Iterative Synthesis of Extenders of Uniform Chain Lengths for Making Thermo-Reversible Polyurethane Supramolecules

Ming-Chieh Kuo,[†] Ru-Jong Jeng,[†] Wen-Chiung Su,[‡] and Shenghong A. Dai*,[†]

Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan, and Chung-Shan Institute of Science and Technology, Lungtan, Tauyuan 325, Taiwan

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ABSTRACT: An efficient iterative synthesis was utilized to prepare hard-segment extenders of uniform chain lengths with multiple hydrogen-bonding sites for uses in preparation of supramolecular thermoreversible polyurethanes (TRPUs). The unique feature of our iterative synthesis is based on two alternative addition reactions to a dual-functional intermediate, 4-isocyanato-4′(3,3-diethyl-2,4-dioxoazetidino)diphenylmethane (assigned as [MIA]), where (1) the more reactive isocyanate group of [MIA] was reacted first with anilines or secondary amine group of 1-(2-aminoethyl)piperazine followed by (2) addition of a more reactive primary aliphatic amine group of 1-(2-aminoethyl)piperazine to react with the more selective azetidine-2,4-dione group of the [MIA]. With this iterative synthetic approach, three generations of supramolecular extenders were prepared, and each were added to isocyanate-prepolymers of varied chain lengths to form supramolecular "pseudo-triblock" TRPUs with a similar hard segment content of about 41%. It was found that both supramolecular extenders and their respective TRPUs showed distinctive glass transition temperatures (T_g). Thermal degradation temperatures (T_d) of both TRPUs and extenders increase with increasing hard-segment chain lengths. Different degrees of phase-segregation were present in the synthesized TRPUs and have shown to be enhanced in the same general trend. Investigations by variable-temperature FT-IR and circular scanning treatment of DSC on the TRPU [G2-41] with second generation extenders, between 25 and 180 °C revealed thermal reversibility due to the increasing (at room temperature) and diminishing of hydrogen bonding (at 180 °C) among the multiple hydrogen-bonding hard-segment chains. The results of SAXS analyses of TRPUs with first and second generation extenders further showed that these TRPUs formed self-assembling phase-segregated domains. The TRPU [G2-41] was found to exhibit the most prominent phase-segregation observed by SAXS with formation of uniform hard-segment domains of 40 nm. In the meantime, it also behaves like a polyurethane elastomer with a high elongation of 651% possessing the best mechanical properties found among the series. This study further demonstrated that a structural balance between uniform chain-length hard-segment extenders and their connecting soft segment play a dominant role on performances of "pseudo-triblock" polyurethane systems through molecular self-assembling.

Introduction

In 1966, Cooper and Tobolsky[1] discovered that polyurethane is capable of forming a chain-blocked structure of hard- and soft-segment domains. The hard domains made from polar extenders such as 1,4-butadienediol with 4,4′-methylenebis-(phenyl isocyanate) aggregates via hydrogen-bonding can exhibit higher than expected modulus.[2] Since this initial finding, many studies relating to the hard- and soft-phase segregation phenomenon of polyurethanes and poly(urethane−urea)s have advanced.[3−5] Scientists[6−8] have proposed and prepared segmented polyurethanes via prepolymer-based two-step polymerization procedures, resulting in polyurethanes with narrow polydispersity and enhanced performances. Strong evidence indicates that polydispersity and length of hard segments play significant roles in affecting material properties, including mechanical behaviors and thermal properties[9−13] of polyurethanes due to different morphology formations.[14−18] Further investigation of producing well-defined hard-block domains of polyurethanes has become one of the active studies of polyurethane polymers.[19−20] However, the synthesis of precise hard-segment chain lengths and investigations of the chain-length effect on polyurethane morphologies are still rare due to lack of precise and efficient synthetic methodologies.

Earlier synthetic approaches for producing uniform chain-length hard-segment intermediates have been reported in several studies.[21−25] However, all the methods reported so far have drawbacks. Harthcock[26] and his co-workers had to use a cumbersome gel permeation chromatogram process to isolate individual extenders of uniform chain lengths from a random product mixture. Harrell[21] synthesized monodispersed hard segments with uniform chain length, but these prepared compounds did not possess any multiple hydrogen-bonding sites. Wilkes[19] and his co-workers reported a morphological study on polyurethanes involving only one hard-segment block in the molecular chains. However, their syntheses do not appear to be flexible enough to prepare extenders with twice or multiple chain lengths due to intrinsic limitations. Recently, Sijbesma[22,23] et al. reported successful preparation of segmented poly(ether urea)s with uniform chain-length hard segments, but their systems consisted mainly of aliphatic backbones vastly differing from the majority of polyurethanes made from aromatic diisocyanate and malonamide/(urethane urea) systems in our study.

Nakaname and co-workers[27] found that physical properties of materials reach optimum performance when weight ratio of hard segments/soft segments increases to a specific optimal ratio. Any slight deviation from the optimum ratio causes a significant drop off of the properties enhancement. In other words, outside the precise optimum ratio, the properties of polyurethanes do not necessarily rise as hard-segment content increases. There

* Corresponding author. Telephone: +886-4-22840510 ext 412. Fax: +886-4-22874159. E-mail: shdai@dragon.nchu.edu.tw.
[†] Department of Chemical Engineering, National Chung Hsing University.
[‡] Chung-Shan Institute of Science and Technology.

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have been too few examples in the literature to support this hypothesis.

Supramolecules are the compounds of relatively low molecular weight that are capable of interacting among them to form organized assemblies.[28] Recent literature[30,31] indicates that the self-assembling process is essential to enhance physical properties[32,33] such as mechanical behavior, thermal properties, and T_g.[34] Binder[35] et al. established pseudo-block copolymers which utilized hydrogen-bonding-terminated oligomers. These pseudo-block copolymers were shown to form microdomains through hydrogen bondings, and the degree of the hydrogen-bonding interactions is found to be dependent highly upon temperatures. In our preceding paper on this subject, we disclosed our result on supramolecular polyurethanes with terminal dendritic extenders as means of increase hydrogen-bonding interactions.[36−39] In this paper, we would like to report our study of using [MIA] to prepare well-defined linear hard-segment extenders by iterative synthesis (Figure 1). On the basis of this rather simple yet selective synthetic strategy, the iterative synthesis gave three generations of extenders possessing narrow molecular distributions. These extenders were then utilized in synthesis of TRPUs to gain insight into their structure−property relationship.

Experimental Section

Materials. 4,4′-Methylene-bis(phenyl isocyanate), 2-ethylbutyryl chloride, triethylamine, 1-(2-aminoethyl)piperazine, and aniline were obtained from Acros Organics, and all were used after purification by distillation. PTMO 2000 (with averages of about 27 repeating tetramethylene ether groups) and PTMO 1000 (with averages of about 13 repeating tetramethylene ether groups) are commercial polyether diols of DuPont (Terathane) with an average molecular weight of 2058 g/mol and 969 g/mol, which were calculated based on hydroxyl number of 54.504 and 115.791 respectively (as determined by ASTM D4274 and ASTM E222). Both PTMOs were dried under vacuum at 80 °C for 6 h before use.

