A New Generation of Highly Branched Polymers: Hyperbranched, Segmented Poly(urethane urea) Elastomers

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Introduction. Highly branched polymers, which include dendritic, hyperbranched, or multibranched systems, exhibit interesting and versatile performance. Interest in branched macromolecules is due to several unique properties when compared with their linear analogues, which include low solution and melt viscosities, improved solubilities, and the presence of a large number of functional end groups that offers the possibility for further modification for various high-performance applications. On the other hand, several important structural drawbacks of hyperbranched polymers, with the exclusion of dendrimers, include broad molecular weight distributions, irregular arm growth (branching), and a statistical distribution of functional end groups throughout the macromolecule. More importantly, hyperbranched polymers generally display inferior mechanical properties when compared to their linear analogues since segment lengths are much shorter than the critical molecular weight for entanglement (M_c). A number of excellent reviews are available in the literature, which describes the synthetic methodologies for the preparation of a wide variety of hyperbranched and dendritic macromolecules using condensation, addition, and ring-opening polymerizations and their properties.[1−6]

Linear, segmented polyurethanes or thermoplastic polyurethanes (TPU), which consist of alternating hard and soft segments, represent a commercially interesting and versatile class of polymeric materials.[7−9] Thus, TPUs are quite suitable for a wide range of applications in many diverse fields, ranging from protective coatings to elastomeric fibers and biomaterials.[10] Superior mechanical and thermal properties of TPUs are attributed to microphase-separated morphologies and strong hydrogen bonding between the hard segment domains.[11−13] Early reports of the successful preparation of hyperbranched polyurethanes appeared in 1993 when Spindler and Fréchet[14] disclosed AB₂ type monomers which contained a single hydroxyl (A) and two blocked isocyanate groups (B₂). Polymerization was conducted in refluxing THF in the presence of catalytic amounts of dibutyltin dilaurate to produce a high molecular weight product, which was subsequently end-capped with an aliphatic alcohol.

Kumar and Ramakrishnan[15] prepared an AB₂ type monomer and reported the preparation of wholly aromatic hyperbranched polyurethanes using 3,5-dihydroxybenzoyl azide in a Curtius type rearrangement reaction. Moreover, they also reported the one-pot synthesis of hyperbranched polyurethanes containing di- and triethylene oxide spacer segments.[16] The starting material was 3,5-bis(ω-hydroxy oligoethyleneoxy)-benzoyl azide, which is a classical AB₂ type monomer. The ether spacer segments consisted of short di- and tri(ethylene oxide) units. In a similar fashion, Hong et al.[17] also reported the preparation of hyperbranched polyurethanes which were derived from AB₂ monomers that contained very short ethylene oxide units. Several other reports on the preparation of hyperbranched polyurethanes using AB₂ monomers[18−20] and others are also available.[21−24] More recently, Bruchmann and Schrepp[25] described a one-step methodology for the preparation of hyperbranched poly(urethane urea)s, utilizing commercially available A₂ and B₃ type monomers. A₂ monomer was a diisocyanate (isophorone diisocyanate or toluene diisocyanate), and the B₃ monomer was an aminoalkanediol.

The preparation and structure−property behavior of linear segmented thermoplastic poly(urethane urea)s (TPUU) and polyureas with different soft segments have received significant attention over the past three decades.[7−10] Recently, we disclosed the preparation of segmented, hyperbranched elastomers and engineering thermoplastics[26] which displayed mechanical properties comparable to their linear analogues. In the present report, a simple oligomeric A₂ + B₃ approach will be described for the preparation of segmented, hyperbranched polyureas and poly(urethane urea)s with mechanical properties comparable to their linear analogues. This approach utilizes an isocyanate end-capped polyether (PPO or PTMO) as an oligomeric A₂ monomer and a B₃ triamine monomer. This novel approach can easily be extended to a large number of telechelic oligomers (A₂) including poly(dimethylsiloxane) (PDMS) or poly(ethylene glycol) and trifunctional monomer (B₃) combinations for the preparation of a wide range of polymeric materials from elastomers to engineering thermoplastics.

