Low-Modulus Siloxane–Polyurethanes. Part II. Effect of Chain Extender Structure on Properties and Morphology

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ABSTRACT: A series of six polyurethanes were prepared to study the effect of silicon chain extender structure on properties and morphology of siloxane–polyurethanes. Polyurethanes were prepared by a two-step bulk polymerization without a catalyst. The soft segment of the polyurethanes was based on an 80:20 (w/w) mixture of α,ω-bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS, MW 966) and poly(hexamethylene) oxide (MW 714). The hard segment was based on 4,4'-methylenediphenyl diisocyanate (MDI) and a 60:40 molar mixture of 1,4-butanediol (BDO) and a silicon chain extender. Silicon chain extenders (SCE) investigated were 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD), 1,3-bis(3-hydroxypropyl)1,1,3,3-tetramethyldisiloxane (BPTD), 1,4-bis(3-hydroxypropyl)1,1,3,3-tetramethyldisilylethylene (HTDE), 1,3-bis(6-hydroxyethoxypropyl)1,1,3,3-tetramethyldisiloxane (BETD). All polyurethanes were clear and transparent with number average molecular weights between 72,000 to 116,000. Incorporation of the silicon chain extender resulted in polyurethanes with low-modulus and high elongation. This was achieved without significant compromise in ultimate tensile strength in all cases, except BETD. Differential scanning calorimetry (DSC) results showed that the silicon chain extenders did not significantly disrupt the hard segment crystallinity, but exhibited a unique morphological feature where SCE-based hard segments formed separate domains, which may be the primary reason for achieving low modulus without significant compromise in strength. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1092–1100, 2003

Key words: polydimethylsiloxane; silicon chain extender; polyurethanes; morphology; mixed macrodiols; mixed chain extenders

INTRODUCTION

Siloxane–polyurethanes represent a major recent advancement in the development of biostable polyurethanes.[1] These polyurethanes combines the excellent mechanical properties of conventional polyurethanes and biostability of silicon rubber.[2–4] The key strategy used in the development of siloxane–polyurethanes with good mechanical properties and biostability was the mixed macrodiol approach, where a mixture of a siloxane macrodiol such as α,ω-bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS) and a polyether macrodiol poly(hexamethylebne oxide) (PHMO) was used as the soft segment of the polyurethane. PHMO improved the interfacial adhesion between nonpolar siloxane segments and the polar hard segments, largely through the interaction with ethoxypropyl end groups of PDMS. Typically, about 20% PHMO in the soft segment produced polyurethanes with a combination of good biostability and mechanical properties.[2–4] This strategy enables us to overcome the typical incompatibility problems associated with preparing PDMS-based polyurethanes as previously reported in the literature.[5–8] Further, siloxane segments were incorporated as part of the hard segment as well to achieve low-modulus siloxane–polyurethanes. This was achieved using a mixture of 1,4-butanediol (BDO), a conventional polyurethane (PU) chain extender and a silicon chain extender such as 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethylsiloxane (BHTD).[9–11] This enabled the synthesis of low-modulus polyurethane elastomers without compromising biostability or mechanical properties. Such low-modulus biostable polyurethanes are highly sought after for a variety of medical implants, including vascular grafts and heart valves.

The structure of the chain extender has a significant effect on properties and morphology of polyurethanes. For example, diols such as 2,2-diethyl-1,3-propanediol, 1,3-propanediol, and 2,2-dimethyl-1,3-propanediol produce highly phase-mixed, amorphous materials with poor mechanical properties compared to those prepared from conventional PU chain extenders such as BDO. Although these diols can be used along with BDO as chain extenders to produce low-modulus polyurethanes, the biostability of such polyurethanes is generally very

poor.[12] On the other hand, silicon chain extenders such as BHTD [(**I**) where R = $(CH_2)_4$] when used with BDO at certain compositions produce low-modulus, biostable polyurethanes with good mechanical properties.

$$
\begin{array}{ccc}
& CH_3 & CH_3 \\
& | & | \\
HO{-}R{-}Si & {-}O{-}Si & {-}R{-}OH \\
& | & | \\
& CH_3 & CH_3
\end{array}
$$