Measurements. ^{1}H NMR spectra were taken on a Varian Gemini-200 FT-NMR spectrometer with acetone-d_6 or chloroform-d_1 as the solvent depending on sample's solubility. Thermal analysis of the polymers by differential scanning calorimeter (DSC) was performed under N_2 atmosphere on a Seiko SII model SSC/5200 at a heating and cooling rate of 10 °C/min and was held for 5 and 3 min at +180 and −100 °C, respectively. Thermogravimetry analysis (TGA) was carried out on a Seiko SII model SSC/5200 at a heating rate of 10 °C/min. FT-IR spectra over the range from 4000 to 400 cm^{-1}, were recorded on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer. Calibrations for background absorptions were done by recording the blanked KBr disk initially before scanning each of the samples. Melting points (mp) of the samples were run on a Fargo melting point apparatus MP-2D at a heating rate of 3 °C/min. Gel permeation chromatography (GPC) of polymers and hard-segment extenders prepared in this study were performed by a Waters Apparatus using THF as the eluding solvent. The samples were analyzed through Waters Styragel columns at a flow rate of 1.0 mL/min with polystyrene calibration. Fast atom bombardment (FAB) and electrospray ionization (ESI) mass spectrometry were recorded on a Finnigan/Thermo Quest MAT 95XL. The mechanical behavior of the materials was measured by a universal testing machine (HT-8504; Hung Ta Instrument Co., LTD, Taiwan) with a crosshead speed of 50 mm/min at room temperature. Dumbbell-shaped film samples were prepared with gauge section of 20 mm (L) × 5 mm (W) × 0.4 ∼ 0.5 mm (H). Small-angle X-ray scattering (SAXS) measurements were taken on Rigaku D/MAX-2500 equipped with a rotating anode X-ray tube using Cu K radiation (1.54 Å wavelengths) at 40 kV/300 mA. The films of polymer samples were prepared by casting the solution of 10−20% polymers in THF into a Teflon mold followed by drying. The films were stored in PE bags under room temperature before being tested.

Notation. 4-Isocyanato-4′(3,3-diethyl-2,4-dioxoazetidino)diphenylmethane is assigned as [MIA] due to its containing monoisocyanato(azetidine-2,4-dione) backbone, and 4,4-bis(3,3-diethyl-2,4-dioxoaztidino)diphenylmethane is assigned as [BA] due to its containing bis(azetidine-2,4-diones) functional group. All of the well-defined multiple hydrogen-bonding hard-segment extenders and their intermediates are assigned as "[H-G*X*]" and "[H-G*X*-I]" respectively, where *X* represents the generation number of extenders such as the first generation of hard-segment extender as [H-G1] and its corresponding precursor as [H-G1-I]. The notation used for representing the series of TRPUs is identified by "[G*X*-*YY*]", where *X* represents TRPU attached by extender [H-G*X*] and *YY* represents the weight fraction of hard segment in this TRPU. For example, the TRPU [G1-44] is the product made from addition of extender [H-G1] which possesses 44% of the weight fraction of hard segment. [G0] generally donates all samples of zero generation made from isocyanate-terminated prepolymers capped by aniline.

Synthesis of 4-Isocyanato-4′(3,3-diethyl-2,4-dioxoazetidino)-diphenylmethane ([MIA]). Synthesis and isolation of [MIA] with a 3,3-diethyl-substituted group on the azetidine-2,4-dione rings were performed according to the procedures of the previous published method[40] of Martin. However, the method was modified by using ethylbutyryl chloride/triethylamine as the precursors of diethylketene[41,42] (Scheme 1) and the detailed experiments are described as follows: A dried xylenes (120 mL) solution containing 28.1 g (0.278 mol) of triethylamine was added dropwise to a xylene solution (350 mL) of 4,4′-methylenebis(phenyl isocyanate) (50.0 g, 0.2 mol) and ethylbutyryl chloride (26.3 g, 0.2 mol) over 3 h period. The resulting reaction mixture was refluxed for another 4 h after the completion of the addition reaction. Then, the reaction mixture was cooled to −15 °C and was filtered to remove the salt precipitation. The clear filtrate and washings were concentrated under vacuum to remove xylenes. Then, the final product mixture (assigned as [MIA-m]) containing major product, [MIA], and [BA], was obtained by distillation under high vacuum to remove unreacted 4,4′-methylenebis(phenyl isocyanate) (160−170 °C at 0.1 mmHg). The yield of [MIA] calculated from ^{1}H NMR analysis of the product mixture [MIA-m] is about 48% based on initial 4,4′-methylenebis-(phenyl isocyanate).

The characteristic FT-IR spectrum of the product mixture [MIA-m]: 2272 cm^{-1} (−NCO), 1850, 1870, and 1740 cm^{-1} (stretching vibration of −C═O of azetidine-2,4-diones). The characteristic of ^{1}H NMR ($CDCl_3$, δ): 1.01 (t, 18H, $-CH_3$ of [MIA] and [BA]), 1.78 (q, 12H, $-CH_2-$ of [MIA] and [BA]), 3.94 (s, 2H, Ar$-CH_2-$Ar of [MIA]), 3.97 (s, 2H, Ar$-CH_2-$Ar of [BA]), 6.98−7.79 (m, 16H, Ar−H of [MIA] and [BA]). GPC (THF): polydispersity of [MIA] capped by CH_3OH = 1.07, M_n = 239 g/mol, M_w = 253 g/mol; polydispersity of [BA] = 1.06, M_n = 752 g/mol, M_w = 891 g/mol based on GPC analyses. Conveniently, the product mixture was used directly as our building block for iterative synthesis, and the byproduct, [BA], in the mixture was not separated at this stage but was separated in the subsequent step as shown in the procedure describing the synthesis of [H-G1].