Materials, Synthetic Procedures, and Characterization. Bis(4-isocyanatohexyl)methane (HMDI) (Bayer) and cyclohexyl isocyanate (CHI) (Aldrich) with purities greater than 99.5% were used. Poly(tetramethylene oxide) (PTMO) oligomers (Terathane, Du Pont) with number-average molecular weights (M_n) of 2000 (PTMO2) and 3500 g/mol (PTMO3) and α,ω-amine-terminated poly(propylene oxide) oligomer (PPO) (Jeffamine D-2000, Huntsman) with M_n of 2000 g/mol (PPO2) were used as received. Tris(2-aminoethyl)amine (TRIS) (Aldrich), a poly(oxyalkylene)triamine (Jeffamine T-403, Huntsman) (ATA), 2-methyl-1,5-diaminopentane (MDAP) (Dytek A, Du Pont), HPLC grade isopropyl alcohol (IPA), and tetrahydrofuran (THF) (Aldrich) were all used as received. Chemical structures of triamines are depicted in Figure 1.

All reactions were conducted in three-necked, round-bottomed flasks that were equipped with an overhead stirrer, addition funnel, and nitrogen inlet. Isocyanate end-capping reactions of PTMO were conducted in bulk at 80 °C with 50 ppm dibutyltin dilaurate as the catalyst. Isocyanate end-capping reactions of amine-

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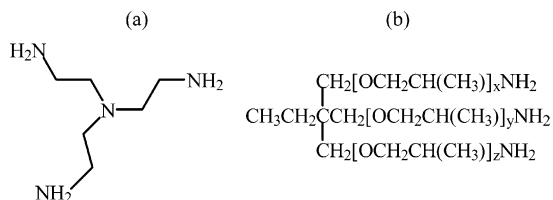* Corresponding author: e-mail telong@vt.edu.

(a)   (b)

H$_2$N

N — NH$_2$

NH$_2$

CH$_2$[OCH$_2$CH(CH$_3$)]$_x$NH$_2$
CH$_3$CH$_2$CCH$_2$[OCH$_2$CH(CH$_3$)]$_y$NH$_2$
CH$_2$[OCH$_2$CH(CH$_3$)]$_z$NH$_2$

Figure 1. Chemical structures of triamines used: (a) tris(2-aminoethyl)amine (TRIS), (b) poly(oxyalkylene)triamine (ATA), where $x + y + z = 5.3$ and $M_w = 440$ g/mol.

Table 1. Average Molecular Weight and Molecular Weight Distribution (M_w/M_n) of the Polymers Formed for the PTMO2 + ATA System as a Function of the Amount of A$_2$ Added and Corresponding B$_3$ Conversion (p_B)

[A$_2$]	[B$_3$]	p_B	M_n (g/mol)	M_w (g/mol)	M_w/M_n
0.69	1.00	0.46	16 000	24 000	1.50
0.81	1.00	0.54	17 000	37 000	2.18
0.95	1.00	0.64	26 000	75 000	2.88
1.02	1.00	0.68	28 000	116 000	4.14
1.10	1.00	0.74	63 000	390 000	6.19
1.12	1.00	0.75	gel	gel	

terminated PPO were performed in IPA at room temperature by the dropwise addition of the oligomer solution into the HMDI solution in 15−20 min.[27] Quantitative conversions were confirmed using FTIR spectroscopy (Nicolet Nexus 870 FT-IR). The segmented hyperbranched polyureas based on PPO were prepared in IPA. PTMO-based polymers were prepared in THF/IPA (25/75 vol/vol) solutions by the dropwise addition of the A$_2$ solution into a solution of B$_3$ at room temperature. Reactions were conducted in dilute solutions, typically at 10−15% solids with very strong agitation. Since equimolar amounts of A$_2$ and B$_3$ (or in terms of equivalents [A]/[B] = 2/3 = 0.67) were used, [B] was always in excess, and gelation was not observed during the reactions. To monitor the growth in the molecular weight of the products, samples were withdrawn from the reactor at different levels of A$_2$ addition and end-capped with CHI prior to GPC analysis. GPC was conducted on a Waters system that was equipped with three in-line PLgel 5 mm Mixed-C columns, an auto-sampler, a 410 RI detector, a Viscotek 270 dual detector, and an in-line Wyatt Technologies miniDawn multiple angle laser light scattering (MALLS) detector at 40 °C in THF at 1 mL min⁻¹ using polystyrene standards. Because of its insolubility in THF, the GPC of the linear TPUU (PTMO2-MDAP) was conducted on a Waters system equipped with Styragel HT colums and an RI detector in NMP containing 0.05 M LiBr, at 40 °C with a flow rate of 1 mL/min. DMA was conducted on Seiko DMS210. Samples were quenched from room temperature to −125 °C and thereafter subjected to a heating rate of 2 °C/min and 1 Hz. A Perkin-Elmer Pyris-1 instrument was used for DSC analysis at 10 °C/min under a helium atmosphere, and all reported data were obtained from the second heating. Stress−strain tests were conducted on an Instron 4400R using dog-bone-shaped samples with 2.9 mm width, 10 mm grip separation distance, and 25 mm/min cross-head speed.

