Thermoreversible Supramolecular Polyurethanes with Self-Complementary Quadruple Hydrogen-Bonded End Groups

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ABSTRACT: In this article, a new type of strongly dimerizing 2-ureido-4-[1H]-pyrimidinone (UPy) with amine group is synthesized and then used as end-group to prepare a novel series of supramolecular polyurethanes (PUs). The effects of strong and well-defined hydrogen bonding on material properties of PUs are studied. In these PUs, the UPy groups consequently serve as thermoreversible associations or the "hard blocks" and the bi-functional PU chains act as the "monomers." This theoretical hypothesis is proved by the results of dynamic mechanical thermal analysis (DMTA) and rheological test. Thermal analysis shows that the strong hydrogen bonds from end groups restrict the formation of their microcrystalline domains. The supramolecular PUs exhibit good mechanical performance and their self-assemble mechanism is discussed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1755–1763, 2012

Key words: 2-ureido-4-[1H]-pyrimidinone; supramolecular polyurethanes; self-complementary; quadruple hydrogen-bonding; thermoreversible

INTRODUCTION

In a novel class of supramolecular polymers, the reversibility of the non-covalent bonds between the monomers gives rise to interesting material properties.[1–3] The self-association of individual molecules can lead to the formation of highly complex and fascinating non-covalent interactions, including metal coordination, electrostatic interactions, van der waals, π–π interactions, and hydrogen bonds.[4,5] Hydrogen bonds play an important role in determining the three-dimensional structure of chemical systems as a consequence of their specificity and directionality. In contrast to covalent bonds, the formation of hydrogen bonds is reversible and their strength depends on their concentration and the chemical environment, such as the solvent or temperature.[6,7]

The 2-ureido-4-[1H]-pyrimidinone (UPy) moiety is known to dimerize via a strong quadruple hydrogen bonding (QHB) array. QHB units with extremely high dimerization constants ($K_{dim} = 6 \times 10^7$ M^{-1} in CHCL₃) have received significant attention for the creation of novel supramolecular architectures.[8–11] Meijer and co-workers have first developed supramolecular polymers by connecting two strongly dimerizing UPy groups as a linker and the "monomers" are bi-functional molecules.[12,13] Long and co-workers have also synthesized a series of well-defined QHB-terminated polymers, such as telechelic polyesters, glassy poly(styrene), rubbery poly(isoprene), and PS-*b*-PI block copolymers. The relationship between end-group structure and physical properties, such as the glass transition temperature, melt viscosity, and morphology, were reported.[14–16]

Following Meijer and Long's pioneer work, UPy has been used extensively by others as binding units for supramolecular polymers, such as polycarbonate, linear telechelic siloxanes, well-defined (meth)acrylic polymers, poly(ethylene/butylene), and copolyesters. The formation of microcrystalline domains between QHB end groups can lead to a dramatic change in the microscopic and macroscopic properties of the resulting supramolecular assemblies, including thermal properties, tensile strength, rheological properties, surface morphology, and dynamic mechanical properties.[17–21] However, the π–π interactions between the end groups are too weak to induce aggregation and no lateral stacking of dimmers was observed in UPy-functionalized polymers, unless additional urethane or urea groups were built into the hard block. The aggregation is attributed to the incompatibility of soft block and hard block, leading to nanophase separation.[22] The presence of lateral urea in UPy-based supramolecular poly(ethylene butylene) will give rise to 1D aggregation of dimerized end groups (long fiber structures), which leads to high melting point (129°C) and noticeable elastic properties.[23]

Besides the widely used UPy, Kim and coworkers have developed a facile, efficient route to synthesize

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a supramolecular material containing QHB sites. This approach, which does not need the selective use of monofunctionalized precursor, involves a single-step reaction between the amine of methyl isocytosine and the epoxy group of polymer, for example, poly(ethylene glycol diglycidyl).[24]

Dimmers of UPy, which act as robust, selective, and directional hydrogen-bonding systems, have a wide range of practical applications: reversible cross-links in cross-linking polymer networks, bioactive scaffolds for tissue engineering, shape-memory materials, thermoplastic elastomers, biomimetic modular polymers, star-shaped polymers, supramolecular dendrimers, peptide modification, and hyperbranched polymers.[25–38]

In this article, we synthesize a type of UPy with amine group and introduce these QHB units into polyurethanes (PUs) as end groups, which can yield a pseudo-high molecular weight linear polymer with good mechanical performance and processability via the thermoreversible association of end groups. The thermal properties, mechanical performance, rheological behavior, and self-assemble mechanism of the supramolecular PUs are characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and universal electromechanical tester and rotational rheometer. The self-assemble mechanism of supramolecular PUs is discussed in detail based on their mechanical properties.