Synthesis of First Generation of Hard-Segment Extenders, [H-G1], and Its Precursor Intermediates, [H-G1-I]. Aniline (5.3 g, 57.5 mmol) was added to a stirred toluene (300 mL) solution containing 41.7 g [MIA-m] which contained 57.5 mmol of [MIA] (as calculated from 48% of [MIA] in [MIA-m]) under dry N_2 ambient at 4 °C. After 2 h, [H-G1-I] precipitate (23.3 g) was collected by suction filtration. [BA] contaminant present in [MIA-m] was unreactive with aniline and remained intact in the toluene solution. The yield of isolated [H-G1-I] was calculated to be 92%. The mp of [H-G1-I] was measured to be 146.0−147.0 °C. Extenders [H-G1] were subsequently prepared in the next step by the reaction of 1-(2-aminoethyl)piperazine (0.3 g, 2.3 mmol) with [H-G1-I] (1.0 g, 2.3 mmol) in dried-DMF (6 mL) at 20 °C under N_2 for 1 h. The resulting reaction solution was slowly added into water, and the white solid precipitate (1.1 g), [H-G1], was gathered by filtration. The yield of dried [H-G1] was 85% (calculated) with mp found between 62.8 and 74.2 °C. The product analysis confirmed that [H-G1] is the selective ring-opening product of [H-G1-I] and 1-(2-

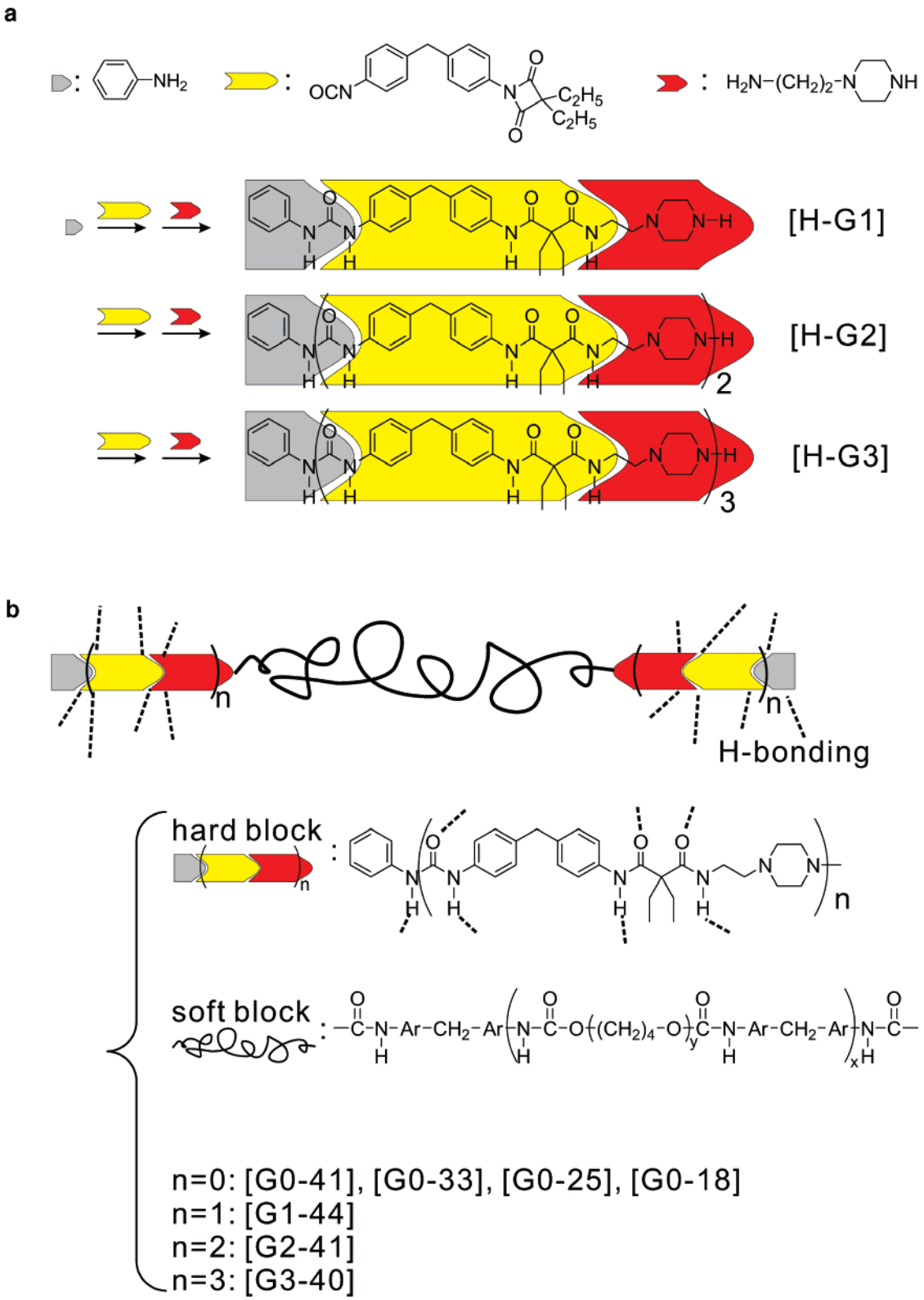


Figure 1. (a) Iterative synthesis: multiple hydrogen-bonding extenders. (b) Pseudo-triblock supramolecular TRPUs.

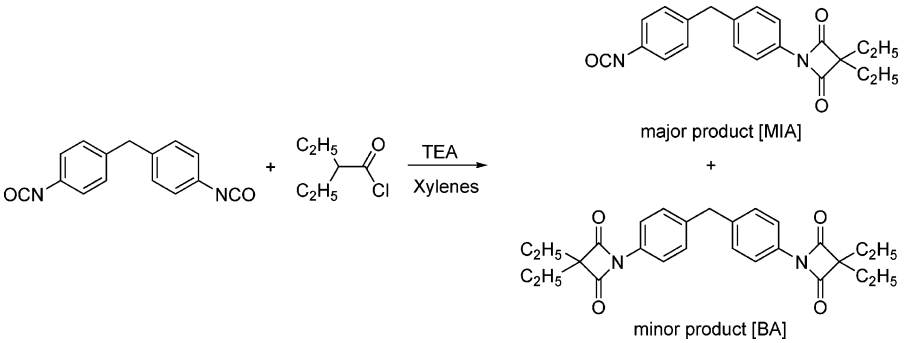
aminoethyl)piperazine through the aminoethyl-group of 1-(2-aminoethyl)piperazine and not the piperazine N−H group.

[H-G1-I]. FT-IR: 3312 cm^{-1} (−NH), 1848 and 1740 cm^{-1} (stretching vibration of -C═O of azetidine-2,4-diones), 1650 am^{-1} (−C═O of urea groups). The ^1H NMR (acetone-d_6, δ): 0.98 (t, 6H), 1.78 (q, 4H), 3.94 (s, 2H), 6.95−7.71 (m, 13H), 8.05 (s, 2H, proton of urea groups). MS (FAB): calcd 441.21; found 442 [M + 1]. GPC (THF): polydispersity = 1.04, M_n = 351 g/mol, M_w = 386 g/mol.

[H-G1]. FT-IR: 3331 cm^{-1} (−NH), 1666 cm^{-1} (−C═O of malonamide groups). ^1H NMR (acetone-d_6, δ): 0.79 (t, 6H), 1.78 (q, 4H), 2.34−2.46 (m, 4H), 2.70−2.79 (m, 6H), 3.34 (q, 2H,), 3.88 (s, 2H), 6.90−7.59 (m, 13H), 8.05 (d, proton of urea groups), 11.08 (s, proton of malonamide groups). MS (ESI): calcd 570.33; found 571 (M + 1). GPC (THF): polydispersity = 1.07, M_n = 530 g/mol, M_w = 568 g/mol.

