HIGHLY BRANCHED, SEGMENTED POLYUREA ELASTOMERS THROUGH OLIGOMERIC A_2+B_3 APPROACH

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Introduction

Highly branched (HB) polymers are tree-like macromolecules which display unique combination of physical and chemical properties. Availability of a large number of reactive end groups offer modification for a large number of specific end-use applications. Low solution and melt viscosities of hyperbranched polymers, as well as high solubilities provide ease of processing. Unfortunately, HB polymers synthesized by conventional methods have broad molecular weight distributions, irregular arm growth and poor mechanical properties. By applying oligomeric A_2+B_3 method with controllable addition of reactants, segmented, HB polyurea elastomers having mechanical properties comparable to their linear analogs can be prepared [1-5]. In this study we investigated (i) role of the concentration of the reaction medium on gelation, (ii) influence of the reaction procedure followed on polymer properties, and (iii) influence of the soft segment structure, chain extender and polymer composition on structure-property behavior.

Experimental

Materials: Bis(4-isocyanatocyclohexyl)methane (HMDI) and 1,6-hexamethylene diisocyanate (HDI) were kindly provided by Bayer, Germany. Cyclohexyl diisocyanate (CHDI) was purchased from DuPont and cyclohexyl isocyanate (CHI) from Aldrich. Purities of isocyanates were greater than 99.5%. Tris(2-aminoethyl)amine (TRIS) and α,ω-aminopropyl terminated poly(tetramethylene oxide) (PTMO) (M_n =1080 g/mol) were purchased from Aldrich. α,ω-Aminopropyl (PDMS-NH_2) oligomers with molecular weights 3200 and 10800 g/mol were obtained from Wacker-Chemie, Germany. Di and trifunctional, amine terminated polyethers; Jeffamine T-3000 (PPO with M_n=3060 g/mol), Jeffamine ED-900 (PEO with M_n=1000 g/mol) and polyoxyalkylenetriamine (Jeffamine T-403) (TRI) (M_n=440 g/mol) were kindly supplied by Hunstman. Poly(tetramethylene oxide) glycol (PTMO) with $<M_n>$=2000 g/mol, (Du Pont), N-butylamine (NBA) (Aldrich), HPLC grade isopropyl alcohol (IPA), and tetrahydrofuran (THF) (Aldrich) were also used. Dibutyltin dilaurate (T-12) was obtained from Air Products.

Gelation studies: All reactions were performed in 3-neck, round bottom flasks equipped with an overhead stirrer and addition funnel. For the determination of the effect of solution concentration on gelation HMDI was used as A_2 and TRI as B_3. Reactions were carried out at room temperature under strong agitation. Reactants were dissolved separately in IPA at specific concentrations and one of the reactants was added over the other one dropwise until the observation of the gelation. When A_2 was added over B_3, TRI was placed in the reactor and HMDI into the additional funnel. Reverse was performed in the case of B_3 addition over A_2.

Synthesis of HB copolymers: All reactions were conducted in dilute solutions, typically at 10-12% by weight solids in IPA and/or THF. To observe the influence of the reaction procedure used on polymer properties, isocyanate end-capped PTMO was prepared in bulk at 80˚C with a catalyst. The prepolymer was dissolved in THF and was added dropwise over B_3 in IPA or B_3 in IPA was added onto prepolymer solution. Polymerizations were terminated by end-capping. CHI was used if there was excess amine in the medium (A_2 over B_3) and NBA was used if there was excess isocyanate (B_3 over A_2). Oligomeric B_3 (T-3000) and ED (ethylene diamine) were used to investigate the effect of the chain extender. In these reactions first T-3000 and ED were introduced into the reactor onto which the diisocyanate was added dropwise. Reactions were terminated by end-capping. Isocyanates used here were HMDI, HDI and CHDI. HB silicone-urea copolymers were prepared by end-capping of amine terminated PDMS oligomers with HMDI followed by the reaction with TRIS. Polymers with ED-900 were also synthesized where HMDI was used for the end-capping of ED-900 and TRIS as B_3.

Polymer films were obtained by pouring the films on Teflon molds. Molds were kept at room temperature for one day and then put in an air oven maintained at 50 ºC until complete evaporation of the solvent.

Instrumentation: Reactions were followed by FTIR spectroscopy on a Nicolet Impact 400D FTIR spectrometer, using thin films cast on KBr disks. Stress-strain tests were conducted on an Instron 4411 using dog-bone-shaped samples at room temperature with a 25 mm/min cross-head speed. Thermal analysis was obtained on a TA Q100 DSC and Q800 DMA:

Results and Discussion

Influence of the reaction procedure and solution concentration on the gel point Monte Carlo simulation and experimental results: In a previous study [1] gel points were determined at different solution concentrations where A_2 (HMDI) was slowly added over B_3 (TRI). This study is extended by determining the gel points when B_3 was slowly added over A_2 and repeating some of the reactions done previously. A sudden increase in the solution viscosity indicated the formation of gels. Solution concentrations and experimental gel point conversions are shown in Table 1.