EXPERIMENTAL

Materials

2,6-Toluene diisocyanate (TDI) was used as received from Bayer MaterialScience. 1,6-Hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) were used as received from Nippon Polyurethane Industry (Japan). Polytetramethylene ether glycol (PTMG) and polybutylene adipate (PBA) were purchased from DuPont and Yantai Huada Chemical Industry, respectively. N,N'-Carbonyldiimidazole (CDI) was purchased from Jingyan Chemicals (Shanghai). N,N-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethyl acetoacetate (EAA), guanidine carbonate, dibutyltin dilaurate (DBTL), ethanol, acetone, and 1,6-hexylenediamime were purchased from China National Medicines. PTMG and PBA were degassed at 100°C for a minimum of 3 h before use. DMF was dried with CaH_2 and purified by vacuum distillation, then kept with 4A molecule sieves. DMSO was dried under 4A molecular sieves for a minimum of 3 days. Other chemicals were used without further purification unless stated otherwise.
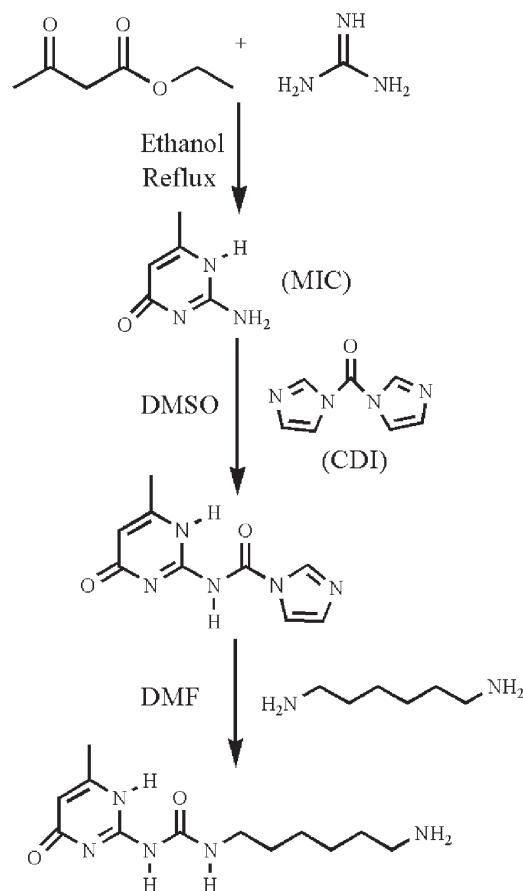

Scheme 1 Synthesis route of 2-ureido-4[1H]-pyrimidinone with amine group.

Synthesis of 2-amino-4-hydroxy-6-methylpyrimidine (MIC)

The route was shown in Scheme 1. A suspension of EAA (71.6 g, 0.5 mol) and guanidine carbonate (45.1 g, 0.55 mol) in dry ethanol (600 mL) was refluxed overnight. The reaction mixture was cooled down, and the resulting precipitate was filtered and washed with ethanol, water, and acetone to yield MIC (58.4 g, 93%). The product was obtained as a white powder and dried in vacuo at 30°C for 2 h. ^{1}H-NMR (400 MHz, [D$_6$] DMSO, δ): 10.85 (s, 1 H), 6.66 (s, 1 H), 5.48 (s, 1 H), 1.97 (s, 3 H). FTIR: γ = 3335, 3074, 2945, 1661, 1499, 1388, 1360, 1279, 1176, 829 cm^{-1}.

Synthesis of 2-ureido-4[1H]-pyrimidinone with amine group (UPy)