Synthesis of Second Generation of Hard-Segment Extenders, [H-G2], and Its Precursor Intermediates, [H-G2-I]. [H-G1] (3.0

Scheme 1. Synthesis of Two Different Functional Starting Materials, 4-Isocyanato-4′(3,3-diethyl-2,4-dioxoazetidino)biphenylmethane [MIA] and 4,4-Bis(3,3-diethyl-2,4-dioxoazetidino)diphenylmethane [BA] (a Minor Compound)



g, 5.30 mmol) was added to a stirring [MIA-m] acetone (10 mL) solution containing [MIA] (1.8 g, 5.30 mmol as calculated from 3.75 g [MIA-m]) at ambient temperature under dry N_2. After stirring for 0.3 h, the product was purified by repeated cyclohexane-washings, and then a white solid adduct (4.5 g), [H-G2-I], was isolated by filtration. It was found that this purification process had removed [BA] completely from the product mixture. The yields of [H-G2-I] were 93% with mp of 102.0−133.0 °C. Then, in a similar synthetic procedure described for that of [H-G1], 1-(2-aminoethyl)piperazine (0.28 g, 2.18 mmol) was added to a stirring dried-DMF (9 mL) solution containing 2.00 g of [H-G2-I] at 20 °C under dry N_2 until complete dissolution of the starting materials. The reaction lasted for 60 min as monitored by TLC when [H-G2-I] was consumed completely. The resulting solution was then slowly poured into 500 mL of water to give a white solid [H-G2] (1.6 g; 70%) by filtration. The mp of [H-G2] measured between 110.0 and 130.0 °C.

[H-G2-I]. FT-IR absorptions: 3333 cm^{-1} (−NH), 1870, 1850, and 1735 cm^{-1} (stretching vibration of −C═O of azetidine-2,4-diones), 1650 cm^{-1} (−C═O of urea groups). The ^1H NMR absorptions (acetone-d_6, δ): 0.80 (t, 6H), 0.97 (t, 6H), 1.78 (q, 8H), 2.40−2.60 (m, 6H), 3.40−3.50 (m, 6H), 3.90 (s, 2H), 3.94 (s, 2H), 6.90−7.75 (m, 21H), 7.87 (s) and 8.04 (d, proton of urea groups), 10.95 (s, proton of malonamide groups). MS (FAB): calcd 918.48; found 920 (M + 2). GPC (THF): polydispersity = 1.10, M_n = 1081 g/mol, M_w = 1193 g/mol.

[H-G2]. FT-IR absorptions: 3329 cm^{-1} (−NH), 1666 cm^{-1} (−C═O of malonamide groups), 1654 cm^{-1} (−C═O of urea groups). ^1H NMR absorptions (acetone-d_6, δ): 0.79 (t, 12H), 1.79−1.95 (m, 8H), 2.34−2.50 (m, 12H), 2.70 (t, 4H), 3.39−3.45 (m, 8H), 3.85 (s, 2H), 3.87 (s, 2H), 6.85−7.58 (m, 21H), 7.87 (s) and 8.00 (d, proton of urea groups), 10.90 (d, proton of malonamide groups). MS (ESI): calcd 1047.61; found 1048 (M + 1). GPC (THF): polydispersity = 1.20, M_n = 1152 g/mol, M_w = 1382 g/mol.

Synthesis of Third Generation of Hard-Segment Extenders, [H-G3], and Its Precursor, [H-G3-I]. Preparation of [H-G3-I] and [H-G3] were carried out by similar procedures but instead of acetone, a dried-THF was used due to better solubility. The yields for [H-G3-I] and [H-G3] were 76% and 77%, respectively. The mps of solid [H-G3-I] and [H-G3] were observed over wider ranges than previous generations with the former founded between 135.1 and 154.1 °C and the latter 132.3−153.4 °C.

[H-G3-I]. FT-IR absorptions: 3333 cm^{-1} (−NH), 1870, 1852, and 1737 cm^{-1} (stretching vibration of -C═O of azetidine-2,4-diones), 1663 cm^{-1} (−C═O of urea groups). The characteristics of ^1H NMR (acetone-d_6, δ): 0.80 (t, 12H), 0.97 (t, 6H), 1.78 (q, 12H), 2.02 (q, 12H), 2.45 (m, 12H), 3.46 (s, 12H), 3.84 (s, 2H), 3.87 (s, 2H), 3.91 (s, 2H), 6.91−7.70 (m, 29H), 7.84 (d) and 8.04 (d, proton of urea groups), 10.95 (s, proton of malonamide groups). MS (ESI): calcd 1395.76; found 1396 (M + 1). GPC (THF): polydispersity = 1.18, M_n = 1563 g/mol, M_w = 1850 g/mol.

[H-G3]. FT-IR absorptions: 3325 cm^{-1} (−NH), 1662 cm^{-1} (−C═O of malonamide groups), 1653 cm^{-1} (−C═O of urea groups). The characteristics of ^1H NMR (acetone-d_6, δ): 0.80 (t, 18H), 1.83 (q, 12H), 2.35−2.55 (m, 18H), 2.70 (t, 4H), 3.45 (s, 14H), 3.85−3.87 (d, 6H), 6.88−7.60 (m, 29H), 7.83 (s) and 8.00 (d, proton of urea groups), 10.95 (d, proton of malonamide groups). MS (ESI): calcd 1524.89; found 1525 (M + 1). GPC (THF): polydispersity = 1.29, M_n = 1269 g/mol, M_w = 1644 g/mol.

Table 1. Formulary of Materials.

	molar ratio[c] 4,4-MDI/PTMO/[H-GX]	added reactants, g	hard-segment content,[d] wt %
[G0-41][a]	2/1/2	1.54/3.00/0.58	41
[G0-33][a]	3/2/2	1.16/3.00/0.29	33
[G0-25][b]	2/1/2	0.73/3.00/0.27	25
[G0-18][b]	3/2/2	0.54/3.00/0.14	18
[G1-44][b]	2/1/2	0.73/3.00/1.66	44
[G2-41][b]	3/2/2	0.54/3.00/1.52	41
[G3-40][b]	4/3/2	0.49/3.00/1.48	40

[a] Soft-segment parts: PTMO 1000. [b] Soft-segment parts: PTMO 2000. [c] X = 0 (aniline), 1, 2, 3. [d] Hard-segment content (wt %) = $((W_{MDI} + W_{[H-GX]})/(W_{MDI} + W_{PTMO} + W_{[H-GX]})) \times 100\%$.

Preparation of Isocyanate- (NCO-) Terminated Prepolymers. Polyurethane isocyanate prepolymers were prepared by reacting 4,4′-methylenebis(phenyl isocyanate) with PTMO 2000 or PTMO 1000, respectively, in 12 w/v % THF solution. The NCO/OH molar ratios of three NCO-terminated prepolymers were at 2/1, 3/2, and 4/3 respectively. Di-*n*-butyltin dilaurate (T-12), was used as catalyst in all cases under dried N_2 at 60 °C and the reactions were completed within 2 h based on the disappearance of diol OH-groups (at 3333 cm^{-1}) of the reaction mixtures monitored by FT-IR.