Table 1. Influence of the concentration of reaction medium on gel point in HB polyureas formed by the slow addition of HMDI (A_2) over TRI (B_3) in IPA and vice versa at room temperature (* From [1]).

Solution concentration (wt %)	**A_2 over B_3** A_2 added at gel point (mol %)	**B_3 over A_2** A_2 consumed at gel point (mol %)
5	no gel	no gel
7.5	120.5*	102.6
10	109.4	85.4
15	97.2*	84.8
20	89.9	81.3
25	77.7	67.2

At 5% solution concentration no gelation was observed in either method (A_2+B_3 or B_3+A_2). As expected and can be seen from Table 1 as the solution concentration increased the conversion at gel point decreased. Additionally, at the same solution concentration, less amount of reactant was used in the case of B_3 over A_2 addition in comparison to the amount of reactant used in A_2 over B_3 addition.

Monte-Carlo simulations were also performed to understand the molecular weight development in polymers obtained by B_3 over A_2 addition, assuming different cyclization ratios (to mimic solution concentration). Figure 1 illustrates the growth of number average molecular weight with respect to B_3 conversion.

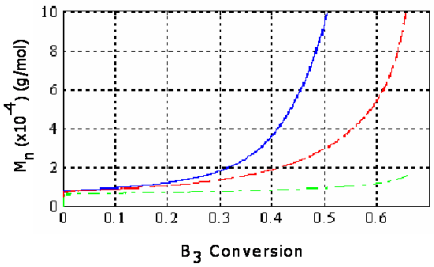


Figure 1. Development of number average molecular weight as a function of B_3 conversion for the addition of B_3 over A_2. (—) 1% cyclization, (—) 10% cyclization, (—) 100% cyclization

As can be observed from the above figure, when cyclization is less than 1%, gelation occurs at about 50% addition of B_3, which is the theoretical gel point for B_3 addition on A_2. On the other hand, in case of 10% cyclization, gelation occurs at about 65% addition of B_3. At a very high cyclization ratio of 100%, polymer molecular weight does not increase and gelation is not formed, as expected (e. g. 5% by weight solution). These results show that the amount of cyclic structures formed and the amount of the reactant to be added on the other is closely related with the concentration of the reaction medium.

Comparison of the mechanical properties of HB poly(urethane urea) polymers prepared by A_2+B_3 and B_3+A_2 approach: In this part, PTMO-2000 based HB poly(urethane urea) (PUU) copolymers containing the same amounts of hard segments were synthesized by the addition of A_2 over B_3 and

B_3 over A_2. In both reactions solution concentrations were about 10% by weight (in IPA and THF) and hard segment ratios were 25%. Chemical compositions of these copolymers are given in Table 2.

Table 2. Chemical compositions of PTMO-2000 based HB poly(urethane urea) copolymers synthesized by A_2+B_3 and B_3+A_2 methods

Method	PTMO(2K) (g)	HMDI (g)	TRIS (g)	NBA (g)	CHI (g)	HS (%)	Solution conc.(%)
A_2+B_3	7.088	1.711	0.408	--	0.285	25.3	10
B_3+A_2	7.012	1.889	0.262	0.251	--	25.5	10

Figure 2 gives the stress-strain behavior of these polymers obtained by two different methods. It is interesting to note that HB PUU prepared by A_2+B_3 approach displays nice elastomeric properties, with a tensile strength of 12.7 MPa, Young's modulus of 5.0 MPa and elongation of 905%. On the other hand, polymer having the same chemical composition formed by the addition B_3 over A_2 displayed lower mechanical properties. This polymer had 43% of the tensile strength and 80% of the modulus of the homologous PUU synthesized by A_2 over B_3 approach. Elongation at break was 880%.