The route was shown in Scheme 1. MIC (16 g, 128 mmol) and CDI (29 g, 179 mmol) were suspended in DMSO (800 mL) and stirred for 2 h at 80°C. The reaction mixture was cooled down, and the resulting precipitate was filtered and washed with ethanol to yield CDI-activated MIC. The intermediate was obtained as a white solid and dried in vacuo at 30°C for 1 h. Then CDI-activated MIC (23.2 g, 105 mmol)
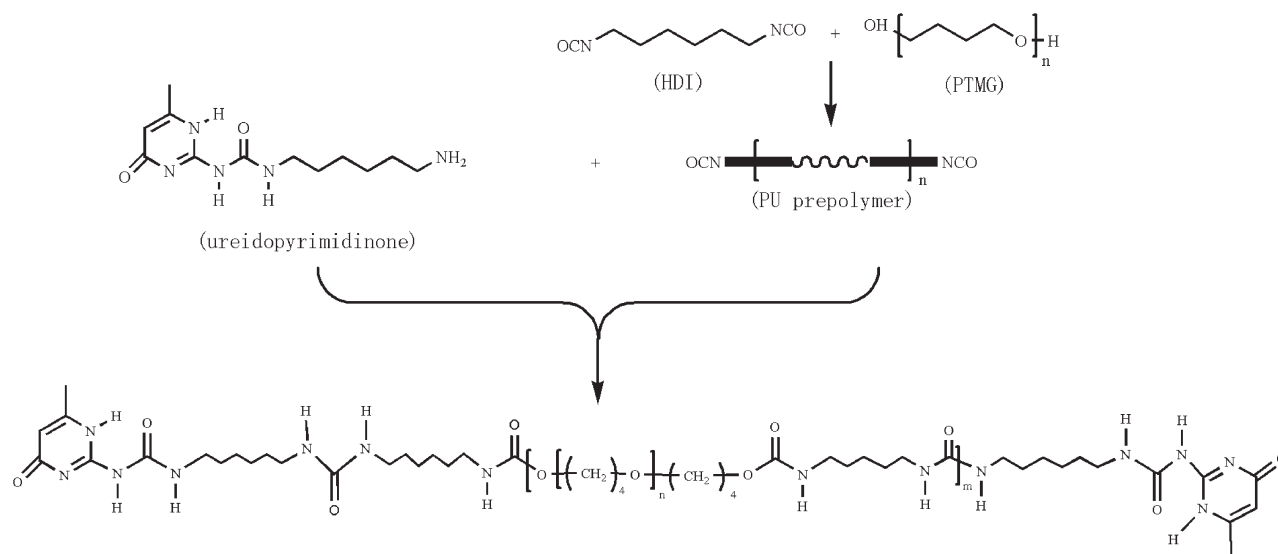
Scheme 2 Synthesis route of UPy-functionalized supramolecular PUs.

and 1,6-hexylenediamime (61.4 g, 528 mmol) were suspended in DMF (200 mL) and stirred for 2 h at room temperature. The reaction mixture was filtered and washed with water and ethanol to yield UPy (19.2 g, 57%). The product was obtained as a white powder and dried *in vacuo* at 30°C for 2 h. ^{1}H-NMR (400 MHz, [D_6] DMSO, δ): 13.12 (s, 1 H), 11.86 (s, 1 H), 10.21 (s, 1 H), 5.51 (s, 1 H), 3.17 (q, 2 H), 2.67 (t, 2 H), 2.00 (s, 3 H), 1.46 (m, 4 H), 1.33 (m, 4 H). FTIR: γ = 3222, 2933, 2859, 1713, 1668, 1603, 1543, 1477, 1433, 1336, 1319, 1264, 1196, 1138, 1028, 968 cm^{-1}.

Synthesis of UPy-functionalized supramolecular Pus

The route was shown in Scheme 2. According to the feed ratio of diisocyanate to polyether glycol (or polyester glycol), a certain amount of diisocyanate was loaded in a three-necked round-bottom flask. Then, PTMG (15 g), DMF (40 mL), and DBTL (two drops) were slowly injected into the flask. The mixture was stirred in N_2 atmosphere and reacted at 70°C for about 2.5 h. To a solution of PU prepolymer, DMF (80 mL) and an excess (1.2 equiv.) of UPy were added to the flask. The mixture was stirred in N_2 atmosphere and reacted at 70°C for 20 h. The completeness of the reaction was checked with Fourier Transform Infrared Spectrometer (FTIR) and the infrared absorption band of —NCO group (2270 cm^{-1}) disappeared after reaction at 70°C for 20 h. The mixture was filtrated to remove the remaining solid powder and the DMF was removed in blast oven at 70°C for 1 day. The resulting material was dried at 70°C for 4 h under reduced pressure. It is not necessary to remove the trace amounts of catalyst and UPy due to its extremely low solubility in DMF. The structure was determined by ^{1}H-NMR (400 MHz, [D_6] DMSO) spectrum (Fig. 1).

Characterization

The FT-IR spectra were recorded on a Perkin–Elmer 1000 FT-IR spectrometer with a resolution of 2 cm^{-1} and the dilute solution was cast onto potassium bromide disc for measured. ^{1}H-NMR spectra were recorded on an Avance-400 spectrometer (Bruker, Switzerland) in DMSO at 25°C, and chemical shifts were reported in ppm relative to tetramethylsilane (TMS). The composition of UPy were analyzed for C and N contents on a Perkin–Elmer 2400 series II CHNS/O analyzer. The sample type was solid and the accuracy is 0.3%. Gel permeation chromatography (GPC) was performed on a Perkin–Elmer Series 200, using DMF as the eluent. Sample concentrations were 2 mg/mL in DMF, and all molecular weights were relative to polyethylene glycol (PEG) standards.
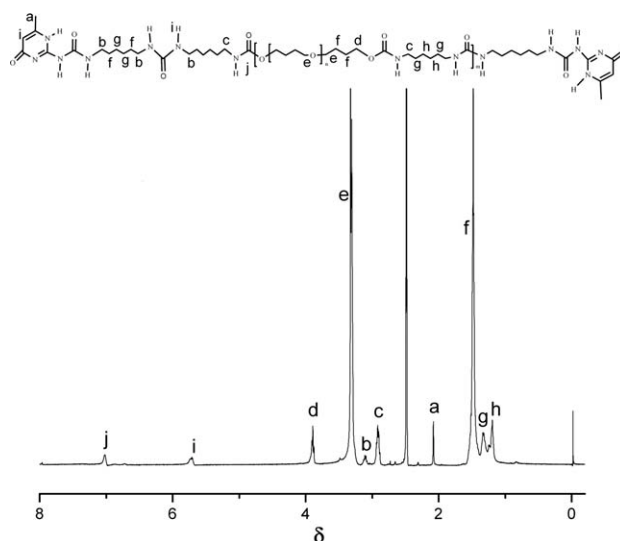