Preparation of Supramolecular TRPUs. In order to obtain supramolecular PUs with identical hard-segment contents of about 41%, PTMO with molecular weights of both 1000 and 2000 g/mol were used as soft segments and they were then reacted with 4,4′-methylenebis(phenyl isocyanate) to form NCO-terminated prepolymers. When the NCO-terminated prepolymer was capped with stochiometric amounts of aniline, they are assigned as [G0] series. Four [G0] PU products, [G0-41], [G0-33], [G0-25], and [G0-18] were prepared with different molecular weights, which were used for as our comparative study. Supramolecular TRPUs made from higher generation of extenders such as [H-G1], [H-G2], and [H-G3] with isocyanate prepolymers having approximate the same hard-segment/soft-segment ratios of 41% were similarly synthesized. Table 1 showed the relative molar ratios used in each study with detailed reaction conditions. In each case, the NCO-terminated prepolymers were added into a dried-THF solution containing an extender with stirring under dried nitrogen at 60 °C for 10 min until the complete consumption of isocyanate. The resulting solutions were cooled and then poured into a Teflon mold to form the polymer films for testing.

Results and Discussion

Synthesis and Reactions of 4-Isocyanato-4′(3,3-diethyl-2,4-dioxoazetidino)diphenylmethane. Synthesis of 4-isocyanato-4′(3,3-dimethyl-2,4-dioxoazetidino)diphenylmethane has been described previously in our paper.[41,42] Since the isolated yields of recrystallized 4-isocyanato-4′(3,3-dimethyl-2,4-dioxoazeti-

Table 2. Characteristics of Multiple Hydrogen-Bonding Hard-Segment Extenders with Uniform Chain Lengths

	melting point (°C)	T_g (°C)	ΔC_p (mJ deg^{-1} mg^{-1})	T_d (°C)	PD
[H-G1-I]	146−147	55.2	0.340	222	1.04
[H-G1]	63−74	60.0	0.336	198	1.07
[H-G2-I]	102−133	98.3	0.269	233	1.10
[H-G2]	110−130	100.0	0.393	224	1.20
[H-G3-I][a]	135−154	122.5	0.293	256	1.18
[H-G3][a]	132−153	122.1	0.339	251	1.29

[a] Extenders were exactly synthesized and had a broad polydispersity (PD).

dino)diphenylmethane were generally low, in the range of only 25−35%, we turned our efforts in this study to synthesis of [MIA] in hopes of improving yield. This approach was based on our observation that dimethyl ketene generated from isobutyryl chloride/triethylamine solution seems to be more volatile and reactive. Hence, some of the dimethyl ketene might have been lost during the reaction process and some appears to have undergone self-oligomerization. In our hand, diethyl ketene generated from 2-ethylbutyryl chloride/triethylamine did undergo cycloaddition with isocyanates in better selectivity.[43] We also found that the reaction mixture after removal of 4,4′-methylene-bis(phenyl isocyanate) though still contaminated with [BA], can be applied conveniently in our synthetic for urea derivation by addition of aniline or any compounds with secondary amine to make our extenders (see Figure 1). Separation of the solid extenders from [BA] was accomplished simply by a filtration step. By so doing, overall yields of [MIA] in the mixture were estimated to be at least 48% based on the extender isolated.

Synthesis of Multiple Hydrogen-Bonding Hard-Segment Extenders. Three structurally well-defined multiple hydrogen-bonding hard-segment extenders, [H-G1], [H-G2], and [H-G3] (shown in Figure 1), had been synthesized using [MIA], aniline, and 1-(2-aminoethyl)piperazine via the iterative syntheses. Since all the reactions involved are simple repetitive addition reactions, these syntheses were straightforward, efficient and high-yielding.[43] The preparations of the first and second generations of supramolecular extenders, [H-G1] and [H-G2], were especially simple and precise, and both resulted in formation of supramolecular extenders exhibiting low polydispersity of 1.04−1.20, respectively, in GPC analysis. These data imply that these extenders possess narrowed molecular weight distributions. In addition, mass spectral data measured of extenders matched the structural assignments. Although the synthesis of a third generation of supramolecular extenders, [H-G3], met with slight complications due to the presence of trace smaller molecular-weight byproducts in its GPC analysis and had a slightly larger polydispersity of 1.29, the mass spectra of the product still showed the expected molecular weight.

GPC and Thermal Properties of Multiple Hydrogen-Bonding Hard-Segment Extenders. The detailed data of ^{1}H NMR, FT-IR, and mass spectroscopy confirmed that these synthesized supramolecular extenders possessed well-defined structures as shown in Figure 1. GPC and thermal analysis data for the extenders, [H-G1], [H-G2], and [H-G3], and those of their corresponding precursors, [H-G1-I], [H-G2-I], and [H-G3-I], were compiled together in Table 2 for comparison. In Table 2, the data clearly indicated that melting points of these extenders increased with increasing chain length. However, melting ranges of the higher generation extenders in [H-G2] and [H-G3] series became wider. These general trends are consistent with the structural effects of the growing number of hydrogen-bonding sites due to the presence of more urea and amide groups in the main chain.[44] For example, 13 hydrogen-bonding sites are present in [H-G2] while only seven exists in those of [H-G1]. The growth in hydrogen-bonding sites is expected to cause major change in their respective molecular chain interactions as well as chain mobility as proven in data in Table 2.

In Table 2, the T_g for each generation of extenders was determined by DSC. These low-molecular-weight extenders showed distinctive glass transitions especially after taking the second scanning. The glass transition behaviors of these extenders appeared to resemble motions of long-chained polymers,[44−46] and indicated that the prepared extenders possessed supramolecular performance. Thus, the extenders could be considered to be "pseudo-polymers". The variations can also be due largely to degree of differences in the chains' intimate hydrogen-bonding which exists between interchain interactions.[47] Furthermore, data in TGA analysis, shown in Table 2, indicated that T_d (5% weight loss) of the extenders also have been enhanced with an increase in chain lengths. These results indicated that highly hydrogen-bonding molecules such as the uniform chain-length extenders, [H-G2] and [H-G3], synthesized in this research, can be expected to possess molecular reinforcement capability through supramolecular assembling.