(**I**)
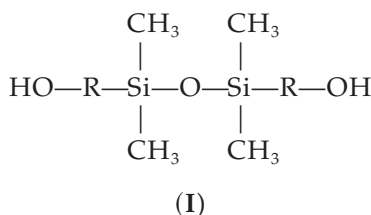
We have previously reported the effect of BDO and BHTD composition on polyurethane properties and morphology, and showed that a 60:40 molar composition of BDO:BHTD yields polyurethanes with both good mechanical properties and excellent biostability.[10,13,14] The objective of this study was to investigate the effect of SCE structure on properties and morphology. Two main structural variations were investigated. The first was the structure of the alkyl group [R in (I)] where the effect of the propyl, butyl, and ethoxypropyl substituents were studied, and the second was the siloxane linkage, where —SiOSi— was replaced with disilylethylene —Si—CH_2CH_2Si—. The silicon chain extenders used to achieve these structural variations were 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethylsiloxane (BHTD), 1,3-bis(3-hydroxypropyl)1,1,3,3-tetramethylsiloxane (BPTD),1,3-bis(6-hydroxyethoxypropyl)1,1,3,3-tetramethyldisiloxane (BETD), and 1,3-bis(3-hydroxypropyl)1,1,3,3-tetramethyldisilylethylene (HTDE). Polyurethanes were prepared by a two-step bulk polymerization procedure and were formulated to have a constant hard segment weight percent of 40. The soft segment of the polyurethane was based on an 80/20 (wt/wt) mixture of PDMS and PHMO and the hard segment was 4,4′-methylenediphenyldiisocyanate chain extended with a mixture of BDO and each of the silicon chain extender. This paper reports on the effect of the silicon chain extender structure on properties and morphology when used as a mixture with BDO in a 40–60 molar ratio.

MATERIALS

PDMS (Shin-Etsu X22-160AS) was obtained from Japan. PHMO was synthesized using a method reported previously.[15] 1,4-butanediol (BDO), General Aniline Film (GAF) was dried over activated molecular sieves, distilled under vacuum and middle fraction used for polymerization. All silicon chain extenders except HTDE and BETD were obtained from Silar Laboratories and degassed at room temperature under a vacuum of 0.1 torr for 6 h to remove cyclic impurities. HTDE and BETD were synthesized by the hydrosily-

lation of 1,1,3,3-tetramethyldisilylethylene with allyl alcohol and 1,1,3,3-tetramethyldisiloxane with hydroxyethoxypropene using Wilkinson and Karstedt catalysts, respectively.[16,17] The purity of HTDE and BETD were characterized by their NMR (^{1}H, ^{13}C, and ^{29}Si spectra recorded in CDCl$_3$ at 250, 62.5, and 50.0 MHz, respectively).

HTDE: 1H (δ, ppm): 0.01 (s, 12H, 4XSiCH$_3$), 0.38 [s, 4H, Si(CH$_2$)$_2$Si], 0.42–0.51 (m, 4H, 2XSiCH$_2$), 1.44–1.60 (m, 4H, 2XSiCH$_2$CH$_2$), 2.0 (s, 2H, 2XOH), 3.60 (t, 4H, 2X CH$_2$OH). ^{13}C (δ, ppm): −3.99, 6.95, 10.13, 27.14, 65.77. 29Si (δ, ppm): 4.62 [s, Si(CH$_2$)$_2$Si] .

BETD: ^{1}H (δ, ppm): 0.01(s, 12H, 4X SiCH$_3$), 0.41–0.50 (m, 4H, 2XSiCH$_2$), 1.51–1.61 (m, 4H, 2X SiCH$_2$CH$_2$), 2.71 (s, 2H, 2XOH), 3.39 and 3.48 (t, ea, 8H, 2XCH$_2$O and 2X OCH$_2$), 3.68 (t, 4H, 2XCH$_2$OH). ^{13}C (δ, ppm): 0.21, 14.10, 23.32, 61.64, 71.78, 73.79. 29Si (δ, ppm): 7.68 (s, SiOSi).

Both macrodiols PDMS and PHMO were dried thoroughly under a vacuum of 0.1 torr at 105°C for at least 12 h prior to synthesis.

4,4′-Methylenediphenyldiisocyanate (MDI, Suprasec MPR from Orica) was used as received.

Hydroxyl number

Hydroxyl number of the macrodiols was determined by phthalic anhydride reflux method in accordance with ASTM method D2849.

Synthesis of polyurethane elastomers

Polyetherurethanes were synthesized by a two-step bulk polymerization procedure without catalyst. A typical two-step bulk polymerization procedure used for the synthesis of polyurethane based on BHTD/BDO chain extender mixture is described below.

A mixture of predried macrodiol PDMS (120.0 g, MW 965.6) and PHMO (30.0 g, MW 714.8) was degassed at 80°C for 1 h under vacuum (0.1 torr). Molten MDI (77.65 g) was placed in a three-necked flask fitted with a magnetic stirrer, a nitrogen inlet, and an addition funnel. The macrodiol mixture (150 g) was added to MDI dropwise through the addition funnel over a period of 30 min under a slow stream of dry nitrogen. After the addition was over, the reaction mixture was heated to 80°C for a period of 2 h with stirring. The prepolymer thus obtained was then degassed under vacuum (0.1 torr). The prepolymer (220 g) was weighed into a 500 mL polypropylene beaker to which was added a mixture of 1,4-butanediol (7.05 g) and BHTD (14.53 g) and stirred rapidly for about 3 min. The viscous polymer was then poured into a Teflon-coated metal pan and cured for 4 h at 100°C in a nitrogen-circulating oven.