Figure 1 ^{1}H-NMR spectrum of supramolecular PUs.

TABLE I
The Chemical Composition of UPy Determined by CHN Analysis

	Theoretical value	Measured value
N/mass %	26.18	25.42
C/mass %	53.86	53.57
C:N	2.06 : 1	2.11 : 1

DMTA was performed on a TA Instruments DMA2980 in film tension mode to determine the storage modulus (G') and loss factor (tan δ). Samples were characterized at 1 Hz from $-100°C$ to the temperature limit at which the elastic modulus was experimentally inaccessible and the heating rate was $3°C/min$. The thickness, length, and width of the films were about 0.5 mm, 12 mm, and 5 mm, respectively.

TGA was performed on a TA Instruments Q5000IR from 40 to $600°C$ under N_2 flow (40 mL/min) and the heating rate was $20°C/min$. DSC measurements were performed on a TA Instruments Q2000 under N_2 flow (50 mL/min). The heating and cooling rates were $20°C/min$. The thermal history of all samples were eliminated by being heat to $180°C$ under N_2 atmosphere, then all samples were placed for 2 weeks at room temperature before DSC test.

Rheological measurements were performed on a TA Instruments AR G2 at a strain of 1% and a shear frequency of 1 Hz. A parallel plate fixer, that is, plate diameter = 25.0 mm and gap = 800 μm, was used. Samples were characterized from 90 to $180°C$ and the heating rate was $3°C/min$. Tensile properties were measured on the Instron 4465 Universal Electromechanical Tester equipped with a 2 kN load cell in the air at room temperature. The thickness, length, and width of the films were about 0.5 mm, 20 mm, and 4 mm, respectively. The crosshead speed was 200 mm/min and five samples were evaluated to determine stress and strain at break.

RESULTS AND DISCUSSION

A new type of UPy with amine group (Scheme 1) and self-complementary QHB supramolecular PUs (Scheme 2) were successfully synthesized. The chemical composition of UPy was determined by CHN analysis (Table I). The carbon and nitrogen contents of UPy were 53.57% and 25.42%, respectively. The C:N ratio of the sample (measured value) was in agreement with the theoretical value. The structure of final polymer product was confirmed by ^{1}H-NMR spectrum (Fig. 1). Molecular weight, molecular weight distribution and composition of supramolecular PUs, and unfunctionalized PUs were listed in Table II.

Unfunctionalized PUs **U-HPTMG1000-4.9** was a kind of semicrystalline and sticky material with low glass transition temperature ($T_g \approx -80°C$) and melting point ($T_m \approx 20°C$) because of its low molecular weight. However, functionalized PUs **F-HPTMG1000-4.4** became an elastic solid (Fig. 2) and showed distinct properties of thermoplastic elastomers (TPEs) due to the formation of their pseudo-high molecular weight. The viscosity of solution was very high when **F-HPTMG1000-4.4** was dissolved in chloroform, but was very low when **F-HPTMG1000-**

TABLE II
Composition, Molecular Weight, and Thermal Properties of Various PUs

Type	Entry	PUs[a]	M_n[b] (kg/mol)	PDI[b]	T_m[c] (□)	ΔH[c] (J/g)
Unfunctionalized PUs	1	**U-HPTMG1000-4.9**	4.9	2.3	–	–
	2	**U-HPTMG2000-3.9**	3.9	2.3	–	–
Functionalized Supramolecular PUs	3	**F-HPTMG2000-4.6**	4.6	2.5	–	–
	4	**F-HPTMG2000-5.5**	5.5	2.5	–	–
	5	**F-HPTMG2000-7.8**	7.8	2.5	–	–
	6	**F-HPTMG1000-2.9**	2.9	2.5	None[d]	None[d]
	7	**F-HPTMG1000-4.4**	4.4	2.6	29	6.2
	8	**F-HPTMG1000-6.4**	6.4	2.5	–	–
	9	**F-HPTMG1000-8.3**	8.3	2.5	33	8.4
	10	**F-HPTMG1000-10.9**	10.9	2.3	33	8.7
	11	**F-HPTMG1000-13.1**	13.1	2.3	37	12.8
	12	**F-HPTMG1000-14.8**	14.8	2.0	39	14.6
	13	**F-HPTMG1400-7.5**	7.5	2.5	–	–
	14	**F-HPBA2000-7.6**	7.6	2.3	–	–
	15	**F-TPTMG2000-5.3**	5.3	2.5	–	–
	16	**F-IPTMG2000-6.0**	6.0	2.5	–	–

