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ARTICLE *in* PROGRESS IN ORGANIC COATINGS · JULY 2009

Impact Factor: 2.36 · DOI: 10.1016/j.porgcoat.2009.02.007

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Structure–Thermomechanical Property Correlations of Highly Branched Siloxane–Urethane Networks

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Supporting Information

ABSTRACT: A series of B_3 core-terminated highly branched siloxane–urethane polymers was synthesized through the $A_2 + B_3$ route. Isophorone diisocyanate (IPDI)-terminated polydimethylsiloxane (PDMS) was used as the A_2 unit and triethanol amine as the B_3 core. Size exclusion chromatography (SEC) studies revealed decreasing number-average molecular weights for the branched polymers and increasing tendency toward lower molecular weight species formation with increased proportion of B_3 core in the branched polymers. The degree of branching and fraction of dendritic units, evaluated from ^{1}H NMR, increased monotonically with increasing B_3 core in the branched polymers. Cross-linked networks of the highly branched polymers were prepared by reaction of the terminal hydroxyl groups with tetraethoxysilane (TEOS) at room temperature. The sol fractions obtained for the networks from solvent extraction studies were consistent with the non-network-forming low molecular weight fractions obtained from the deconvoluted SEC traces. The solubility parameter, Flory–Huggins interaction parameter, and cross-link density of the networks were evaluated from swelling studies. FTIR spectroscopy was used to evaluate the degree of hydrogen bonding of the branched networks. The thermomechanical properties of the networks were evaluated by stress–strain measurements and dynamic mechanical analysis, and the results were correlated with the structural parameters, such as degree of branching, extent of hydrogen bonding, and cross-link density.

INTRODUCTION

Hyperbranched polymers represent a class of highly branched soluble macromolecules, which has attracted a lot of attention during the past decade. This has resulted in development of several new and simpler synthetic approaches for their preparation.[1−7] Branched polymers containing urethane or urea groups within the backbone are well established as precursors for various polyurethane (PU) resins, foams, and coatings and thus have high industrial importance.[8−13] In general, isocyanate chemistry is thoroughly studied for polymers due to the high versatility and potential to tailor material characteristics by varying the structure of the monomers, monomer combinations, as well as morphology and branch point density control. Hydrogen bonding plays a critical role in this class of materials, and these noncovalent secondary interactions often significantly influence the material properties.[14,15]

Spindler and Fréchet first reported the preparation of high molecular weight hyperbranched polyurethanes using AB_2-type monomers containing a hydroxyl (A) and two blocked isocyanate groups (B_2).[16] Kumar et al. also used an AB_2-type monomer and reported the preparation of fully aromatic hyperbranched polyurethane from 3,5-dihydroxybenzoylazides using Curtius-type rearrangement reactions.[17] Since the AB_x approach necessitates rather innovative chemistry approaches due to the high reactivity of the NCO group, researchers resorted to the $A_2 + B_y$ approach for hyperbranched polyureas and polyurethanes to simplify the process and facilitate work with more commonly available monomers. Thus, hyperbranched polyurethane polyols and polyisocyanates could be synthesized based on conventional raw materials, exploiting the differences in reactivity in an $A_2 + CB_2$ or $AA' + CB_2$ (or $AA' + B'B_2$) approach.[18−20] On the basis of the present work, we discuss certain literature reports on the $A_2 + B_3$ approach to prepare hyperbranched polyurethanes. Sheth et al. reported the preparation of segmented hyperbranched polyurethanes by an oligomeric $A_2 + B_3$ approach.[21] They used diisocyanate-capped polyethylene oxide or polypropylene oxide as the A_2 units, while oligomeric triamines were used as the B_3 core. The resulting products with degree of branching in the range 30–50% showed microphase-separated morphologies and mechanical properties close to their linear analogues. Unal et al. demonstrated the preparation of segmented, hyperbranched polyurethaneureas using the same approach,[22] where A_2 was an isocyanate end-capped polyether glycol, such as poly(tetramethylene oxide) glycol (PTMO), and B_3 was an aliphatic triamine. They reported the importance of slow addition of A_2 units onto the B_3 core to control the gelation, structural regularity, and minimization of cyclic species in preparation of branched polyurethanes. Oguz et al. reported the structure development in hyperbranched polymers prepared by the oligomeric method through experimental studies and Monte Carlo simulations.[23] They observed a strong influence of solution concentration on the gel point and the extent of cyclization on the polymers formed. Although there are several such reports on synthesis and characterization of hyperbranched or highly branched polyurethanes and polyureas, studies on further use of end-functionalized polymers to prepare cross-linked networks are limited. Further, in all these

Received: April 2, 2011
Revised: February 1, 2012
Accepted: February 1, 2012
Published: February 1, 2012

   dx.doi.org/10.1021/ie200629w | *Ind. Eng. Chem. Res.* 2012, 51, 3531–3540

reports the oligomeric A_2 unit used is either a polyther or a polyester-type polyol capped with an aliphatic or aromatic disocyanate.

Thus, the objective of the present work is to establish structure−property correlations of networks of end functional highly branched siloxane−urethanes cross-linked with a tetrafunctional cross-linker (TEOS). Hydroxyl end functional highly branched siloxane−urethane polymers were prepared by reacting an isophorone diisocyanate-capped PDMS (A_2) unit with a triethanol amine (B_3) in different proportions using the oligomeric A_2 + B_3 approach. The degree of branching of the polymers was evaluated by ^{1}H NMR using both Frey and Fréchet methods. Heterogeneity in the molar mass distribution of the polymers was evaluated by deconvolution of the GPC traces. The hydroxyl end-functionalized polymers were reacted with tetrethoxy silane (TEOS) at room temperature to prepare cross-linked networks. Swelling studies of the networks were carried out to evaluate the sol−gel fraction and cross-link density. Thermomechanical properties of the networks were evaluated using DMA and stress−strain measurements. FTIR spectroscopy was used to find out the variation of degree of hydrogen bonding of the networks. Structure−thermomechanical property correlation of the networks was carried out in light of the structural parameters evaluated by different techniques.

MATERIALS AND EXPERIMENTAL DETAILS

Materials. Silanol-terminated polydimethyl siloxane ($M_n \approx$ 2000) was purchased from Dow Corning India Pvt. Ltd. Isophorone diisocyanate (IPDI), 10% dibutyltindilaurate in toluene (DBTDL) ,and tetraethoxysilane were purchased from E-Merck and used as received. Triethanolamine (Sigma-Aldrich) was freshly distilled before use. Methyl ethyl ketone (MEK) was purchansed from E-Merck and distilled over anhydrous K_2CO_3 before use.