Polyurethanes are abbreviated based on silicon chain extender. For example, PU-BHTD refers to a PU

Silicon Chain Extender (SCE)	Chemical Structure	Molecular weight
1,3-Bis(4-hydroxybutyl) tetramethyldisiloxaane (BHTD)	HO—(CH₂)₄—Si(CH₃)₂—O—Si(CH₃)₂—(CH₂)₄—OH	278.54
1,3-Bis(3-hydroxypropyl) tetramethyldisiloxane (BPTD)	HO—(CH₂)₃—Si(CH₃)₂—O—Si(CH₃)₂—(CH₂)₃—OH	250.48
1,4-Bis(3-hydroxypropyl) tetramethyldisilylethylene (HTDE)	HO—(CH₂)₃—Si(CH₃)₂—CH₂CH₂—Si(CH₃)₂—(CH₂)₃—OH	262.53
1,3-Bis(6-hydroxyetho-xypropyl) tetramethyld-isiloxane (BETD)	HO—(CH₂)₂O(CH₂)₃—Si(CH₃)₂—O—Si(CH₃)₂—(CH₂)₃O(CH₂)₂—OH	338.59

Figure 1 Structure of silicon chain extenders.

prepared from a mixture of PDMS/PHMO (80/20) containing 40 mol % BHTD whereas the control material is referred as PU-BDO. The structure of all the silicon chain extenders and their molar compositions are shown in Figure 1 and Table I, respectively.

Size-exclusion chromatography

Size exclusion chromatography (SEC) of polyurethane materials was carried out on a Water Associates Chromatograph using $0.05M$ lithium bromide in N,N'-dimethylformamide as the mobile phase at 80°C. The flow rate was 1.0 mL/min. The stationary phase consisted of a set of three μ-Styragel HT columns (10^5, 10^3, and 500 Å). The system was calibrated with polystyrene standards. Results are expressed, therefore, as polystyrene-equivalent molecular weights.

Sample preparation

After drying for 15 h at 70°C in vacuum (0.1 torr), polyurethane samples were compression molded into flat sheets at temperature between 180 and 190°C under a nominal load of 8 tons. The sheets had dimensions of 60 × 100 mm and were 1 mm thick. They were cut into dumbbells of 3 cm in length and 1 cm in width; the narrow section was 1.2 cm in length and 0.4 cm in width. For flexural modulus tests, rectangular specimen (12.7 × 3 × 72 mm; width × thickness × length) was used. Test specimens for tear strength measurement were cut using a standard trouser leg die.

All samples were inspected under cross-polarizers to determine if internal stress was present. All samples

TABLE I
Molar Ratios of Polyols, MDI, and Mixed Chain Extenders

Sample code	Polyols: MDI+BDO+SCE
PU-BDO	1: 2.04: 0.988
PU-BHTD	1: 1.86: 0.812
PU-BPTD	1: 1.88: 0.834
PU-HTDE	1: 1.87: 0.824
PU-BETD	1: 1.82: 0.768

TABLE II
GPC Results of Synthesized Polyurethanes

Sample code	$\bar{M}_n$	$\bar{M}_w$	PD
PU-BDO	118612	307475	2.5
PU-BHTD	116490	340645	2.9
PU-BPTD	79612	204775	2.5
PU-HTDE	80135	201570	2.5
PU-BETD	72484	201155	2.7

were stress free and exhibited no birefringence under cross-polarizers. Dumbbells were stored under ambient conditions for at least 1 week before tensile tests and hardness measurements were performed.

Mechanical properties

Mechanical testing was carried out with an Instron Model 4032 Universal Testing machine. A 1 kN load cell was used and the crosshead speed was 500 mm/min. The result reported is the median values for 5 replicates. Hardness measurement was carried out using a calibrated Shore A Durometer. The flexural modulus measurement were performed using a three-point bend configuration with a 52.8 mm spacing. A 1 kN load cell was used with a cross head speed of 14 mm/min, and the results reported are the mean values of three replicates. Tear strengths were measured according to ASTM D-624 method using a crosshead speed of 200 mm/min and results reported are the median values for three replicates.