[a] H means HDI, T means TDI, and I means IPDI.
[b] Determined by GPC in DMF.
[c] Determined by DSC in the second heating run.
[d] Did not show any melting peak in DSC curves.

Figure 2 Images of **U-HPTMG1000-4.9** (left) and **F-HPTMG1000-4.** (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

4.4 was dissolved in polar solvent (such as DMF or DMSO) since polar solvent could break the multiple hydrogen-bond. The results indicated the reversibility of UPy groups to solvent's polarity and the high dimerization constants of UPy moiety.

TGA data (Fig. 3) showed that **U-HPTMG2000-3.9** and **F-HPTMG2000-5.5** exhibited an onset of weight loss at 254°C. In contrast to **U-HPTMG2000-3.9,** which has no second degradation, the degradation mechanism appeared to involve two steps for **F-HPTMG2000-5.5**. The first degradation step (328°C) corresponded to the elimination of UPy units since the Δweight-loss (8%) as compared to **U-HPTMG2000-3.9** was close to the theoretical weight of UPy end groups. The second degradation step corresponded to the degradation of the polymer backbone, which appeared at 415°C and 425°C for **F-HPTMG2000-5.5** and **U-HPTMG2000-3.9**, respectively. It indicated that the introduction of UPy into PUs as end groups had a slightly negative effect on their thermal stability.
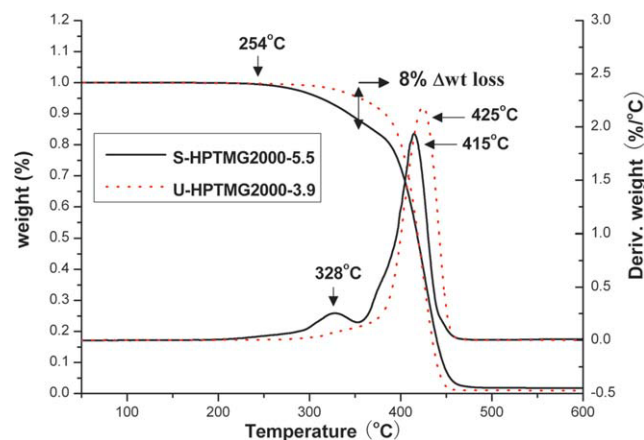
In the DMTA curves of **F-HPTMG1000-4.4** (Fig. 4), a distinct glass transition at −60°C was observed, and a rubber plateau at a high G' value was discernible between −60°C and 90°C. The results indicated that supramolecular structure were formed by the aggregation of dimerized end groups and the "virtual" molecular weight was extremely high in supramolecular PUs. With the increase of temperature, the melting of the polymer backbone was visible by the drop in G' and finally the polymer transferred to viscous flow state at around 135°C. A slight drop in G' at around 33°C was induced by the melting of PTMG soft segments. It was evident that this material dispalyed typical TPEs characteristics at room temperature. The remarkable improvement of mechanical performance was due to the QHB aggregations, which induced the interchain interactions including microcrystalline domain and physical crosslink. For all supramolecular PUs, a gradual decrease in G' was observed from glass to rubber and finally to melting state. With the increase of
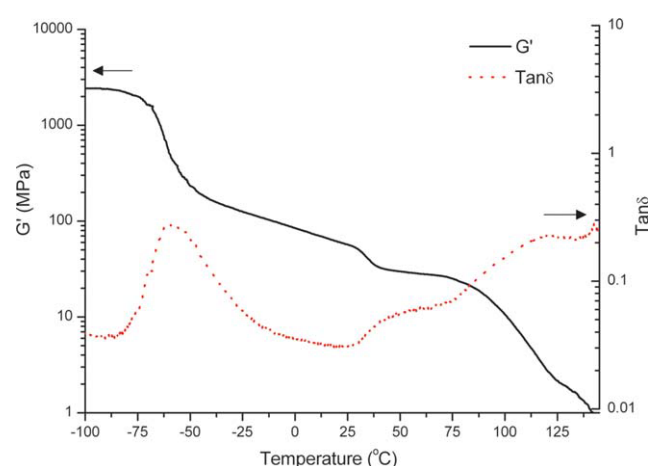