Synthesis. Synthesis of the highly branched siloxane−urethane polymers was carried out in a two-step process: capping of silanol-terminated PDMS with IPDI to prepare the isocyanate-terminated PDMS prepolymer followed by reaction of the free isocyanate of the isocyanate-terminated PDMS with triethanolamine to prepare the branched polymers.

Capping of Silanol-Terminated PDMS with Isophorone Diisocyanate. A 100 g amount of silanol-terminated PDMS was taken in a dry 250 mL capacity round-bottom flask equipped with a magnetic stirrer. The material was demoisturized under vacuum (50 mmHg) at 100 °C. The flask was cooled to 65 °C, and then 22.2 g of isophorone diisocyanate (OH to NCO molar ratio 1:2) was added along with 2 drops of 10% DBTDL in toluene. The temperature of the mixture was maintained at 70 °C and stirred for 4 h under reduced pressure. The reaction progress was monitored by titrimetry as well as FTIR spectroscopy.

Synthesis of Highly Branched Siloxane−Urethanes. The highly branched siloxane−urethanes were prepared by an oligomeric A_2 + B_3 approach. In this method three different branched polymers were prepared by varying the molar ratio of the isocyanate-capped PDMS prepolymer (A_2 moiety) and triethanolamine core moiety (B_3) in an A_2:B_3 (molar ratio) of 1:1, 1:1.5, and 1:2. All reactions were carried out in a 3-necked round-bottom flask equipped with an overhead stirrer, an addition funnel, and a nitrogen inlet. Polymerization reactions for preparation of branched polymers were carried out in methyl ethyl ketone (MEK) solutions at room temperature under strong agitation. During the reactions oligomeric A_2 solution was always added dropwise into B_3 solution. In order to prevent gelation the solid content for the reaction was maintained at 15% for all cases. Reaction progress was monitored by tracking the isocyanate content and FTIR spectroscopy through the course of the reaction. After completion of the reaction the solvent was evaporated in a rotary evaporator setup and degassed for 4 h under vacuum to isolate the polymers.

Hyper 1:1: ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.91($Si-CH_3$), 0.91−1.04 ($-CH_3$), 1.23−1.90 ($-CH_2$), 2.20 ($-CH_2-C-$), 2.76 ($N-CH_2$), 3.52 (−CH−), 3.70 ($-CH_2-O-$), 4.09 ($-CO-O-CH_2-$), 5.00−6.00 (−NH−).

Hyper 1:1.5: ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.06−0.17 ($Si-CH_3$), 0.91−1.24 ($-CH_3$), 1.24−1.68 ($-CH_2$), 2.50 ($-CH_2-C-$), 2.70−2.88 ($N-CH_2$), 3.53−3.58 (−CH−), 3.71 ($-CH_2-O-$), 4.10 ($-CO-O-CH_2$), 5.00−6.00 (−NH−).

Hyper 1:2: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05−0.17 ($Si-CH_3$), 0.85−1.05 ($-CH_3$), 1.13−2.01 ($-CH_2$), 2.69−2.88 ($N-CH_2$), 3.58−3.53 (−CH−), 3.71−3.67 ($-CH_2-O-$), 4.10 ($-CO-O-CH_2-$), 5.00−6.00 (−NH−).

Preparation of Cross-Linked Networks. The synthesized branched siloxane−urethane polymers were used for preparation of cross-linked networks. The hydroxyl-terminated branched polymer was mixed with a stoichiometric amount of tetraethoxysilane (TEOS) in chloroform as solvent with a solid content of 40% (w/v) using dibutyltindilaurate as catalyst (0.4 wt % of branched polymer). The mixture of branched polymer, TEOS, and catalyst in chloroform was then cast in a Teflon mold and allowed to cure at room temperature. In a typical formulation, Hyper 1:1 network was prepared by dissolving 10 g of Hyper 1:1 branched precursor in 25 mL of chloroform followed by addition of 0.49 g of TEOS and 0.04 g of DBTDL and subsequently casting the homogenized mixture in a Teflon mold. The progress of the cross-linking reaction was monitored by tracking the evolution of gel fraction with time.

CHARACTERIZATION

Isocyanate Content of Prepolymer. The isocyanate content of the prepolymer, formed by capping reaction of silanol with IPDI, was measured by titration of the free isocyanate content according to ASTM D 2572-97 standard. According to this method the prepolymer was reacted with an excess of di-*n*-butylamine in toluene for 15 min to ensure completion of the reaction. The excess di-*n*-butylamine was determined by back-titration with standard hydrochloric acid solution.

Calculation for NCO content is as follows

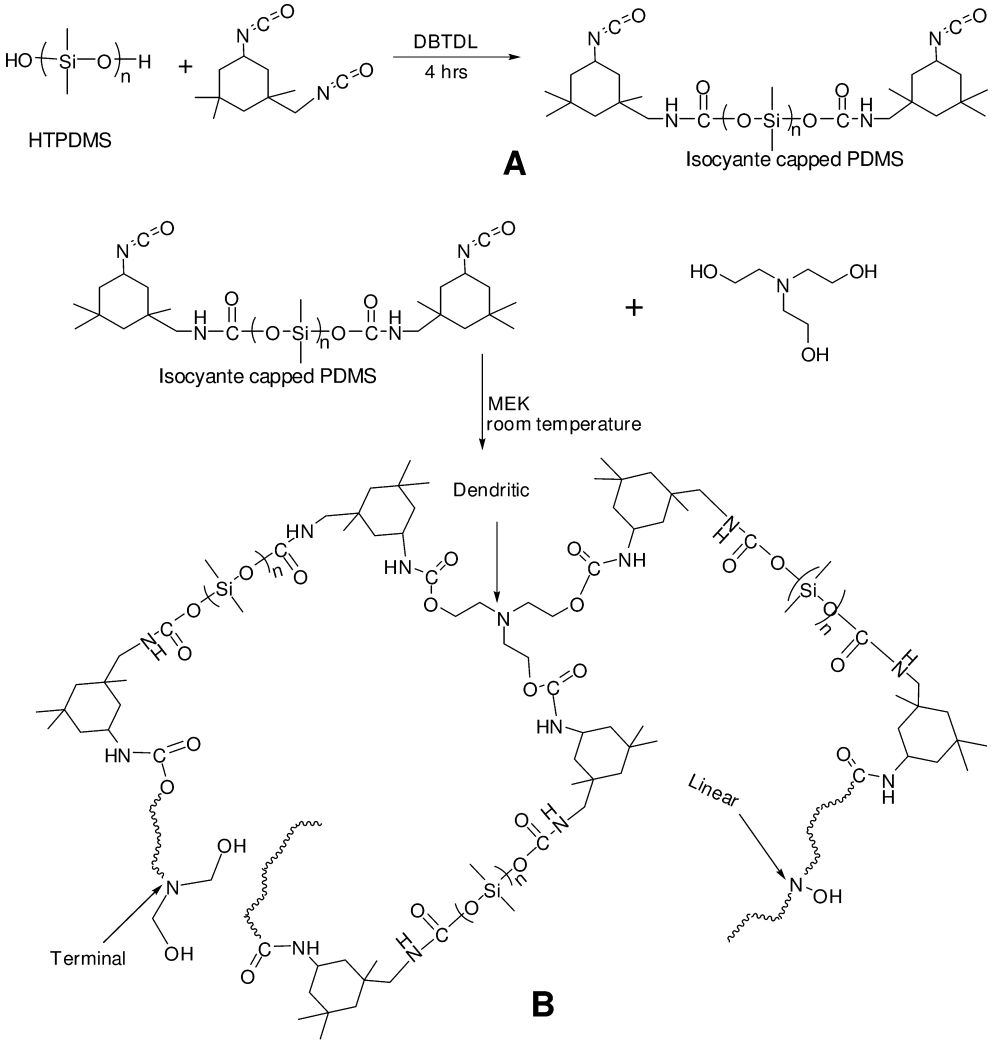
$$\text{NCO}\ (\%) = ((B - V) \times N \times 0.042)/W \times 100$$