Thermal analysis

DSC analysis over the temperature ranges −150–220°C was performed using a Mettler DSC 30. The experiments were carried out at a heating rate of 10°C/min under nitrogen. Sample weights were 20–25 mg. The samples were dried at 65°C for 48 h under vacuum (0.1 torr). Annealing was carried out on predried samples in a nitrogen-circulating oven at 100°C for 1 h and samples were allowed to cool to room temperature in the oven prior to testing. Dynamic mechanical thermal analysis was performed on a Rheometric dynamic thermal mechanical analyzer DMTA IV equipped with bending head and reducing force option. The analysis was car-

ried out only on predried as-molded materials with a heating rate of 2°C at a 14 (Hz) frequency setting.

RESULTS AND DISCUSSION

The polymerization in all cases proceeded to yield clear and transparent polyurethane elastomers. The molecular weight of the as-synthesized polyurethanes are shown in Table II. The number average molecular weight varied between 72,000 and 11,600, while polydispersity varied between 2.5 and 2.9. The MW was dependent on the SCE structure; except for BHTD, the other silicon chain extenders produced significantly lower molecular weight polymers than the control PU-BDO. BETD, which was the most polar of the SCEs, produced the lowest molecular weight. Further, SCE-based polyurethanes had broader molecular weight distributions than that of the control PU-BDO. Although the solubility parameters (see Table IV) of silicon chain extenders were significantly different from that of BDO, their effect on polymerization was not considered significant since the polymerization was carried out in two steps.

Mechanical properties

The tensile properties and Shore hardnesses of the polyurethanes are shown in Table III. The stress strain curves are shown in Figure 2. The results clearly demonstrated that the silicon chain extender structure has a significant effect on properties of polyurethanes. The major effect is in making polyurethanes more flexible and low modulus compared with the BDO chain extended PU, as illustrated by high elongation at break, low Young's and flexural modulus, as well as low Shore hardness. Associated with this was some compromise in ultimate tensile and tear strength. However, this compromise was not so significant for BHTD and BPTD. It is noteworthy that for BHTD and BPTD, the flexural modulus decreased over 70% but the corresponding ultimate tensile strength UTS decrease was less than 15%. BETD produced PUs with significantly low UTS compared with others in the series, where the decrease was nearly 50%. All four SCEs with the siloxane backbone showed similar moduli as

TABLE III
Tensile Properties of Synthesized Polyurethanes (As-Annealed)

Sample	Elong (%)	UTS (MPa)	YM (MPa)	Stress 100%	Tear S N/min	FM (MPa)	Shore H (A)
PU-BDO	317 ± 4	23 ± .9	32 ± 3	11.6 ± .4	61 ± 4	36 ± 2	85
PU-BHTD	391 ± 5	19.8 ± .4	7.8 ± .4	5.1 ± .13	43.2 ± .6	9.8 ± .5	70
PU-BPTD	410 ± 10	20.6 ± .7	6.9 ± .7	5.3 ± .05	44.3 ± .3	9.1 ± .7	72
PU-HTDE	436 ± 19	16.7 ± 1	10.6 ± .2	6.6 ± .1	46.6 ± 1	13 ± .9	72
PU-BETD	414 ± 49	13 ± 1.6	7.5 ± .4	5.2 ± .2	41.1 ± 4	9.5 ± .4	69

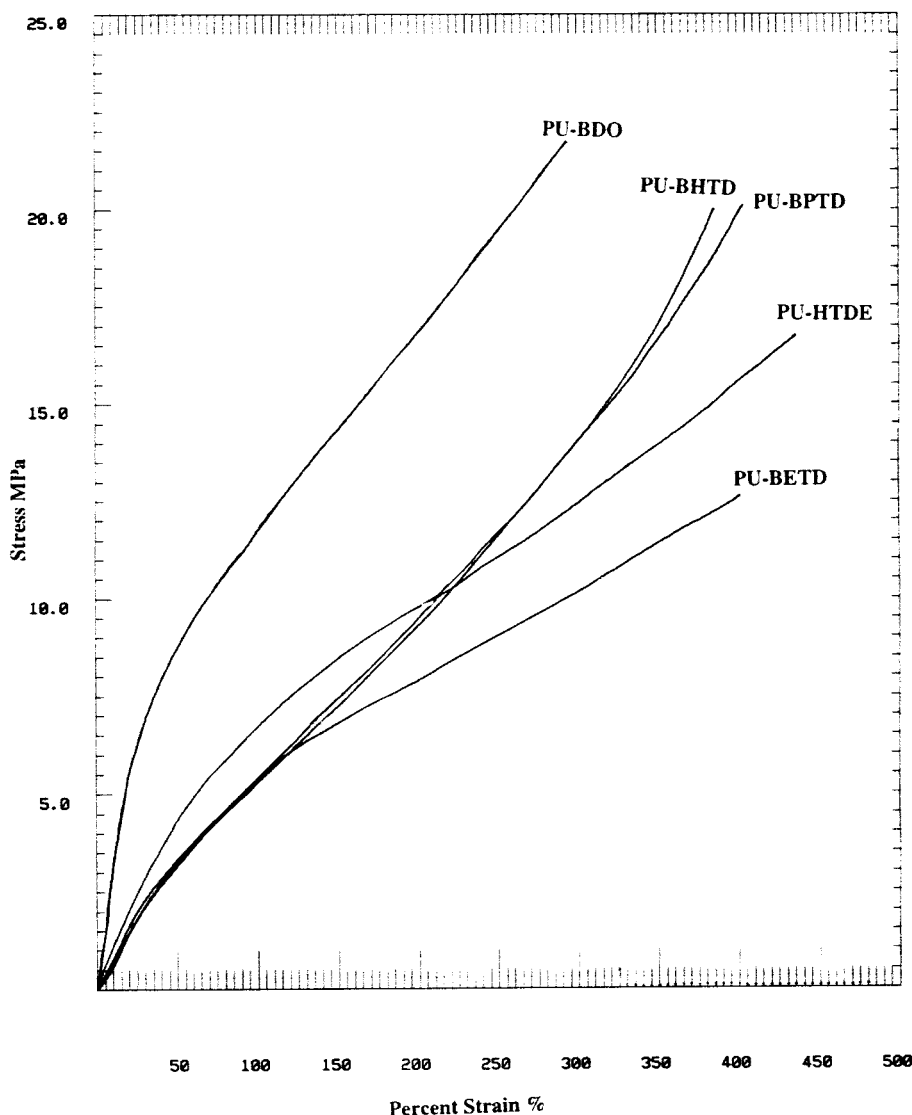YM: Young's modulus; Tear S: tear strength; FM: flexural modulus.