Figure 3 Thermogravimetric analysis of **U-HPTMG2000-3.9** and **F-HPTMG2000-5.5**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 DMTA curves of **F-HPTMG1000-4.4.** [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
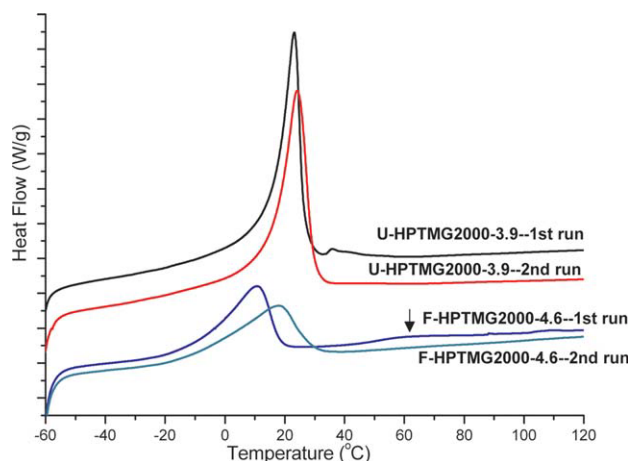
Figure 5 DSC traces of **U-HPTMG2000-3.9** and **F-HPTMG2000-4.6** at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weight, their glass transition temperature (T_g) were all at around −60°C, or were not related to their molecular weight.

The thermal properties of supramolecular PUs were investigated using DSC. **F-HPTMG2000-4.6** showed two melting peaks in the first heating run (Fig. 5), and the second peak at 60°C was probably originating from the melting of the UPy-hexyl-urea dimmer hard-blocks. However, this second melting peak of UPy dimmer would move to about 135°C if the samples were placed at 70°C for 28 h, which could be also observed in the DMTA curves. After the thermal history of DSC samples was eliminated, the microcrystalline domains in supramolecular PUs were melted. In contrast with the samples that were placed at 70°C for 28 h, the lateral stacks in DSC samples were less densely packed and the end-group aggregations were not complete. It indicated that the end-group mobility was too low to form complete microcrystalline domains due to inadequate chain flexibility at room temperature, even if the relaxation time was long enough (2 weeks).

After the functionalization of UPy units, the melting temperature of polymer backbone shifted from 23 to 10°C and a distinct decrease in the melting enthalpy (ΔH decreased from 57 to 24 J/g) was observed since the end-group aggregations were formed. The end-group aggregations would decrease the chain mobility to lower the crystallization, and also restricted the arrangement of PTMG chains at the juncture. With the increase of molecular weight, their ΔH and T_m increased clearly in the second heating run and **F-HPTMG1000-2.9** didn't show any melting peak at all (Table I). This might be due to the content decrease of end-group hard blocks and their restriction effect on PTMG crystallization was reduced.

As mentioned above, a "virtual" high molecular weight was obtained through the formation of end-group aggregations in supramolecular PUs. Despite low molecular weight of the PU chains, excellent mechanical properties were observed below the melting point due to a combination of supramolecular polymerization and nanophase segregation. The degree of polymerization (DP), which was directly proportional to tensile strength of supramolecular PUs, was mainly determined by two factors: end-group concentration and chain flexibility. Their mechanical properties were studied by tensile test and the results were showed in Fig. 6. With the increase of molecular weight, the maximum applied stress increased gradually, reaching the peak at 14.4 MPa for **F-HPTMG1000-13.1**, and then decreased to 11.9 MPa for **F-HPTMG1000-14.8**. When the molecular weight was lower than 13.0 kg/mol, the chain flexibility played a key role in determining their DP. The end groups became more mobile to result in higher DP since the flexibility became better due to the increase of PU chain length. When the molecular weight was higher than 13.0 kg/mol, the end-group concentration became quite low and the end groups could hardly encounter to form microcrystalline domains. So, their DP was low and their maximum applied stress declined. On the other hand, the maximum strain of supramolecular PUs increased significantly with the increase of their molecular weights since the concentration of end-group hard blocks decreased. It could be observed that supramolecular PUs became tougher and exhibited TPEs-like properties. In addition, conventional high molecular-weight PUs ($M_n \approx 30$ kg/mol) were also prepared and the chain-extender was 1,4-butanediol. This PU was a kind of sticky material and showed extremely poor mechanical performance.
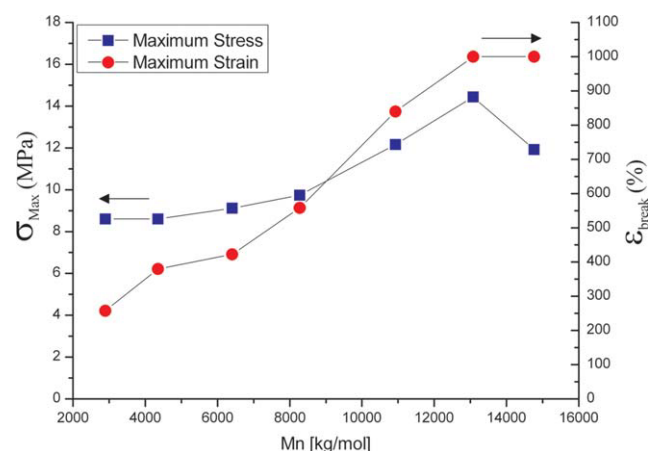