where B is the volume of HCl for titration of the blank (mL), V is the volume of HCl for titration of the specimen (mL), N is the normality of HCl, and W is the specimen weight (g).

Hydroxyl Value of Branched Polymer. The hydroxyl values of the B_3 core-terminated branched polymers were determined by refluxing the samples with acetic anhydride in the presence of pyridine. After completion of acetylation, excess acetic anhydride was hydrolyzed with water. The acetic acid formed was titrated with standard potassium hydroxide solution up to the end point. The end point was determined by the inflection point on the titration curve.

dx.doi.org/10.1021/ie200629w | Ind. Eng. Chem. Res. 2012, 51, 3531−3540

Scheme 1. Capping Reaction of Silanol-Terminated Polydimethyl Siloxane with IPDI and Polycondensation Reaction of IPDI-Capped Siloxane with Triethanol Amine Yielding the Hyperbranched Siloxane−Urethanes



The hydroxyl value of the polymer sample was calculated from the titer value using the formula given below

$$\text{hydroxyl value (mg/g)} = ((B - A) \times N \times 56.1)/W$$

where B is the blank reading, A is the sample reading, N is the normality of the standard NaOH solution, and W is the sample weight

Density. The density of branched networks was determined by weighing them in air and ethanol using an analytical balance (Mettler AE 200) and a homemade device similar to the Mettler density kit ME-33360 following the equation

$$\rho = \frac{\rho_{Et} M}{M - M_1} \quad (1)$$

where ρ is the sample density, ρ_{Et} is the density of ethanol, M is the sample mass in air, and M_1 is its mass in ethanol.

Sol Fraction Measurements. The networks thus prepared were extracted in dry THF, and the amount of soluble (uncross-linked) material was evaluated from the weight differences between the final and the initial dry weights.

Instrumental Characterization. ^{1}H NMR analysis of the branched polymers was carried out in a Bruker 500 MHz FT-NMR spectrometer using $CDCl_3$ as the solvent at ambient temperature.

GPC measurements of the branched polymers were carried out in a Waters system equipped with a Styragel HT column and a differential refractive index detector using THF as the solvent, and the instrument was calibrated with narrow molecular weight polystyrene standards. The GPC traces were deconvoluted by a Gaussian multipeak procedure available in the ORIGIN v7 program.

Dilute solution viscometry measurements were made with a Schott-Gerate automated viscometer system utilizing a Schotte-Gerate Ubbelohde viscometer tube (bore size 0.46 mm), immersed in a constant temperature water bath at 25 °C.

FTIR spectra of the branched networks were recorded in a Thermo-Nicholet Omnic spectrometer. Each sample was scanned 64 times with a resolution setting of 4 cm^{-1} within the range 400−4000 cm^{-1}.

The soft segment glass transition temperature (T_g), storage modulus (E'), and dissipation factor (tan δ) of the branched networks were determined using a Gabo, Eplexor 100 N, dynamic mechanical analyzer in tensile mode. The temperature

dx.doi.org/10.1021/ie200629w | Ind. Eng. Chem. Res. 2012, 51, 3531−3540

range of analysis was from −150 to 50 °C at a frequency of 1 Hz, a ramp rate of 2 °C min^{-1}, and an initial strain of 0.2%.

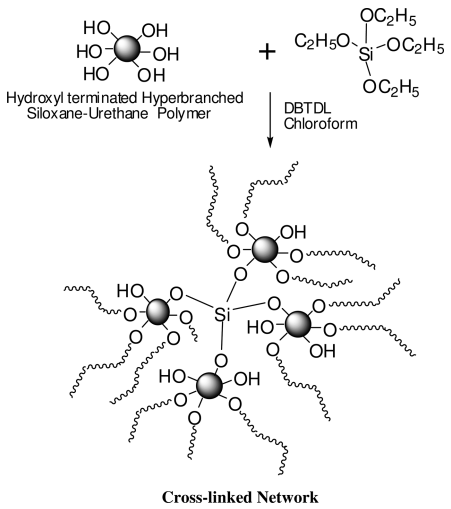
Tensile strength measurements of the branched networks were carried using a Hounsfield Universal Testing Machine according to the specification of ASTM D882. The sample size was 100 mm × 10 mm × 1 mm, and the crosshead speed was set at 500 mm/min. For each data point five samples were tested, and the average was recorded.

RESULTS AND DISCUSSION

Synthesis. In the present study the A_2 + B_3 approach has been adopted for synthesis of highly branched siloxane−urethane polymers. The isocyanate-capped PDMS was used as the oligomeric A_2 moiety and the triethanol amine as the core B_3 moiety. The isocyanate-capped material was prepared by end capping of silanol-terminated PDMS with isophorone diisocyanate. The schematic of the capping reaction is given in Scheme 1A. The isocyanate content of the prepolymer was found to be 3.3% versus the theoretical value of 3.43%, implying completion of the capping reaction. Further, the prepolymer showed urethane peaks at 1710 cm^{-1} due to reaction of the hydroxyl groups with isocyanate of IPDI. Unreacted isocyanate was characterized by the appearance of a peak at 2270 cm^{-1}, while the hydroxyl group of the silanol-terminated PDMS was absent in the prepolymer. This indicated completion of the capping reaction.