Figure 2 Stress–strain curve of synthesized polyurethanes.

shown in Table III and Figure 3. The only chain extender with the longest alkyl chain (BETD) produced PUs with the poorest mechanical properties of the
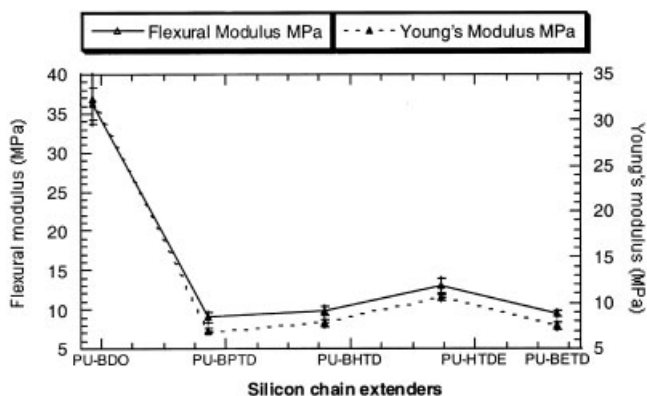

Figure 3 Effect of different silicon chain extenders on Young's and flexural modulus.

series. It should be noted here that this materials also had significantly lower molecular weights than others in the series. HTDE with a disilylethylene backbone yielded slightly more stiff materials, in comparison to those with siloxane backbone. The results therefore indicate that the silicon chain extenders with Si—O—Si— linkages produced softer PUs than that with the —Si—CH$_2$CH$_2$—Si— linkage in the backbone. Further, SCEs with longer alkyl chains produced materials with poor tensile strength. The observed differences could largely be a consequence of the morphology as the chain extender structure should significantly affect the phase separation and ordering in the hard segment.

