29	734	−61	112	−9	−48.2	18	47.5	303	21 860	2.86
D3	25	378	−62	128	−4	−44.1	19	45.1	284	23 880	2.53
D4	9	231	−63	170	−20	−22.3	19	32.7	297	29 400	2.36
D5	6	350	−58	–	−12	−28.5	21	26.8	298	15 880	2.43
D6	59	411	−52	149	−9	−45.6	20	42.4	322	31 550	1.95
D7	8	342	−61	165	−11	−38.9	19	39.6	316	17 440	1.81

[a]PU D1 was a tacky liquid that did not form films and was not subjected to mechanical testing.

Thus, the behavior of the DG and MG series of extenders was dependent on their molecular chain lengths as well as their numbers of malonamide and amide units. Moreover, the values of T_g and T_d for the MG and DG series of extenders did not increase limitlessly upon lengthening their chain lengths. It appears that the highest values of T_g (158 °C) and T_d (356 °C) for the extender DG030 were almost the maximum possible values for such malonamide/amide chain materials.

Preparation of Thermal Elastomeric PUs. Using a strategy and procedures similar to those described for the monoamines, we prepared conventional thermal elastomeric PUs from the diamine extenders. The NCO prepolymer was prepared as a general batch and then it was reacted individually with the extenders DG010, DG020, and DG030. Table 2 reveals that the reactions of a fixed NCO prepolymer with extenders of different chain lengths provided systems D1−D4 with a great variation in hard-segment contents from 17 to 41 wt %. For comparison, we prepared PUs with a hard-segment content controlled at 35 wt % using the three DG series of extenders and 1,4-butanediol (D3 and D5−D7).

Thermal Properties of Thermal Elastomeric PUs. Table 5 reveals that the PUs D1−D4 prepared from the same batch of NCO prepolymer had closely matching melting points of approximately 18 °C, with thermo-stabilities lying closely between 279 and 303 °C. There were no dramatic differences in the glass transition temperatures for their PTMO segments (T_{gS}), which were observed near −62 °C. The glass transitions for their hard segments (T_{gH}), however, varied considerably, with values of 112, 128, and 170 °C for D2, D3, and D4, respectively. The values of T_{gH} of the control polymers prepared using 1,4-butanediol as an extender were not clear for D1 and D5. Furthermore, the values of ΔH_m of these PUs chain-extended with diamines of precise chain length were larger than that of the system chain-extended with 1,4-butanediol. Thus, the great increase in chain length in each generation significantly increased the value of T_{gH} of the PU. Among the systems with a constant hard-segment content of 35% (D3 and D5−D7), the decomposition temperature of PU D6 was the greatest (322 °C), with the glass transition for the hard segments appearing at 149 °C. Thus, the thermostability of the MHB-modified PUs, such as PU D6 and even D7, were superior to those of the 1,4-butanediol−based PU D5 by approximately 20 °C.

Mechanical Properties of Thermal Elastomeric PUs. In Table 5 and Figure 8, for the systems based on the same-length prepolymer, PU D2 exhibited the best elongation (734%) and PU D3 displayed the greatest tensile strength before 400% elongation. Hence, the mechanical properties of the PU D series were greatly influenced by the hard-segment length. With its longer chain extender (DG030) and greater hard-segment