Branched polymer synthesis (Scheme 1B) was carried out with a reactant concentration of 15% to avoid gelation as reported by Unal et al.[22] For preparation of the branched polymers, the B_3 core was always used in excess of the A_2 unit; the lowest molar ratio used was 1:1 of A_2:B_3. In the case of an equimolar ratio of A_2 and B_3 (or in terms of equivalents [A]/[B] = 2/3=0.67), [B] was in excess; hence, no gelation was observed. The reaction progress was monitored by isocyanate content measurements for all polymers. The schematic of the curing reaction to prepare the hyperbranched network is given in Scheme 2. Figure 1A shows FTIR spectra of the branched

Scheme 2. Schematic of Preparation of Cross-Linked Siloxane−Urethane Networks from Hydroxyl-Terminated Hyperbranched Siloxane−Urethane with TEOS



polymers with the magnified −OH stretching peak shown in the inset. From the spectra it is observed that the free isocyante peak at 2270 cm^{-1} is absent for all samples, implying completion of the condensation reaction. The peaks due to the urethane hard segments are seen around 3300 cm^{-1} (−NH stretching) and a broad band from 1690 to 1710 cm^{-1} (−C═O stretching). Other characteristic absorption peaks are seen at 1260 ($-CH_3$ bending), 1020 and 1100 (−Si−O−Si− stretching), and 860 and 810 cm^{-1} ($-CH_3$ rocking of $-Si(CH_3)_2-O-$), attributable to the PDMS soft segment. FTIR spectra thus verified the synthesis and structure of the branched polymers. The intensity of the −OH stretching peak (from peak area) is found to increase with increasing B_3 core in the branched polymer. Quantitative evaluation of the hydroxyl content of the branched polymers was carried out by titrimetry, and the values are shown in Table 2. The hydroxyl values of the branched polymers are in the order Hyper 1:2 (69.7) > Hyper 1.1.5 (63.4) > Hyper 1:1 (53.9) and consistent with the FTIR observation of increasing hydroxyl peak intensity with increasing B_3 core content in the branched polymers. However, it must be noted that the increase in hydroxyl value with increasing B_3 core content is not commensurate with the theoretical values based on the stoichiometry of the A_2 and B_3 moieties. This can be attributed to the increasing cyclic species formation with increased core moiety (B_3) during A_2 + B_3 polycondensation reactions.[22] Detailed quantification of the cyclic species formation is discussed in the molar mass characterization of the branched polymers by GPC.

The cross-linking reaction of the precursor branched polymers and TEOS catalyzed by 0.4 wt % DBTDL (at RT) was monitored by periodic measurement of the gel fraction by solvent extraction with THF. A typical plot for evolution of the gel fraction with time for Hyper 1:2 network formation is shown in Figure 2. From the results it is observed that 80% gel fraction is obtained within a reaction time of 300 min (5 h). The gel fraction value stabilizes at ∼83% with no further increase in the value even after 4000 min. The gel fraction values for Hyper 1:1 and Hyper 1:1.5 networks attained peak values at relatively longer times of 340 and 420 min, respectively.

Degree of Branching (DB) Determination from ^{1}H NMR. The degree of branching of the branched polymers was calculated using the Fréchet and Frey methods using eqs 2 and 3, respectively[3]

$$DB = (D + T)/(D + T + L) \quad (2)$$

$$DB = (2D)/(2D + L) \quad (3)$$

where D is the peak intensity of dendritic unit, T is the peak intensity of the terminal unit, and L is the peak intensity of the linear unit.

^{1}H NMR traces of the branched polymers with assignment of dendritic, terminal, and linear protons are given in Figure 3. The fraction of dendritic, linear, and terminal units and DBs were calculated from the corresponding integrated peaks and are given in Table 1. It is observed that with increasing B_3 core in the branched structures both the DB and the fraction of dendritic core increases monotonically. In the case of the A_2 + B_3 reaction, high sensitivity of the DB on the ratio of the monomers as well as on the sequence of the monomer addition has been experimentally observed and simulated.[24,25] The simulations by Schmaljohann[25] showed that at a 1:1 ratio of A_2/B_3 a strong difference could be observed depending on the sequence of monomer addition. Applying simultaneous stepwise addition of A_2 and B_3, a DB of 0.65 could be achieved, compared to stepwise addition of B_3 to A_2 solution,

dx.doi.org/10.1021/ie200629w | Ind. Eng. Chem. Res. 2012, 51, 3531−3540

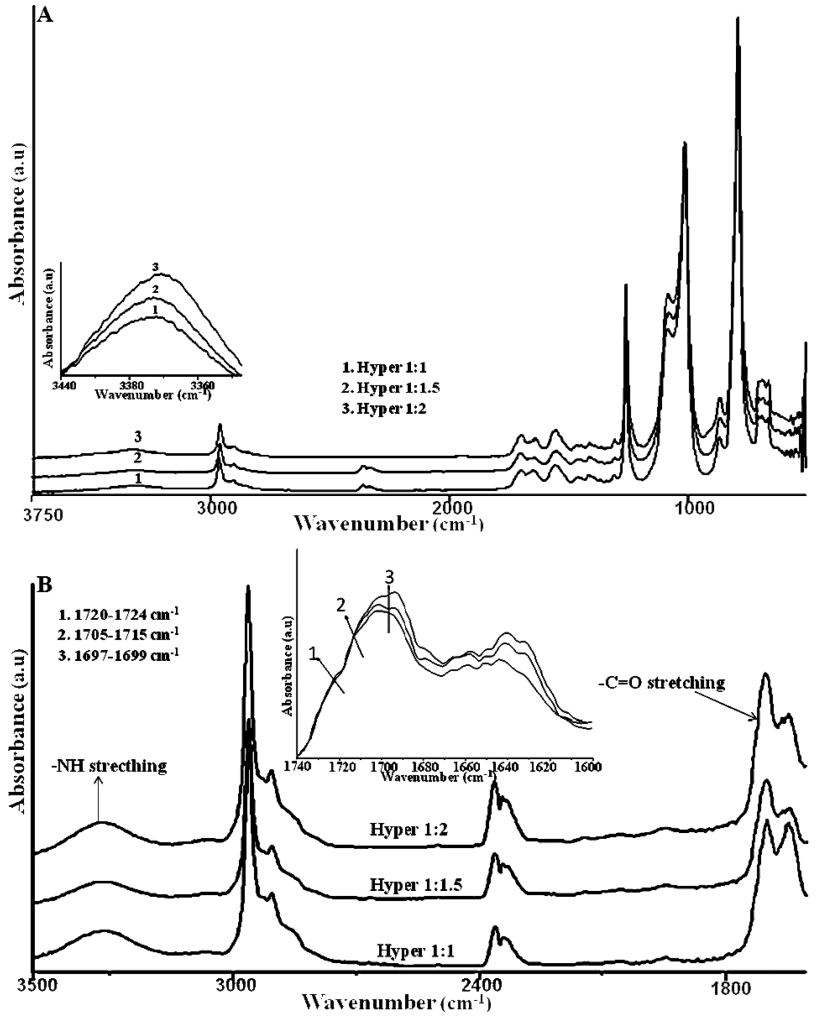


Figure 1. (A) FTIR spectra of the branched polymers; (inset) magnified −OH stretching region. (B) Partial FTIR spectra of cross-linked branched networks; (inset) magnified −C═O stretching region.