Supramolecular Thermoreversible Polyurethane. On Preparation of Supramolecular TRPUs. Information on the detailed composition of seven TRPUs prepared based on the three generations of uniform chain-length extenders synthesized and the controlled samples (using only aniline as the [H-G0] extender), is listed in Table 1. In our formulation design, the targeted "pseudo-triblock" systems were prepared by attaching uniform chain-length extenders to both ends of the NCO-terminated prepolymers (b of Figure 1). In order to achieve hard-segment content of 41% in each series, different ratios of 4,4′-methylenebis(phenyl isocyanate) and PTMO had to be formulated with extenders as shown in Table 1. As the result, the TRPUs are characterized by small chain-length of about ∼17 000 g/mol for [H-G1] extender, medium chain-length of ∼30 000 g/mol for [H-G2] extender and the longest chain-length of ∼80 000 g/mol for [H-G3] extender. They were compared with four [G0] samples of the respective similar molecular weights, and with each other in terms of the effect of hard-segment length on overall physical properties under similar hard-segment content of ∼41%. Since the uniform chain-length hard-segment extenders possessed polar hydrogen-bonding sites, their intrinsic properties are different from those of the long-chained polyether components of the soft segment especially in polarity and in degree of chain interactions. Thus, the TRPUs constructed from them are essentially similar to segmented polyurethane elastomers excepted that their molecular weights are smaller in comparison.

Mechanical Properties of Supramolecular TRPUs. Polyurethane prepolymers of low molecular-weights were generally tacky viscous liquids[48,49] and lack of strength and tough mechanical properties. Recent studies indicate that functionalization of end group polyurethane oligomers with multiple hydrogen-bonding groups will result in great enhancement of their physical properties.[50−52] The stress−strain behavior of the prepared TRPU films is shown in Figure 2. The results of their yield strengths, tensile strengths, elongations, and Young's module of the TRPUs were compiled in Table 3. In Figure 2, superior mechanical behaviors of TRPU [G2-41] can be clearly distinguished from those based on [G1-44] and all of the [G0] series. As can be seen in Table 3, [G0-41] material was too brittle to be tested by conventional mechanical testing. The yield

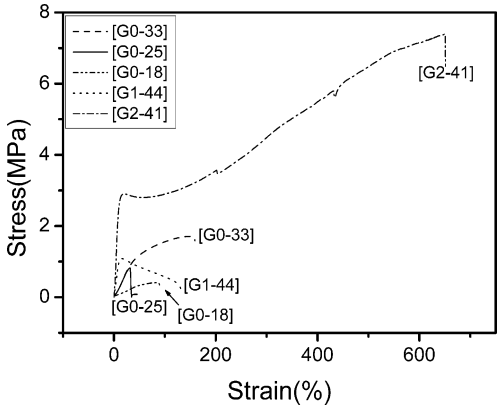


Figure 2. Stress−strain behaviors of TRPUs.

Table 3. Mechanical Behaviors of TRPUs.

	M_p[a] (g mol^{-1})	tensile strength (MPa)	elongation (%)	yield strength (MPa)	Young's modulus (MPa)
[G0-41]	13 497	N/A	N/A	N/A	N/A
[G0-33]	15 878	1.7	159	N/A	N/A
[G0-25]	42 166	0.8	45	N/A	N/A
[G0-18]	62 443	0.4	90	N/A	N/A
[G1-44]	17 261	1.2	131	1.2	8
[G2-41]	30 422	7.4	651	2.9	19
[G3-40]	80 136	N/A	N/A	N/A	N/A

[a] GPC instrument printed peak value.

Table 4. Thermal Properties of TRPUs

	T_{gS} (°C)	ΔC_{pS} (mJ deg^{-1} mg^{-1})	T_{gH} (°C)	ΔC_{pS} (mJ deg^{-1} mg^{-1})	T_m (°C)	T_c (°C)	ΔH_c (mJ mg^{-1})	T_d (°C)
[G0-41]	−51.0	0.419	N/A	N/A	16.3	N/A	N/A	272
[G0-33]	−48.0	0.588	N/A	N/A	8.1	−30.6	−23.0	285
[G0-25]	−47.0	0.021	N/A	N/A	26.2	1.9	−65.8	290
[G0-18]	−54.0	0.091	N/A	N/A	27.0	−13.1	−59.4	320
[G1-44]	−50.2	0.035	96.4	0.087	34.5	−3.5	−32.9	273
[G2-41]	−55.6	0.059	141.6	0.136	42.5	−8.4	−40.9	304

stress of TRPU [G2-41] was 2.4 times greater than that of TRPU [G1-44]. In the meantime, the elongation, Young's Modulus, and tensile strength of TRPU [G2-41] were 5, 2.4, and 6.2 times higher than those of materials based on [G1-44] respectively. Though [G2-41] is only half the molecular weight of [G0-18], its mechanical properties are much greater than [G0-18]. These results clearly imply that the mechanical properties of TRPU materials are greatly influenced by composition and especially by the hard-segment length and overall chain length. In this study, the superior performance of TRPU [G2-41] can be attributed to the increase in total number of hydrogen-bonding sites from seven in [G1-44] to 13 in [G2-41] in the hard segment portion of supramolecular materials. Furthermore, these hydrogen-bonding sites are expected to form physical interchain networks with the supramolecular structures. Thus, the degree of physical-cross-linking in TRPU [G2-41] is also higher than that in TRPU [G1-44]. So far, there are no reports in the literature for elastomeric materials that have shown these outstanding mechanical properties as those of TRPU [G2-41] simply through physical interactions of multiple hydrogen bondings.

In this study, it appears that structural composition between hard and soft segment lengths has achieved the optimal balance or close to it in the case of TRPU [G2-41]. Further increase in the chain lengths of hard segment to [H-G3] and in the meantime increase of the soft segment to 80 000 g/mol (the hard-segment content kept at 41%) ended up with a material having poor mechanical properties. The TRPU [G3-40] failed to form elastic films for physical measurements. In spite of having the highest molecular weight and the longest hard-segment extender of polymers in this study, TRPU [G3-40] was a tacky rubbery material with little strength. Thus, mechanical testing data for TRPU [G3-40] in the thermal analysis were not available (Table 3 and 4). The reason for this failure is still uncertain but may be due to several possible reasons. Structural imperfections of the [H-G3] extender as evidenced from extender's larger polydispersity of 1.29 could be a contributing factor. However, the morphological weakness resulting from its long soft-segment chain-length could be the more likely cause. A long hard extender if connected to an extremely long soft-segment as in the case of [G3-40]'s A−B−A system resembling traditional triblock system[53] would not achieve further performance advancement. The overall properties actually fell substantially. The retardation of self-assembling process in [G3-40] could be a major reason.

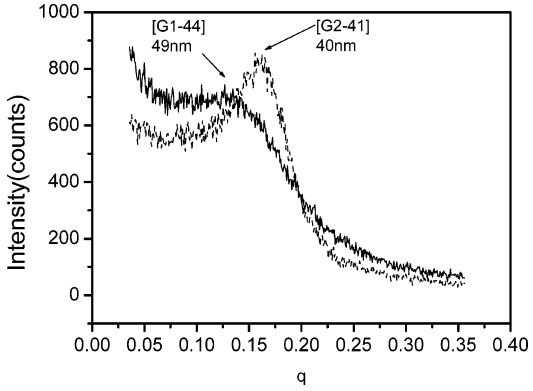


Figure 3. SAXS graph of TRPUs.