Figure 6 Tensile properties of **F-HPTMG1000-2.9** to **F-HPTMG1000-14.8**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
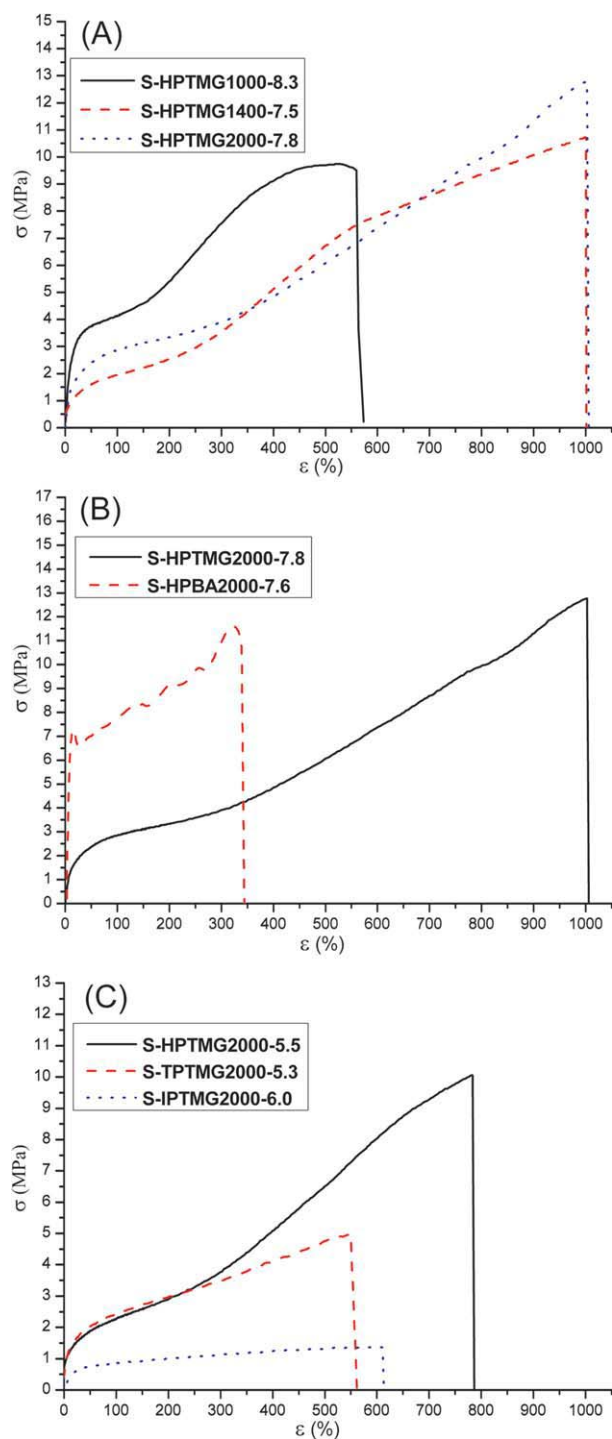
Figure 7 Stress–strain curves of various supramolecular PUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The self-assemble mechanism of supramolecular PUs could also be further testified via adjusting their soft/hard segments. In the **F-HPTMG1000-8.3**, **F-HPTMG1400-7.5**, and **F-HPTMG2000-7.8** [Fig. 7(A)], soft-segment molecular weights were 1000, 1400, and 2000, respectively. Though the hard-segment (HDI) concentration in **F-HPTMG1000-8.3** was the