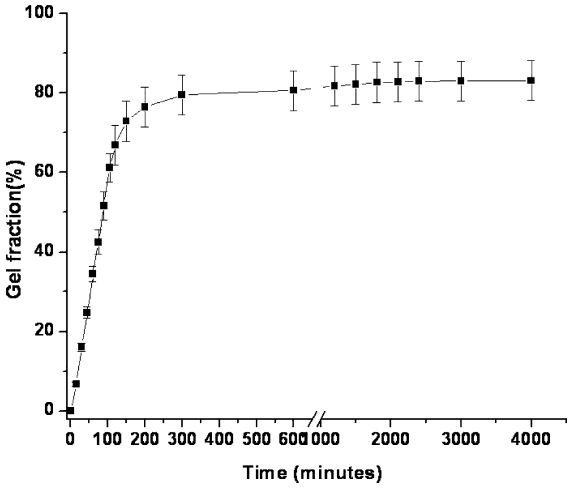


Figure 2. Evolution of gel fraction with time during cross-linking of Hyper 1:2 branched polymer with TEOS at RT.

which leads to a DB of 0.91. In the present case, although the slow addition technique has been adopted the DB was found to be in the range 0.5−0.67, implying only highly branched polymer formation. It is thus clear that the benefits of slow addition are not evident in the present case. This could be attributed to the fact that the B_3 moiety used here is a hydroxyl functional; hence, its reaction with NCO-terminated A_2 will be rather slow at room temperature. Therefore, slow or fast addition of A_2 would not make any difference to the structure of the branched polymers unlike in cases of fast reactions involving a amine-terminated B_3 moiety.[9,21−23] Besides the equal reactivity of the different functional groups, the low extent of side reactions is crucial for achieving a statistical DB. Cyclization is the most investigated side reaction in AB_x or A_2 + B_y polymerization processes.[26−30] Kricheldorf carried out extensive investigations on these structures and developed a cyclization theory in order to account for the deviations of the hyperbranched structures from the cascade theory of Flory.[31] The low DB for the branched polymers in the present case could be attributed to such cyclization possibilities, which is further discussed in the SEC results on the heterogeneous molar mass distribution of the hyperbranched polymers.

Molar Mass Characterization. Figure 4 shows the size exclusion chromatogram (SEC) traces of the branched polymers. It is observed that the peak position shifts toward higher retention times with increasing B_3 core in the branched polymers, implying a decrease in molecular weight. One characteristics feature of all the traces is that the peak shape is not perfectly Gaussian; rather they are skewed toward the right. Thus, the molar mass distribution of the polymers is rather

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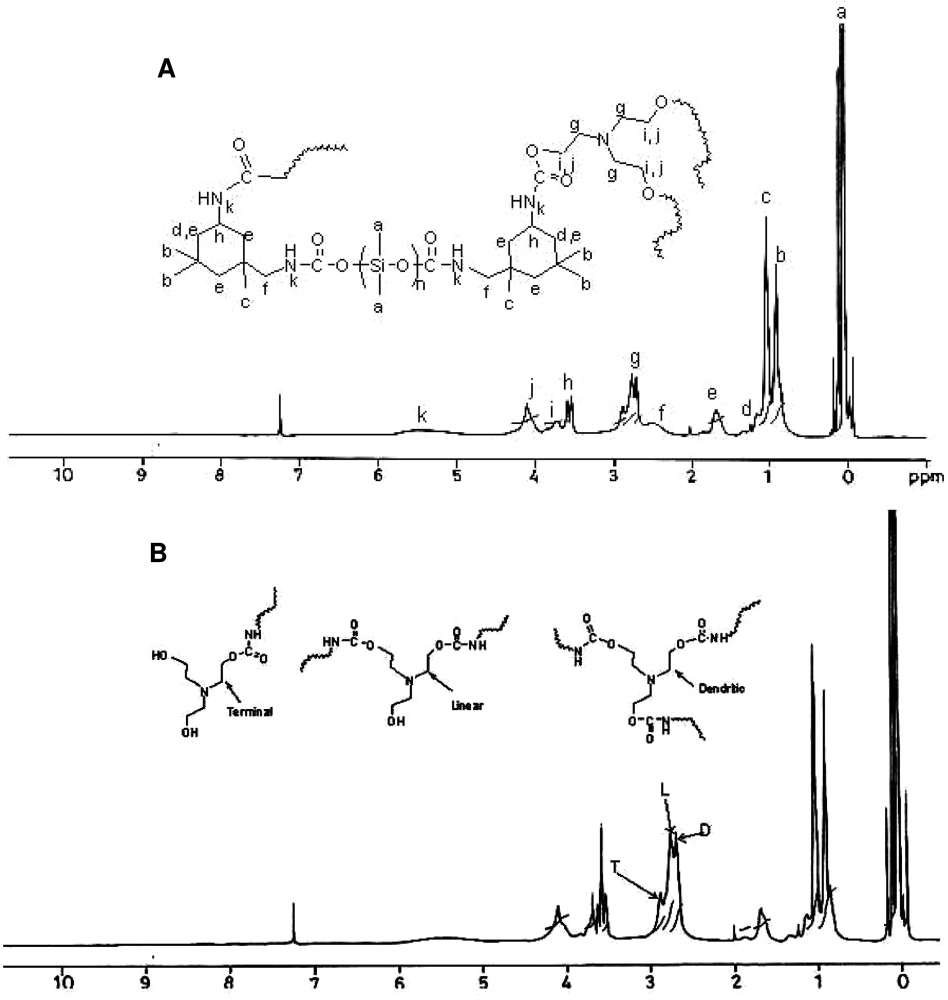

Figure 3. (A) ^{1}H NMR trace of Hyper 1:1. (B) Assignment of linear, dendritic, and terminal units of Hyper1:1 from ^{1}H NMR trace.