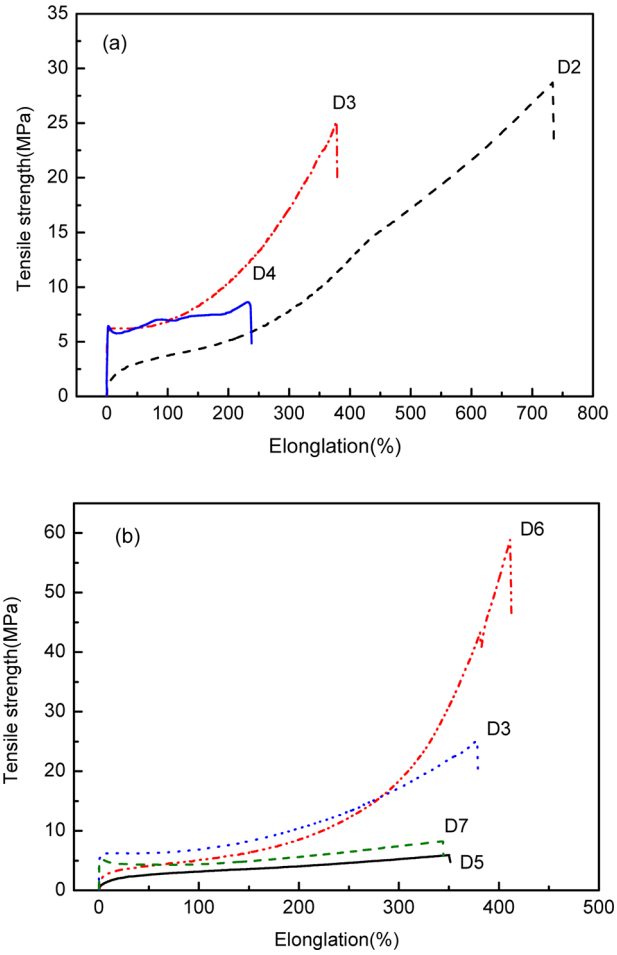

Figure 8. Stress−strain curves of the PU elastomers (a) D2−D4, prepared from the same prepolymer, and (b) D3 and D5−D7, with a hard-segment content of 35%.

content (41%), D4 displayed the same initial tensile strength, but lower elongation (230%). In the stress−strain curves, the PUs D2 and D6 chain-extended with DG010 displayed good elongation; the PUs D3, D4, and D7 displayed high stiff yield points, with Young's moduli of 1 MPa. Upon increasing the length of the hard segment, the mechanical behavior of the PU transformed from that of a ductile elastomer to that of a stiff plastic. Among all of the samples featuring a hard-segment content of 35%, PU D6 had the highest tensile strength (59 MPa), presumably because it featured the most suitable hard-segment length and was the PU with the highest molecular weight. We conclude that DG010, having a molecular weight of 928 g mol^{-1}, was the optimal extender for the D series. Thus,

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the critical hard-segment length in the PU chain appears to be approximately 1428 g mol^{-1}, a result of the combination of two 4,4′-MDI units and one DG010 moiety. A longer chain length did not improve the overall mechanical properties of the PU. In general, crystalline and rigid hard segments provide PUs with greater stiffness. The PUs extended with DG010 (M2, M4) displayed the largest enthalpies (ΔH_c and ΔH_m in Table 5), implying that DG010 possessed the optimal crystalline characteristics. The crystalline structures of the hard segments were not readily formed in the PUs when the hard segments became too long. Conversely, when the length of the hard segment was too short, the total number of available hydrogen bonding sites was too low for noncovalent association.[15] Therefore, this study revealed the optimal chain length of the hard segment in PU elastomers.

CONCLUSION

We have synthesized DEDA-BC, a dual-functional building block that possesses a highly reactive acid chloride unit and a highly selective azetidine-2,4-dione group in the same molecule, both (i) indirectly from *p*-tolyl isocyanate and (ii) directly from 4-isocyanatobenzoyl chloride. By starting with the monoamine aniline or the diamine 4,4′-MDA, we used an alternating step-by-step approach to build, at room temperature under catalyst-free conditions, six new supramolecular extenders of various chain lengths (n = 1−3), without the need for tedious purification. We prepared these supramolecular extenders with mono- and di-functional benzylamine end groups in high yield (77−98%). These prepared extenders, which could take part in multiple hydrogen bonds, displayed narrow monodispersities (1.01−1.12), as determined using GPC. The thermal stabilities, transition temperatures, and numbers of hydrogen bonding sites all improved upon increasing the chain lengths of the amine extenders. The gelation behavior of the supramolecular extenders in organic solution, induced by intermolecular hydrogen bonding, was also dependent on the chain lengths. PU elastomers incorporating these extenders exhibited thermoreversible properties, as observed using variable-temperature FTIR spectroscopy. The physically cross-linked networks existing in these PUs disappeared at temperatures above 90 °C, but reappeared upon cooling to below 70 °C. Because they incorporated hard-segment extenders with precise chain lengths, both the MHB-terminated PUs and thermal elastomeric PUs (M_n = 17 000−43 000 g mol^{-1}) prepared in this study possessed excellent thermal stability at temperatures greater than 300 °C. Morphologically, SAXS analysis revealed that the prepared MHB PUs featured well-defined microdomains having an average period of 39−48 nm. The optimal molecular masses of the extenders, confirmed through mechanical testing, were 1188 g mol^{-1} (MG030; n = 3) for the MHB-terminated PUs and 928 g mol^{-1} (DG010; n = 1) for the thermal plastic PUs. Using an efficient and iterative synthetic approach, we have systematically prepared supramolecular extenders with variable, yet precise, hard-segment contents, and then used them to synthesize elastomeric PUs to gain insight into their structure−property relationships, directed by reversible noncovalent interactions. Our study also found that triblock A−B−A PU elastomer systems appears to have a greater propensity to achieve phase-segregation in polymers than those of traditional PU elastomers where hard segments are en-restricted in both ends.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures of difunctional extenders from DG020 to DG030, PU structures, and ^{1}H NMR and MALDI−TOF mass spectra for extenders MG030 and DG030. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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