Thermal Properties of Supramolecular TRPUs. To study the thermal properties of these TRPUs except for [G3-40], DSC and TGA measurements were carried out (Table 4). TGA results indicated that TRPUs with the specific hard-segment extenders all distinguished themselves with remarkable thermostabilities in cases where T_d measured at around 270 °C. T_d of [G2-41] at 304 °C was the highest in this series.

The T_g of pure PTMO as soft segments (1000 or 2000 g/mol molecular weight) was found at about −85 °C. From our DSC thermograms of the TRPU materials, T_g of soft segments (T_{gS}) of [G1-44] and [G2-41] were shifted upward to −50.2 and −55.6 °C, respectively. With increasing generations and longer hard segment lengths, the T_{gS} appeared to be shifted downward toward the T_g of pure PTMO. This data further supports that [G2-41] exhibited a more prominent phase-segregation morphology than either [G1-44] or others [G0] series. This trend also suggests that the longer the length of multiple hydrogen-bonding hard segments in TRPU materials up to the second generation, the more segregated the phases between hard- and soft-domains. Judging from the additional hydrogen-bonding sites that are available for interaction in [G2-41] than those of lower generations, the greater interactions of hard-segment in [G2-41] through hydrogen-bonding and chain-length seems apparent and beneficial.

The same reasoning can be extended to explain the changes of T_g of uniform chain-length hard segments (T_{gH}) observed in this TRPU series. Multiple hydrogen-bonding extenders bonded to both terminals of NCO-terminated prepolymers limiting their molecular motions. In the [G0]-series, no hard-segment glass transition could be detected. Interestingly, T_{gH} of [G1-44] and [G2-41] were found at 96.4 and 141.6 °C respectively and both have been shifted upward from those of their individual extenders measured at 60.0 and 100.0 °C respectively. These

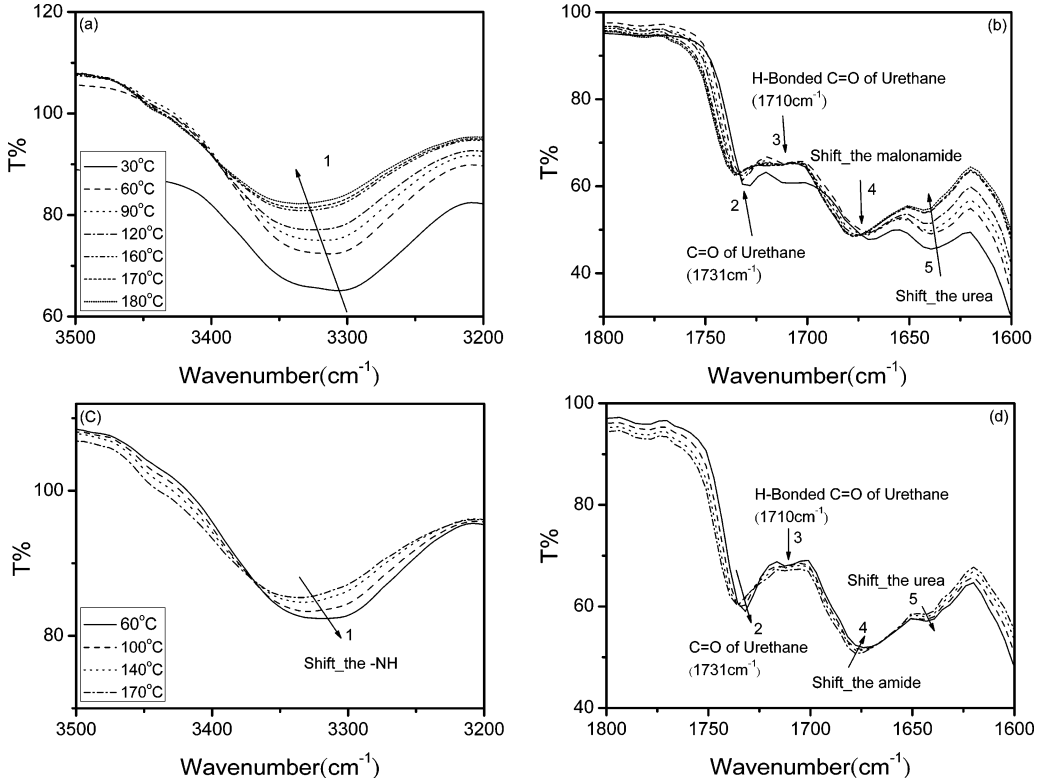


Figure 4. Variable-temperature FT-IR of TRPUs: (a and b) heating process of [G1-44]; (c and d) cooling process of [G1-44].

results could be interpreted to mean that the aggregation of terminal supramolecular hard segments is assisted by the soft segment of polyurethanes. In other words, TRPU [G2-41] had formed highly organized phase-domains among all of our series studied.

Morphology. In order to better differentiate the morphology and performances of the TRPUs of our study, SAXS of TRPU samples were analyzed (Figure 3). The maximum scattering vectors (q) used in analysis for sample [G1-44] and [G2-41] were 0.1268 and 0.1559, respectively. Using the equation $d = 2\pi/q$ as our basis, the average period of microdomain in the lamellar structure can be calculated to be 49 and 40 nm for [G1-44] and [G2-41] respectively. The intensity of the peak signal for [G2-41] was, however, more distinct than that of [G1-44]. The X-ray observation showing a well-defined phase-segregated microdomain due to well-defined hard segments in [G2-41] is consistent with the results discussed in DSC analysis, as well as with our previous conclusion and other art.[36−39]

Thermoreversible Behaviors of Supramolecular TRPUs. The study of thermoreversible behaviors of our novel supramolecular elastomeric polyurethane were focused on changes in the samples' variable-temperature FT-IR spectra and circular scanning treatments on DSC. The results were recorded and presented in Figure 4 and Figure 5, respectively. In Table 5, the details of FT-IR shifting due to hydrogen-bonding effects observed on the variable-temperature FT-IR were compiled. The absorptions of −NH− and carbonyl (−C═O) of malonamide groups have been found to undergo the most obvious changes in the TRPUs due to the temperature change. The formation and degradation of hydrogen bonding between inter-polymer chains and intra-polymer chains was observed during the thermal heating and cooling cycles. During the slow elevation of sample temperature, the −NH− characteristic peak located initially at 3300 cm^{-1} was found to shift gradually toward 3340 cm^{-1} as indicated in arrow 1 of part a of Figure 4. Conversely, the 3340 cm^{-1} peak observed for −NH− absorption at 170 °C would gradually return back toward the original absorption of 3300 cm^{-1} as indicated by part c of Figure 4 upon cooling of the sample to the ambient temperature. This reversible FT-IR shifting phenomenon can be repeated consistently. Extensive hydrogen bonding between inter- or intra-polymer chains was evident at room temperature, but gradually weakened during the temperature elevating process. Similarly, the characteristic absorptions of urethane and urea groups in the TRPUs all shown to exhibit the same phenomena as indicated by arrows of 2−5 in Figure 4. As evidenced from the above variable-temperature FT-IR observations, these TRPU materials possess optimal mechanical and physical properties at ambient temperatures because of highest density of physically "psudo-cross-linked" networks via hydrogen bonding. In our prior report,[36] a similar phenomena of physical "psudo-cross-linked" via hydrogen bonding through dendritic supramolecular interaction in PUs had also been observed. However, the reversibility of polyurethane systems appeared to be especially more rapid in the linear TRPUs of [G1-44] and [G2-41] than those of the dendritic samples reported earlier.