Table 1. Quantification of Structural Units from ^{1}H NMR

sample	% L	% T	% D	DB (Frey)	DB (Frechet)
Hyper 1:1	52	20.4	27.3	0.47	0.51
Hyper 1:1.5	51	20.2	28.4	0.48	0.52
Hyper 1:2	43	19.0	37.7	0.57	0.63

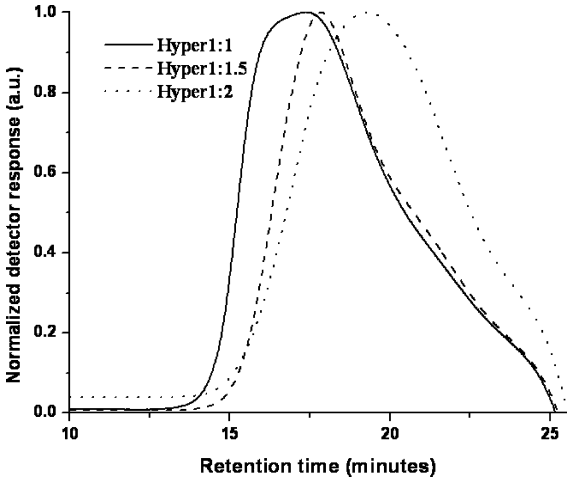

Figure 4. SEC traces of the hyperbranched polymers.

heterogeneous in nature. A definitive presence of low molecular weight fractions might contribute to the broadening of the traces in the higher retention time region corresponding to low molecular weight fractions. As already mentioned, cyclization is the most investigated side reaction in AB_x or A_2 + B_y polymerization processes. SEC separation of the broadly distributed samples can reveal important information regarding the distribution of intramolecular ring formation within the complex mixture of branched macromolecule.[3] In order to quantify the molar mass distributions we performed deconvolution of the SEC traces. Figure 5 shows typical deconvoluted spectra of Hyper 1:1 and Hyper 1:2 traces, and detailed parameters of the molar mass distribution are shown in Table 2. From the results we observe that the Hyper 1:1 sample shows three Gaussian bands pertaining to three different molar mass distributions: a very small fraction of high molecular weight species corresponding to the peak molecular weight (M_p) of 39 200, the main branched structure with an M_p of 12 800, and molar masses at a higher retention time corresponding to an M_p of 590. The molar masses corresponding to the higher retention time of 22 min are attributed to formation of low molecular weight cyclic species formed during the polycondensation reaction. The Hyper 1:1.5 and Hyper 1:2 samples show only two Gaussian bands corresponding to the main branched structure and the cyclic species. The fraction of low molecular weight species, due to the cyclic products, increases

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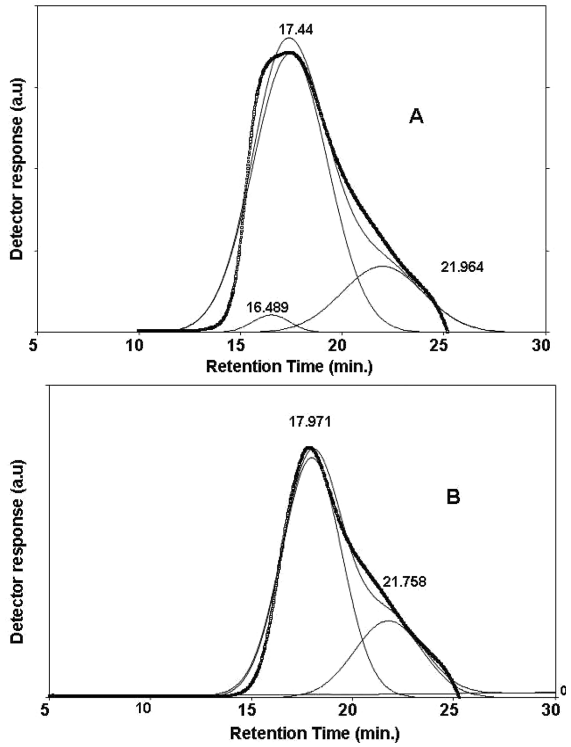

Figure 5. Deconvoluted SEC traces of (A) Hyper 1:1 and (B) Hyper 1:1.5.

Table 2. Molar Mass Distribution of the Branched Polymers from Deconvoluted SEC Traces, Intrinsic Viscosity, and Hydroxyl Value of the Branched Polymers

sample	centroids of retention time Gaussian peaks (minutes)	peak molecular weight (M_p) g/mol	area (%)	width (min)	intrinsic viscosity (dL/g)	hydroxyl value (mg of KOH/g)
Hyper 1:1	16.48	39 200	2.4	4.3		
	17.44	12 800	78.3	8.6	0.135	53.9
	21.75	590	16.3	9.4		
Hyper 1:1.5	17.95	7600	82.9	6.8	0.092	63.4
	21.9	474	15.1	7.9		
Hyper 1:2	18.2	6400	79.2	7.2	0.111	69.7
	22	380	18.8	7.2		

with increasing B_3 incorporation into the structures. These findings are consistent with the observation of reported multimodal characteristics of hyperbranched poly(arylester)s prepared by the $A_2 + B_3$ polycondensation method by two different tpes of GPC equipment.[32] Furthermore, the decreasing intrinsic viscosity values of the highly branched polymers (Table 2) with increasing B_3 core testifies the increased amount of cyclic species formation and decreasing molecular weight of the highly branched polymers.

Sol Fraction and Swelling Studies of Highly Branched Networks. The sol fraction of the branched networks thus prepared (Table 3) is found to increase with increasing B_3 content. The results are consistent with the SEC findings of increasing low molecular weight cyclic species in the networks. It is thus evident that the cyclic species formed during the condensation reactions act as non-network-forming species and

Table 3. Sol Fraction, Flory–Huggins Interaction Parameter, and Cross-Link Density of the Branched Networks Determined from Swelling Studies and the Plateau Modulus of DMA Plots at 25°C

sample	sol fraction	χ_{MEK} (eq 5)	V_2	$\upsilon_{swelling}$	υ_{DMA}
Hyper 1:1	9.2	0.374	0.337	9.31×10^{-4}	3.1×10^{-3}
Hyper 1:1.5	10.8	0.379	0.686	8.6×10^{-3}	3.7×10^{-3}
Hyper 1:2	12.3	0.382	0.720	3.4×10^{-2}	

contribute to the sol fraction. It must be mentioned that pure silanol itself contains some inert dimethylsiloxane cyclics generally present in PDMS samples according to chromatographic measurements.[33] In the present case we found the value to be 6.5%, consistent with the supplier values. Since these species might contribute to the sol fraction values of the networks, the actual sol fraction values are reported after accounting for the cyclic species of the silanol itself.