Results and Discussion. Segmented, hyperbranched poly(urethane urea) elastomers were prepared using an oligomeric A$_2$ + B$_3$ approach, where isocyanate end-capped PTMO oligomers (A$_2$) were slowly added to a triamine (B$_3$) solution at room temperature. It is well-known that aliphatic amines react with isocyanates instantaneously at room temperature.[7,9,27] Table 1 summarizes the growth of the number- and weight-average
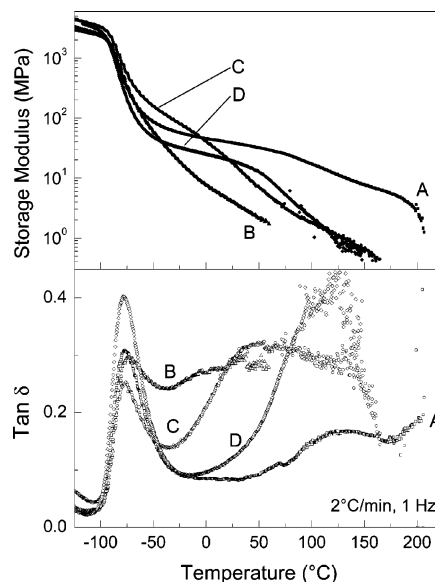

Figure 2. Dynamic mechanical behavior of hyperbranched, segmented poly(urethane urea) elastomers and a linear TPUU: (top) storage modulus−temperature curves and (bottom) tan δ−temperature curves (A) PTMO2-MDAP*, (B) PTMO2-ATA*, (C) PTMO2-ATA, and (D) PTMO2-TRIS (* = no CHI end-capping).

molecular weights of the polymeric products for a PTMO2 + ATA (A$_2$ + B$_3$)-based system as a function of the amount of added A$_2$. As expected, a gradual increase in M_n was observed as more A$_2$ was added to B$_3$ in the polymerization reactor.

It is also interesting to note that a dramatic increase in molecular weight distribution (M_w/M_n) of the product was observed as A$_2$ was added. This observation supports the formation of branched systems. Assuming complete reaction of A groups with B groups upon addition, the gel point for the system, where [A$_2$] = [B$_3$], is at $p_A = 0.87$ or $p_B = 0.58$ (neglecting internal cyclization),[28,29] where p_A and p_B are the conversion of A and B groups, respectively. Table 1 shows that gelation was observed above $p_B = 0.75$, which was much higher than the critical value of 0.58. This clearly indicated internal cyclization, which is typical for A$_2$ + B$_3$ polymerizations.[1−4,29−31] The data presented in Table 1 support the formation of fully soluble, hyperbranched segmented polymers under these reaction conditions. Chemical compositions of the segmented, hyperbranched PUUs and the corresponding linear TPUU are provided in Table 2. Representative average molecular weights and molecular weight distributions (M_w/M_n) of the hyperbranched polymers are provided in Table 3. Again, these results clearly indicate the formation of high molecular weight polymers with broad molecular weight distributions, which are typical for hyperbranched polymers.