Polyurethane morphology

Differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and Fourier trans-
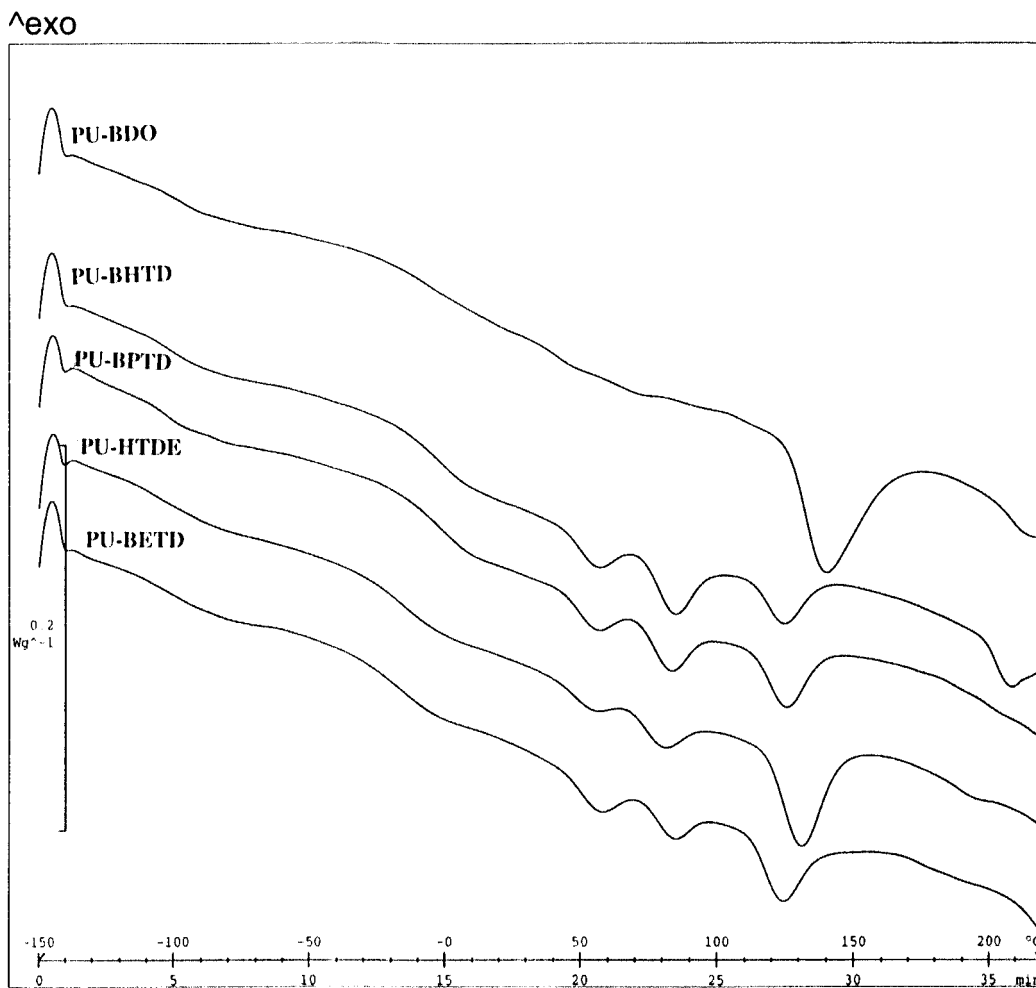
Figure 4 DSC thermograms of synthesized polyurethanes (as-annealed).

form infrared (FTIR) spectroscopy were used to study the effect of chain extender structure on polyurethane morphology. All tests were carried out using test specimens obtained from compression molded and annealed films. The annealing was carried out at 100°C for 10 h to minimize any thermal effects.

Figure 4 shows the DSC traces of the series of polyurethanes. PU-BDO showed a sharp melting endotherm at 138°C, which is assigned to melting of hard domains based on primarily MDI_2BDO segments, the hard segment formed from two MDI and one BDO. In contrast, all SCE-based polyurethanes showed three melting endotherms and the peak melting temperatures are summarized in Table V. Since all mixed SCE-based polyurethanes have 60 mol % BDO as the other chain extender, the higher temperature melting endotherm could be assigned to hard domains based on MDI_2BDO segments. The second melting endotherm around 80°C is attributed to hard domains based on the silicon chain extender. The third melting endotherm could be assigned to single MDI linkages (MDI linked to polyol without chain extender). Since the molar ratio of polyol to MDI in SCE-based PUs is

less than 2 (see Table I), there will always be single MDI linkages in the polyurethanes. DSC results suggests that the hard segments containing SCE form distinct domains, and it does not appear that SCE-based hard segments mix with BDO-based segments. This incompatibility may be due to two reasons. The first is the significant structural dissimilarity between SCE and BDO, causing MDI_2BDO and MDI_2SCE (hard segment with two MDI and one SCE) segments, not to form ordered domains. The second is the difference in solubility parameters of the respective segments. Table IV summarizes the calculated solubility parameters of reagents used in PU synthesis. Due to lower solubility parameters of silicon chain extenders, it is expected that MDI_2SCE segments would have significantly lower solubility parameters compared to MDI_2BDO. Accordingly, these two hard segments would not mix nor form common hard domains with mixed segments. The presence of distinct domains as evidenced by DSC results is consistent with this rationale.