The cross-link density of the networks was determined using the equilibrium swelling measurements. Cured samples of size 1 mm × 5 mm × 5 mm were soaked in dried MEK. After 48 h, the swollen samples were taken out and weighed. The cross-link density was calculated according to the Flory–Rehner equation[34]

$$-[\ln(1 - v_2) + v_2 + \chi {v_2}^2] = \frac{\rho}{M_c} V_s \left[{v_2}^{1/3} - \frac{v_2}{2} \right] \quad (4)$$

where v_2 is the volume fraction of polymer in the swollen mass, ρ is the density of polymer network sample, χ is the Flory–Huggins solvent interaction parameter, and V_s is the molar volume of the solvent.

The volume fraction of polymer in the swollen network was evaluated using the equation

$$v_2 = \frac{w_p}{w_p + w_s \frac{\rho_p}{\rho_s}} \quad (5)$$

where w_p is the weight of polymer in the swollen mass and ρ_p and ρ_s are the density of polymer networks and solvent, respectively.

Following the method proposed by Herrera et al., the Flory–Huggins interaction parameter, χ, estimating the interaction energy between the solvent and the polymer network, was calculated using eq 6[35]

$$\ln a_i = \ln \varphi_i + (1 - \varphi_i) + \chi (1 - \varphi_i)^2 \quad (6)$$

where a is the activity of solvent and φ is the volume fraction of solvent in the swollen network. When the sample is immersed in pure solvent, the solvent activity becomes unity and eq 6 can be rewritten as

$$\chi = -\frac{\ln \varphi_i + \ln(1 - \varphi_i)}{(1 - \varphi_i)^2} \quad (7)$$

The values of the interaction parameters obtained (Table 3) are found to increase with increasing core content in the branched networks. The interaction parameters were also calculated from an empirical relationship between the interaction parameter and the solubility parameter of the polymer networks proposed by Bristow and Watson[36,37] (see Supporting Information).

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The cross-link density of the networks were then calculated from the Flory–Rehner equation using the χ values obtained from eq 7 and are given in Table 3. The results suggest that the cross-link density of the branched networks increases with increasing core content in the network. This is a direct consequence of the increasing hydroxyl end functional concentration with increasing B_3 core incorporation into the branched networks, evident from the increasing hydroxyl value of the branched polymers given in Table 3.

Hydrogen-Bonding Characteristics from FTIR. Figure 1B shows the partial FTIR spectra of the highly branched networks with the magnified −C═O region shown in the inset. In order to evaluate the hydrogen-bonding characteristics of the highly branched networks, we relied on the intensity differences in the broad band of the carbonyl region from 1670 to 1750 cm^{-1}. It has been established that the strongly hydrogen-bonded carbonyls are responsible for the absorbance at lower wave numbers of 1700–1705 cm^{-1}.[38] In the present case the same is observed at 1696 cm^{-1} for the Hyper 1:1 network. The free carbonyl band is noticed at 1726 cm^{-1}, while the absorbance at 1707 cm^{-1} corresponds to the loosely hydrogen-bonded carbonyl peak.[39] No discernible trend in the peak position shifts of the various bands with increasing core moiety in the network is noticed. However, with increasing core moiety incorporation into the network, the relative intensity of strongly hydrogen-bonded carbonyl fraction increases, implying a higher degree of phase separation of the networks with increasing B_3 core content.

Dynamic Mechanical Analysis. Figure 6A shows the storage modulus (E') vs temperature plot of Hyper 1:1 and Hyper 1:1.5 networks. Measurements on the Hyper 1:2 sample could not be carried out, as the sample could not sustain the dynamic ramp and broke during analysis. The temperature response of E' could be categorized to four different temperature regimes. The first temperature regime is the glassy plateau which extends from −150 to −120 °C with typically higher E' values. The glassy plateau is followed by a sharp descent in E', corresponding to the glass-transition temperature of the siloxane soft segments, which marks the second temperature regime of E' response. A transient increase in the modulus is followed in the third temperature regime attributed to cold crystallization of the siloxane segments[40] followed by a drop at −50 °C due to melting of the soft segment crystallites. Finally, the fourth temperature regime is the rubbery plateau which extends from −50 to 100 °C.

Sheth et al. carried out extensive studies on the effect of siloxane soft segment molecular weight (SS MW = 7000, 2500, and 900) on the dynamic mechanical properties of hyperbranched siloxane–urethane and urea polymers.[40] They observed crystallization of the PDMS soft segment (SS) for the segmented polyurethane and polyurea copolymers for SS molecular weight of 7000 only.[40] Observation of crystallization of SS in the present case with SS molecular weight of 2000 could be explained on the basis of the differences in hard segment content and the structure of the soft segment. The hard segment contents for the Hyper 1:1 and Hyper 1:1.5 networks are 22% and 25%, respectively, while the systems probed by Sheth et al. have a hard segment content of 30–40%. It is well established that the number of restrictions on the SS increase with higher hard segment content because of higher a degree of phase mixing. Further, the SS used in the present case is a silanol, devoid of any methylene ($-CH_2-$) groups at the end of PDMS chains, which promotes phase mixing. The

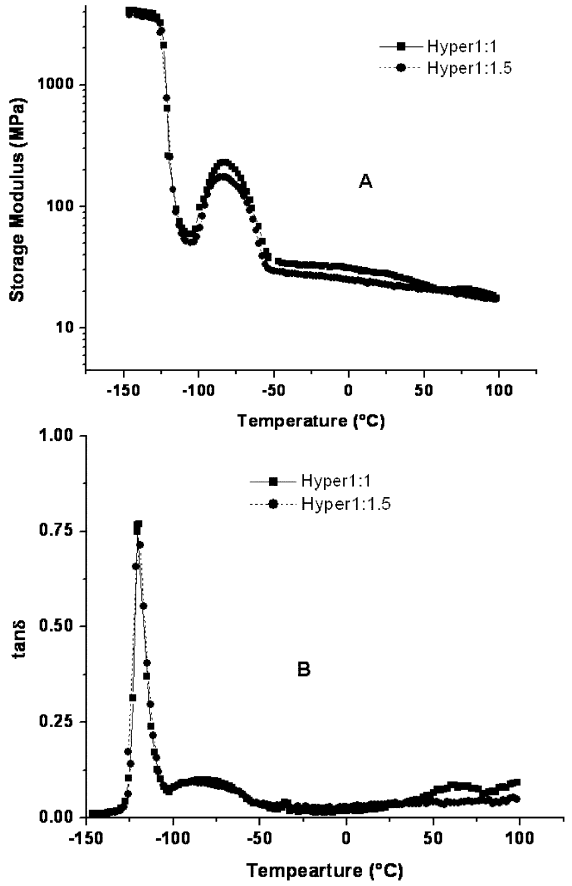

Figure 6. DMA plots of the branched networks: (A) storage modulus vs temperature and (B) tan δ vs temperature.

degree of phase separation thus is relatively higher in the present case due to the absence of methylene spacers and lower hard segment content, which in turn leads to observation of SS crystallization.