These novel, segmented, hyperbranched polymers also display excellent thermomechanical and tensile properties as a function of the chemical composition. Figure 2 depicts the comparative DMA behavior of hyperbranched elastomers, PTMO2-ATA* (uncapped), PTMO2-ATA and PTMO2-TRIS (both end-capped with CHI), and the linear TPUU (PTMO2-MDAP). It should be noted that PTMO2- and ATA-based hyperbranched elastomers (PTMO-ATA and PTMO-ATA*) and the linear TPUU (PTMO2-MDAP) have similar hard segment contents while the hyperbranched elastomers

Table 2. Chemical Compositions of Segmented, Hyperbranched Poly(urethane urea)s and a Homologous Linear TPUU (PTMO2-MDAP) (* = No CHI End-Capping)
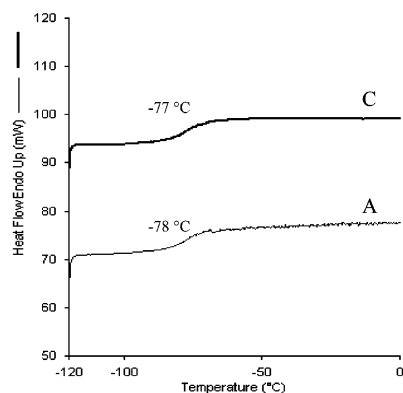
	soft segment			triamine			
sample	HMDI (g)	M_n (g/mol)	amount (g)	type	amount (g)	CHI (g)	HS (%)
PTMO2-ATA*	17.70	2000	67.50	ATA	14.85		33
PTMO2-ATA	17.00	2000	64.70	ATA	14.25	4.05	35
PTMO3-ATA	11.45	3500	76.25	ATA	9.60	2.70	24
PPO2-ATA	17.00	2000	64.70	ATA	14.25	4.05	35
PTMO2-TRIS	18.80	2000	71.55	TRIS	5.20	4.45	28
PTMO2-MDAP*	26.90	2000	65.00	MDAP	8.10		25

Table 3. Average Molecular Weight and Molecular Weight Distribution (M_w/M_n) of Various Segmented Hyperbranched Polymers ([A]/[B] = 0.67) End-Capped with CHI and a Homologous Linear TPUU (* = No CHI End-Capping)

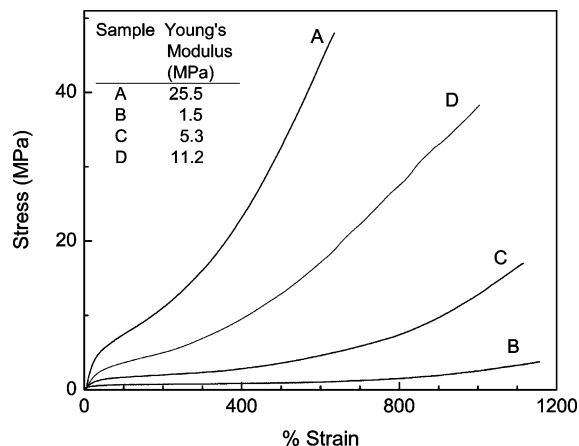| sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PTMO2-ATA	33 000	111 000	3.36
PTMO3-ATA	42 500	179 000	4.21
PPO2-ATA	25 000	110 000	4.40
PTMO2-MDAP*	27 000	42 000	1.56

PTMO3-ATA and PTMO2-TRIS have a lower amount of hard segment content. All polymers displayed two-phase behavior with the PTMO soft segment transition occurring at approximately −75 °C. As depicted in Figure 3, DSC analysis of PTMO2-ATA and PTMO2-MDAP also showed similar soft segment transitions at −77 and −78 °C, respectively, and a significant shift from the pure PTMO T_g (−79 °C) was not observed. The linear TPUU exhibited a much more extended rubbery plateau reaching to about 200 °C and a higher plateau modulus than the hyperbranched polymers. While a lower plateau modulus could suggest a lower entanglement density, it must be recognized that these hyperbranched polymers have an equal to or lower amount of hard segment content compared to the linear analogue; however, a lower tan δ magnitude is observed at the same T_g peak. If it presumed that this observation is only attributed to entanglement, then why is the magnitude of the PTMO transition depressed compared to the linear analogue? This was presumed to be due to some phase mixing that may account for the changes in plateau modulus. Detailed studies are currently underway in order to better understand this interesting phenomenon in these novel hyperbranched elastomers.