The glass transition temperatures of the PDMS soft segments and amorphous interfacial segments (large-

TABLE IV
Calculated Solubility Parameter

Compounds	Calcd solubility parametere δ (cal/mL)$^{1/2}$
PDMS MW 1000	6.66 ± 0.20
PHMO MW 700	9.34 ± 0.07
MDI	9.94 ± 0.09
BDO	13.98 ± 0.05
BHTD	9.28 ± 0.14
BPTD	9.30 ± 0.21
HTDE	9.00 ± 0.05
BETD	7.59 ± 0.06
Prepolymer of MDI and PDMO 1000	7.52 ± 0.16
(MDI-BDO)$_1$	12.2–12.7[a]

The parameters were calculated using the MSI Amorphous Cell package with the PCFF2 force field.
  [a] From Tonelli et al.[19]

ly PHMO and ethoxypropyl end groups) are summarized in Table V. The T_g of PDMS in all cases vary in a very narrow temperature range. If there was phase mixing involving PDMS, then the glass transition temperature would be expected to increase significantly. Absence of this indicates that in these materials the soft segment PDMS largely remains phase separated. The T_g of the amorphous interfacial regions, however, varied depending on the SCE structure. In PU-BHTD and PU-BPTD, the T_g has shifted to higher temperatures compared to that in PU-BDO, indicating some phase mixing. But the opposite trend was observed for PU-HTDE and PU-BETD, indicating these two are more phase separated. This is supported by the observed heat of fusion for melting endotherms as shown in Table V . The total ΔH was the highest for PU-BDO, and among the other five PU-BETD and PU-HTDE had higher values (7.44 and 6.01, respectively) than the other two. Based on these results, PU-BHTD appear to be the most phase mixed of the series followed by PU-BPTD. Interestingly, these two materials also showed higher tensile strength.

DMTA results generally supported DSC results with respect to morphology as well as the corresponding modulus changes discussed earlier. Figure 5 (a) and (b) show the Tan δ vs temperature and storage
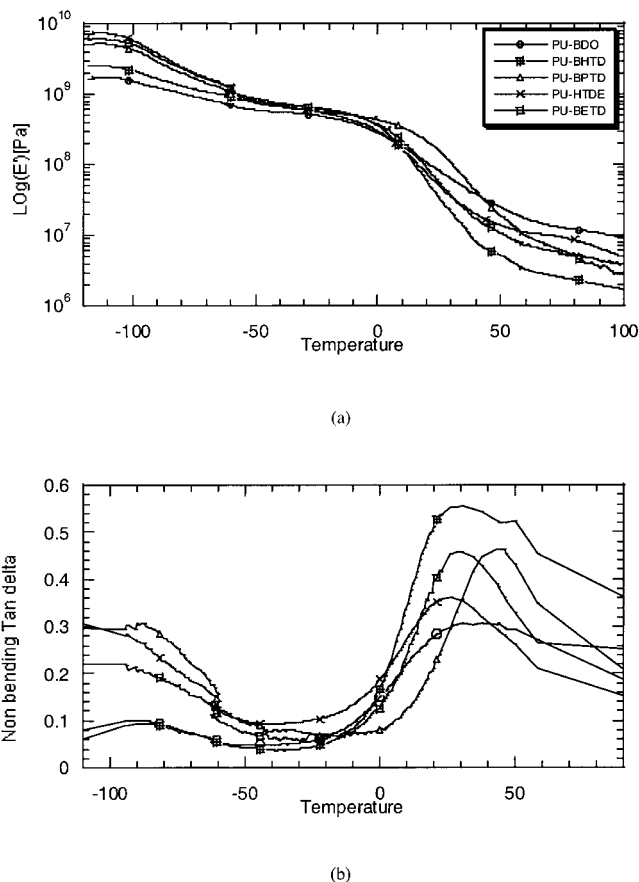

(a)

(b)

Figure 5 DMTA thermal transitions curves: (a) storage modulus (E') and (b) tan δ vs temperature.

modulus vs temperature plots, respectively. Figure 5(a) clearly shows that the modulus of the SCE-based polyurethanes was significantly low compared to PU-BDO in the temperature range 20–100°C and this difference becomes less significant at lower temperatures. The position and the intensity of the tan δ peak [see Fig. 5 (a)] were dependent on the chain extender structure. In all cases tan δ peaks were generally broader, but all SCE-based PUs exhibited lower peak temperatures than that of PU-BDO. Consistent with DSC results, PU-BETD and PU-HTDE had the lowest temperatures in the series. The T_g of PDMS soft seg-

TABLE V
DSC Thermogram of Series Polyurethanes (As-Annealed)

Sample	T_g (PDMS) onset, mid point and end set (°C)	T_g (PDMS end group/comacrodiol) onset, midpoint and end set °C/ ΔC_p, j/g · k	Hard segment endotherms peak temperatures (°C) and heat of fusion ΔH, jg^{-1}
PU-BDO	-107.2, -100.3, -93.2	-20.6, -7.4, 10.19 (0.18)	138.3 (9.95)
PU-BHTD	-113.8, -112.2, -110.5	-13.4, -5.3, 3.7 (0.15)	55.2 (1.1),83.6 (2.26),123.7 (1.94)
PU-BPTD	-109.5, -104.2	-17.88, -5.18 (0.21)	54.7 (1.02),81.8 (1.76),124.3 (2.86)
PU-HTDE	-113.4, -103.6	-28.6, -18.4 (0.15)	53.5 (0.59),79.2 (1.31),129.9 (5.54)
PU-BETD	-114.1, -104.4	-30.6, -20.3 (0.17)	55.9 (1.25),83.1 (1.07),122.8 (3.69)