Circular scanning treatment on DSC further helped to show the thermoreversible behavior of TRPUs prepared. In the actual circular scanning process, the testing materials went through cycles of heating and cooling on DSC scanning. As shown in Figure 5, circular heating/cooling curves generated in our studies superimposed almost identically. Furthermore, with each scan their Δ enthalpy values were maintained nearly the same. The result indicated that, even with an upper temperature limit of 200 °C, essentially no degradation of material was detected during the four heating/cooling cycles. Thus, the results of circular scanning treatment on DSC are consistent with the results of variable-temperature FT-IR study in demonstrating the thermoreversible behaviors for these TRPU materials. Additionally, the T_{gH} of these materials were observed to move to slightly higher temperatures after several heating/cooling cycles. In Figure 5, for instance, T_{gH} of [G2-41] sample has

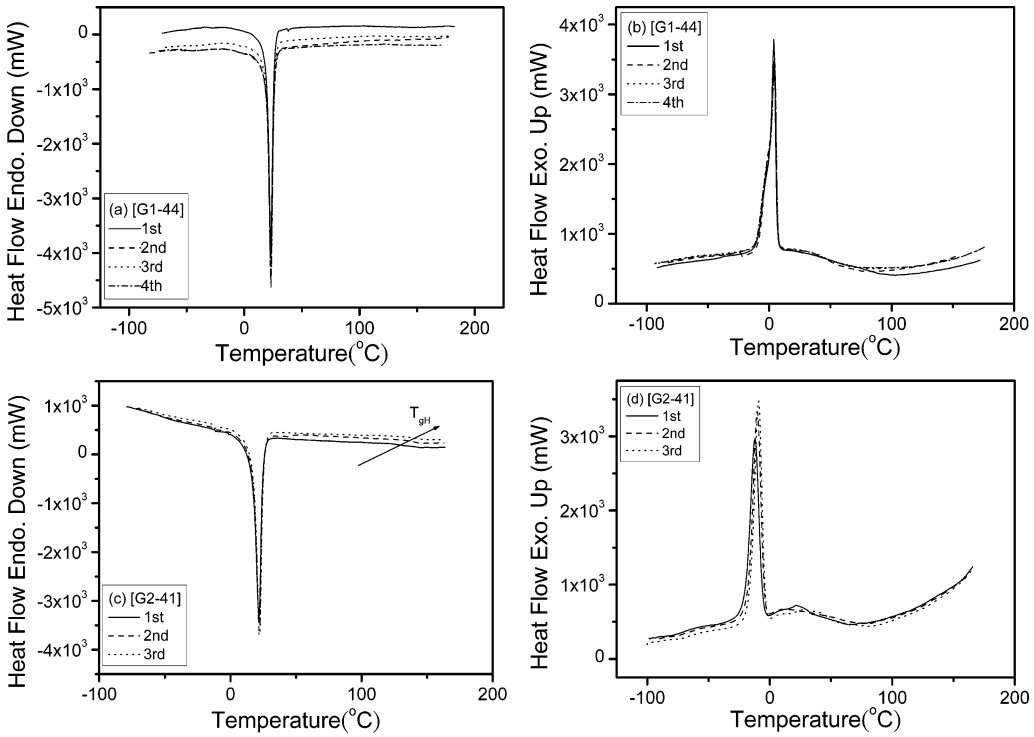


Figure 5. Circular scanning treatments of TRPUs on DSC: (a) heating process of [G1-44]; (b) cooling process of [G1-44]; (c) heating process of [G2-41]; (d) cooling process of [G2-41].

Table 5. Shifting Values of TRPUs for Hydrogen Bonded and Free Hydrogen Bonded

functional group	hydrogen-bonded wavenumber, cm^{-1}	free hydrogen-bonded wavenumber, cm^{-1}
−NH stretch banding in urethane, urea, and malonamide	3300	3340
−C═O in urethane	1710	1731
−C═O in malonamide	1670	1680
−C═O in urea	1639	1645−1680

been moved up from 132 to 141 °C as indicated by the arrow of part c. The above result suggests that the annealing process of TRPUs materials will have a positive effect of enhancing the segregation of soft and hard domains and creating the optimal physical properties.[54]

Conclusion

An efficient iterative synthesis of constructing multiple hydrogen-bonding hard-segment extenders of narrow molecular-weight distribution has been developed based on 4-isocyanato-4′(3,3-diethyl-2,4-dioxoazetidino)diphenylmethane intermediate, aniline and 1-(2-aminoethyl)piperazine. This synthetic methodology allows us to obtain three generations of multiple hydrogen-bonding extenders with molecular weight increment of 477 g/mol in each generation for use in preparation of supramolecular "psedo-triblock" TRPUs. Our results revealed that all three series of TRPUs, [G1-44], [G2-41], and [G3-40], possess narrow-molecular-weight-distribution of multiple hydrogen-bonding hard segments and exert great impact on overall properties of TRPUs. From the TGA and DSC data, thermal stability and glass transition temperatures of TRPUs dramatically increase with increasing chain-length up to the second generation. Increased hydrogen-bonding sites and aromatic contents of the [G2-41] cause more physical cross-linking in uniform chain-length hard segments. SAXS analysis indicated an ability of [G2-41] sample to self-assembly. The second generation extender, [H-G2], was found to be most prominent among the series. The results from mechanical testing revealed that mechanical behaviors of [G2-41] possess superior performance over all TRPUs made in this study. From results of the circular scanning process on DSC and variable-temperature FT-IR, these novel materials all possess thermoreversible behaviors, [G2-41] in particular. Formation and degradation of physical cross-linking due to multiple hydrogen bondings can be readily controlled by temperature changes and has demonstrated consistency for at least four cycles. From above results, polymer possessing two-time-length hard segment with molecular weight of 1047 g/mol, [G2-41], coupled with medium PTMO soft segment of 30 000 g/mol becomes optimal in aspect of phase-segregation morphology and mechanical strength. Compared with our preceding papers,[36−39] the linear-to-end polymer system in this study appears to enhance mechanical properties of materials more effectively those than those with a dendritic approach. This study also provides powerful evidence and workable ranges of what the optimal chain length of multiple hydrogen-bonding hard segments and the connecting soft segment should be. It also points to the possibility of making elastomer materials with memory effect simply through manipulating the multiple hydrogen-bonding hard segments of "pseudo-triblock" polyurethane systems.

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