As expected, a urea end-capped segmented hyperbranched polymer (PTMO2-ATA) displayed better thermomechanical integrity than its uncapped homologue (PTMO2-ATA*) due to increased hydrogen bonding from the strong end group interactions. In fact, such interac-

tions are also reflected in the more extended rubbery plateau of the end-capped polymer, which reaches to nearly 100 °C, whereas the uncapped analogue only extends to about 50 °C. In addition to end-capping, a significant influence of the triamine structure on the thermomechanical behavior was observed based on the DMA analysis of the urea end-capped, TRIS-based polymer (PTMO2-TRIS), which displayed a well-developed rubbery plateau extending to approximately 75 °C, as shown in Figure 2.

Stress−strain curves and the data for both linear and hyperbranched TPUUs are shown in Figure 4. The linear TPUU, which contained 35 wt % urea hard segments, as expected, was a very strong elastomer with a modulus of 25.5 MPa, tensile strength of 42.0 MPa, and an elongation at break value of 620%. The uncapped segmented hyperbranched elastomer based on ATA trimer (PTMO2-ATA*) was weak and displayed modulus and tensile strength values of 1.50 and 3.10 MPa, respectively, but extended to over 1100% at break. It is important to note that although this sample is not end-capped with CHI, it still displays excellent recovery following 1100% elongation. Urea end-capping (PTMO2-ATA) improved the tensile properties significantly and resulted in the formation of a relatively strong elastomer which displayed modulus and tensile strength values of 5.3 and 15.7 MPa, respectively, and an elongation at break value over 1000%. Similar to the uncapped homologue (PTMO2-ATA*), following the 1100% elongation, PTMO2-ATA also exhibits excellent recovery. This behavior is an important signature in providing valuable information about entanglements and relaxation time features in these novel elastomers. A detailed investigation of the hysteresis behavior of the segmented hyperbranched poly(urethane urea)s is in progress. It is noted that the chemical structure of the

Figure 3. Differential scanning calorimetry of a hyperbranched, segmented poly(urethane urea) elastomer and a linear TPUU: (A) PTMO2-MDAP*, (C) PTMO2-ATA.

Sample	Young's Modulus (MPa)
A	25.5
B	1.5
C	5.3
D	11.2

Figure 4. Comparison of the stress−strain behavior of hyperbranched, segmented poly(urethane urea) elastomers and a homologous linear TPUU: (A) PTMO2-MDAP*, (B) PTMO2-ATA*, (C) PTMO2-ATA, and (D) PTMO2-TRIS (* = no CHI end-capping).

triamine had a significant influence on the mechanical properties. As shown in Figure 4, a urea end-capped PTMO2-TRIS-based hyperbranched PUU displayed a modulus of 11.2 MPa, an ultimate tensile strength of 38.2 MPa, and an elongation at break of 1000%, although it contained a lower urea hard segment content of 28 wt % compared to PTMO2-ATA (35 wt %). As can be noted from Figure 4, the tensile behavior of the PTMO2-TRIS-based hyperbranched PUU approaches that of the linear sample (PTMO2-MDAP) despite the fact that this sample contains only 28 wt % hard segments as compared to the 35 wt % in the linear sample. It is also interesting to note that the hyperbranched system exhibits strain-induced crystallization when the sample is uniaxially stretched and held at an extension ratio of 4.5× (as confirmed using wide-angle X-ray scattering). Strain-induced crystallization of PTMO (M_w > ca. 2000 g/mol) in linear segmented copolymers is widely known in the literature and forms the basis of many commercial applications of such materials.[32]

Conclusions. Novel segmented hyperbranched polymers were obtained through oligomeric $A_2 + B_3$ chemistry. These compositions exhibited a microphase morphology as denoted by DMA. The similarity in soft segment glass transition behavior and strain hardening character of the hyperbranched systems (at least sample PTMO2-TRIS) with that of the linear system suggests such hyperbranched materials have considerable promise for structural applications. Detailed studies of the preparation, physical properties (including hysteresis, recovery, and relaxation behavior), and the morphological and rheological features of these and other novel, segmented hyperbranched polymers will be forthcoming.[33]

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