TABLE VI
DMTA Thermal Transition Temperatures of Polyurethanes (As-Annealed)

Sample	Tan δ peak temperatures	T_g (PDMS) midpoint °C/from E''	T_g (soft/hard interfacial regions) midpoint/°C from E''
PU-BDO	−93.0, 29.66	−100.86	2.17
PU-BHTD	−95.94, 24.46	−101.84	2.46
PU-BPTD	−102.06, 25.71	−102.23	26.7
PU-HTDE	14.10	−104.1	19.0
PU-BETD	17.64	−102.2	19.2

ment phase estimated based on E'' vs temperature plots (see Table VI), although higher than those determined by DSC, showed no significant change, confirming that PDMS phase in these materials remains phase separated. The T_g of the amorphous interfacial regions also showed the same trend as that observed in DSC results. BETD and HTDE showed the lowest T_g of the series, indicating these materials are less phase mixed. The higher T_g values observed relative to those determined by DSC may be due to nature of the DMTA technique[8] as well as to the samples used for DMTA analysis, which were as-molded opposed to annealed samples used for DSC analysis.

Further support for the observed morphology differences were obtained from FTIR analysis of the polyurethanes. The transmission FTIR spectra were obtained from uniform thin films (2.5 μm) sectioned from compression-molded sheets after similar thermal treatments as for DSC test specimens. The height of the carbonyl peaks were normalized against the urethane N—H bending and C—N stretching bands near 1532 cm^{-1} as the main reference peaks.[18] The relative

intensities of the bonded 1702 cm^{-1}) and nonbonded carbonyl (1730 cm^{-1}) were used to estimate the extent of phase mixing. The percentage of nonbonded carbonyls were calculated from peak heights and the results are shown in Figure 6. A higher percentage of nonbonded carbonyl indicates a high level of phase mixing, since such carbonyls would likely to be in the interfacial regions. The higher percentages nonbonded carbonyls for all SCE-based polyurethanes indicated that there is increased phase mixing in these materials than that in PU-BDO, but the increase was only marginal. These results are consistent with DSC and DMTA results.

Overall, DMTA and FTIR results corroborated DSC results, and confirmed that of the chain extenders studied BHTD and BPTD produced PUs that are relatively more phase mixed the others.

CONCLUSION

The results in this study clearly indicated that the structure of silicon chain extender significantly affected the polyurethane properties. In general, all silicon chain extenders investigated were found to be suitable for preparing low-modulus siloxane-based polyurethanes. But BHTD and BPTD produced low-modulus polyurethanes without significant compromise in tensile strength. The siloxane segment in the chain extender backbone produced softer materials compared to having disilylethylene.

The effect on morphology was unique in that there was very little hard segment mixing between BDO- and SCE-containing segments, resulting in the formation of distinct domains based on hard segments from respective chain extenders. The PDMS soft segment in these polyurethanes largely remained phase separated. This unique morphology may be the primary reason for achieving low-modulus polyurethanes without significant compromise in strength.

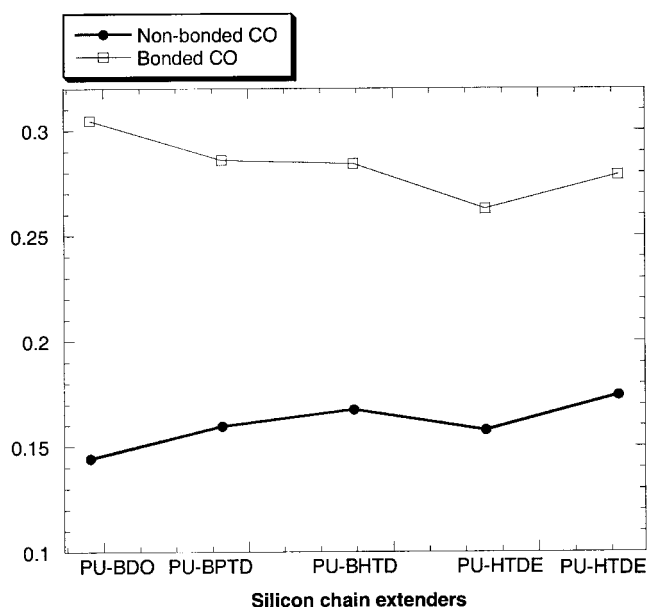**Figure 6** Peak heights of bonded (CO$_b$) and nonbonded carbonyl (CO$_n$) absorption of polyurethanes containing different silicon chain extenders.

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