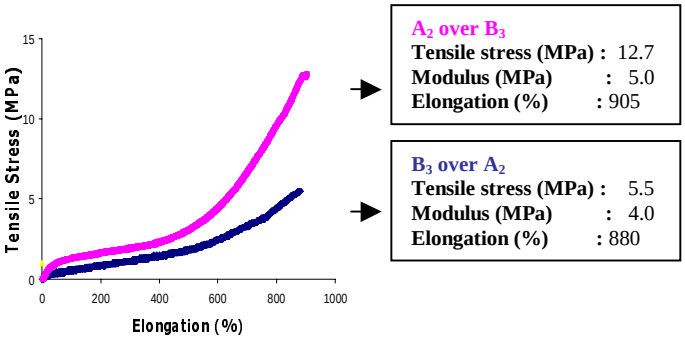


Figure 2. Tensile behavior of the PUU prepared by A_2+B_3 and B_3+A_2 method

Investigation of the influence of end-capping on tensile behavior: Amine terminated PTMO was used to investigate the influence of end-capping on mechanical properties. Chemical compositions of these copolymers are given in Table 3.

Table 3. Chemical compositions of the PTMO-NH_2 based HB polyurea copolymers with and without end-capping

Polymer	Method	PTMO* (g)	HMDI (g)	TRIS (g)	CHI (g)	HS (%)	Solution conc.(%)
	A_2+B_3	3.264	1.571	0.458	0.376	42.5	10
	A_2+B_3	2.240	1.099	0.321	--	38.7	10

The solution concentrations were again 10% by weight in IPA and THF. However, hard segment ratios were higher than the PTMO-2000 based polymers. One of the polymers was synthesized by capping the reactive ends with CHI whereas the other was not end capped. Figure 3 gives the comparative tensile behavior for these HB polymers. Tensile strength of the end-capped polyurea was 25.0 MPa whereas for the uncapped polymer it was measured as 18.9 MPa. Additionally, modulus of the capped one was 125.3 MPa but it was 70.4 MPa for the uncapped one. From these results, it can clearly be seen that end-capping strongly improves the mechanical properties, which is expected.

Investigation of the influence of chain extender on tensile behavior: Trifunctional T-3000 oligomer was reacted with difunctional HMDI and ED (chain extender) for the investigation of the effect of the chain extender in mechanical properties of the hyperbranched polyureas. Chemical compositions of these elastomers are provided on Table 4. IPA was used as the solvent, where solution concentrations were kept around 10% in both reactions.

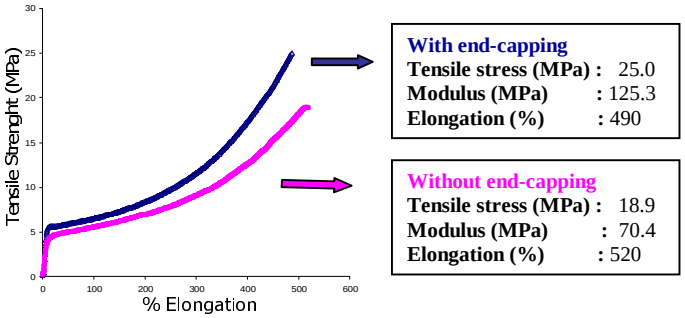


Figure 3. Tensile properties of the copolymers with and without end-capping

Table 4. Chemical compositions of HB polyurea elastomers synthesized by using oligomeric B_3 (T-3000), HMDI as A_2 and ED chain extender

Method	T-3000 (g)	HMDI (g)	ED (g)	CHI (g)	HS (%)	Solution conc.(%)
A_2+B_3	6.121	1.067	0.131	0.137	17.9	10
A_2+B_3	6.121	1.585	0.242	0.262	25.4	10

Hard segment ratio increases from 17.9% to 25.4% with the incorporation of the chain extender. **Table 5** gives the tensile properties of chain extended polyureas, with different amounts of ED chain extender. As expected, chain extension improves the tensile properties, since it increases the hard segment content. Tensile stress was 3.50 MPa in the polymer containing higher amount of ED, more than twice of the tensile stress of the other polymer. On the other hand, modulus increased from 2.0 MPa to 8.2 MPa and elongation increased from 105% to 190%.

Table 5. Stress-strain behavior of the polyurea copolymers having different amounts of chain extender

Method of synthesis	Urea hard segment (%)	Tensile stress (MPa)	Elastic modulus (MPa)	Elongation (%)
A_2+B_3	17.9	1.45	2.0	105
A_2+B_3	25.4	3.50	8.2	190

Conclusions

Highly branched, segmented polyureas were formed through oligomeric A_2+B_3 approach, where A_2 was slowly added over B_3 or vice versa. As expected, gel point determination studies showed that as the concentration of reaction medium decreases gelation is delayed. This is probably due to increased internal cyclization. Polymers prepared by the addition of A_2 over B_3 display better mechanical properties than those prepared by B_3 over A_2 addition. Urea end capped polymers show better mechanical strength than their uncapped counterparts due to stronger hydrogen bonding in the capped systems. Increasing the amount of chain extender increases the tensile strength of branched polymer obtained.

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