highest among three samples, its maximum applied stress (9.7 MPa) was the lowest. It indicated that the highest hard-segment concentration led to the worst chain flexibility to restrict the formation of the end-group aggregations. In the **F-HPTMG2000-7.8** and **F-HPBA2000-7.6** [Fig. 7(B)], their soft segments were PTMG 2000 and PBA 2000, respectively. Though the mechanical strength of PBA 2000 (polyester diol) was better than that of PTMG 2000 (polyether diol), the maximum applied stress for **F-HPBA2000-7.6** (11.6 MPa) was lower than for **F-HPTMG2000-7.8** (12.7 MPa). It indicated that the chain flexibility played a key role in determining their DP in this system. In the **F-HPTMG2000-5.5**, **F-TPTMG2000-5.3**, and **F-IPTMG2000-6.0** [Fig. 7(C)], their hard segments were HDI, TDI, and IPDI, respectively. Though TDI (aromatic diisocyanate) was stiffer than HDI (aliphatic diisocyanate), the maximum applied stress for **F-TPTMG2000-5.3** (5.0 MPa) was much lower than for **F-HPTMG2000-5.5** (10.1 MPa) since its worse flexibility led to its lower DP. Finally, Figure 7(C) showed that the maximum applied stress
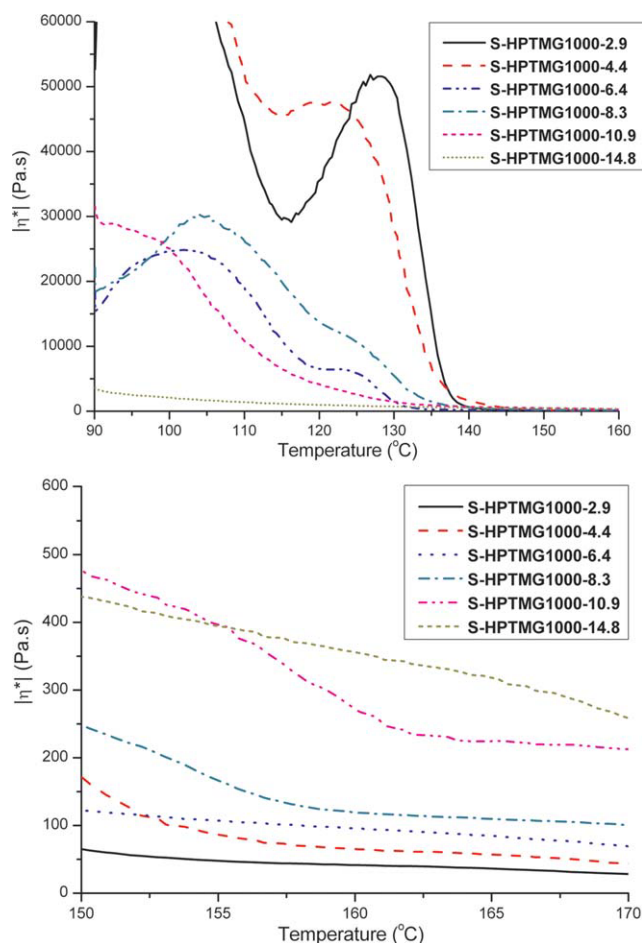

Figure 8 Absolute complex viscosity of various PUs at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for **F-IPTMG2000-6.0** (1.4 MPa) was extremely low because the cyclic structure of IPDI had remarkable steric effect on the formation of end-group aggregations. On the other hand, the maximum strains for **F-HPTMG1000-8.3, F-HPBA2000-7.6,** and **F-TPTMG2000-5.3** were 452%, 330%, and 553%, respectively.

In contrast to the conventional high molecular-weight PUs, thermoreversible supramolecular PUs with a high "virtual" molecular weight showed excellent processability due to their strong temperature dependency of the melt viscosity (Fig. 8). When the temperature was below the melting point, the end-group aggregations led to their good mechanical performance. Supramolecular PUs with lower molecular weight had higher end-group concentration and showed higher absolute complex viscosities. When the temperatures increased to above 155°C, all end-group stacks were melted and supramolecular PUs displayed sharp melting transitions. In Figure 8, there was a distinct increase in viscosity before the sharp melting transition since the "virtual" molecular weight increased. In this process, adequate mobility was obtained for end groups and PU chains rearranged to result in higher DP at the critical temperature. Then, the end-group aggregations were melted with the increase of temperature. In the melting state, supramolecular PUs with lower molecular weight showed lower melting viscosities to guarantee good processability.

CONCLUSIONS

The QHB units were introduced into low molecular-weight PUs as end groups, which were aided by hydrogen bonding of lateral urea groups to make the materials from the sticky to tough. In this new type of supramolecular PUs, reversible end-group interactions between PU chains were formed via microcrystalline domains and physical crosslink. The supramolecular PUs exhibited TPEs-like properties, including a distinct glass transition temperature, a rubber plateau of storage modulus, high melting temperature, and good mechanical performance. Especially, they combined excellent mechanical performance (high tensile strength) and good processability (low melting viscosity). The results indicated that the chain flexibility, and the time/temperature of relaxation process played a vital role in the completely formation of end-group microcrystalline domains. Their self-assemble mechanism was studied and the degree of polymerization (DP), which was directly proportional to their tensile strength, was mainly determined by end-group concentration and chain flexibility.

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