Predominantly, two transitions pertaining to the glass transition and melting of the siloxane segments have been reported for linear siloxane–urethane polymers, wherein the modulus drop was significantly higher during melting than during T_g, which is quite reasonable.[41] In the present case the drop in E' is much higher during the soft segment T_g compared to the soft segment melting transition. The difference in the temperature dependency could be attributed to the contribution of physical cross-links in linear segmented polyurethanes, while in the present case it is due to the covalently cross-linked chains; the drop in the modulus during the melting process is significantly lower. Hence, the plateau modulus is found to be considerably higher compared to the linear segmented siloxane–urethane polymers. On comparison of E' response of the networks, one notes that the Hyper 1:1.5 network exhibits a slightly higher plateau modulus compared to the Hyper 1:1 network due to the higher cross-link density.

The dynamic relaxations of the networks are further evident from the tan δ vs temperature plot shown in Figure 6B. From the temperature response of tan δ, two different transitions could be seen. A pronounced soft segment transition is evident from the sharp tan δ peak at −120 °C for Hyper 1:1 network, with a tan δ value (height) of 0.72–0.75. The location of the soft segment T_g does not change for the Hyper 1:1.5 network, with only a minor depression in the tan δ intensity. This is

dx.doi.org/10.1021/ie200629w | Ind. Eng. Chem. Res. 2012, 51, 3531–3540

followed by a broad mild transition from −100 to −50 °C, with invariant tan δ values for both networks. Comparison of the tan δ profiles of the branched networks with the PDMS-based linear copolymers reported by Sheth et al.[40] provide more insight into the differences in phase separation behavior. The T_g of the branched networks was found to be −120 °C, versus a value of −118 °C for the linear PDMS polyurethane and polyurea samples with a SS MW of 2500. Further, the tan δ magnitude (peak intensity), a measure of SS mobility, is found to be higher for the networks (0.75) compared to the linear polymers (0.4−0.5). This implies a higher degree of phase separation for the branched networks compared to the linear segmented copolymers and hence a higher extent of phase purity for the PDMS soft segments.

The cross-link density, υ_e, the number of moles of elastically effective network chains per cubic centimeter of sample, can be determined from the DMA data using kinetic theory of rubber elasticity. The E' values at 25 °C were taken to calculate the υ_e according to the equation

$$\upsilon_e = E'/3RT \quad (8)$$

where E' is the modulus at 25 °C, R is the universal gas constant, and T is the temperature in Kelvin.

The cross-link density values obtained from the storage modulus data are given in Table 3. From the results it is observed that the cross-link density values obtained from DMA are higher compared to that obtained from swelling studies. The possible reason for the discrepancy could be that the effect of non-network-forming sol fraction (the cyclic species evaluated from GPC) to the storage modulus is not exactly known. Further, the interference of the sol fraction in evaluation of the swell ratio, volume fraction of the polymer network in the swollen mass, and hence the cross-link density of the networks by swelling studies could not be ruled out.

Stress−Strain Behavior. Figure 7 shows a typical stress−strain plot of the branched networks. From the plot it is evident that Hyper 1:1.5 shows optimum mechanical properties in terms of modulus, tensile strength, as well as elongation at break. On the basis of the cross-link density and degree of hydrogen bonding we expected higher strength and modulus for the Hyper 1:2 network. The counterintuitive poor mechanical properties of the network could be attributed to the presence of a higher amount of non-network-forming low molecular weight species. The latter could act as a plasticizer and also a stress concentrator, leading to premature failure of the specimen during testing. Interestingly, we find the mechanical properties of the Hyper 1:1.5 network are comparable to siloxane−urethane linear polymers reported with similar lower hard segment concentrations.[41]

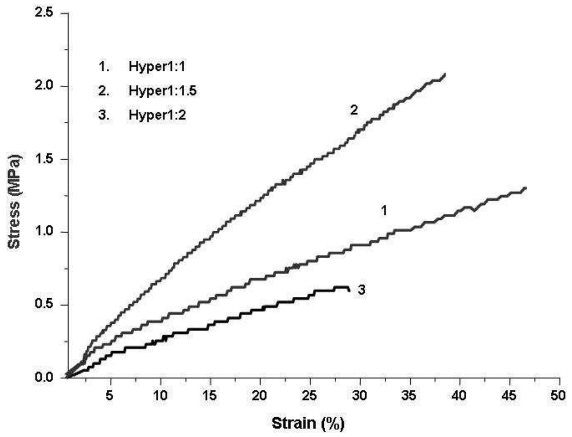

Figure 7. Stress−strain profile of the branched networks.

CONCLUSIONS

A series of highly branched siloxane−urethane networks with varying degrees of cross-link densities was prepared by reaction of hydroxyl functional branched precursors with TEOS. The branched polymers were prepared by the oligomeric A_2 + B_3 approach by varying the stoichiometry of IPDI end-capped siloxane (A_2) and triethanolamine (B_3). Cyclic species formed during preparation of the branched polymers were quantified by deconvolution of SEC traces and found to increase with increasing B_3 content in the highly branched polymers. Characterization of the swelling parameters, hydrogen-bonding characteristics, and thermomechanical properties of the networks were conducted using a range of experimental probes. The extent of strongly hydrogen-bonded fraction and cross-link density of the networks was found to increase with increasing B_3 core content in the branched polymers. DMA studies confirmed the phase-separated morphology of the networks, and a rubbery plateau modulus of 23−25 MPa was observed for the networks at 25 °C. Further studies on the effect of non-network-forming cyclic species, characteristic of the A_2 + B_3 polycondensation approach, on the thermomechanical properties of the networks are underway.

ASSOCIATED CONTENT

Supporting Information

The supporting information deals with determination of the Flory−Huggins interaction parameter of the branched networks obtained from swelling studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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