

Effect of Chain Extender Structure on the Properties and Morphology of Polyurethanes Based on H₁₂MDI and Mixed Macrodiols (PDMS–PHMO)

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ABSTRACT: The effect of chain extender structure on properties and morphology of α,ω -bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS) and poly(hexamethylene oxide) (PHMO) mixed macrodiol-based aliphatic polyurethane elastomers was investigated using tensile testing, differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA). All polyurethanes were based on 50 wt % of hard segment derived from 4,4'-methylenecyclohexyl diisocyanate (H₁₂MDI) and a chain extender mixture. 1,4-Butanediol was the primary chain extender, while one of 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (BHTD), 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane (BPTD), hydroquinonebis(2-hydroxyethyl)ether (HQHE), 1,3-bis(3-hydroxypropyl)tetramethyldisilylethylene (HTDE), or 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (HFPD) each was used as a secondary chain extender. Two series of polyurethanes containing 80 : 20 (Series A) and 60 : 40 (Series B) molar ratios of primary and secondary chain extenders were prepared using one-step bulk polymerization. All polyurethanes were clear and transparent and had number-average molecular weights between 56,000 and 122,100. Incorporation of the secondary chain extender resulted in polyurethanes with low flexural modulus and high elongation. Good ultimate tensile strength was achieved in most cases. DSC and DMTA analyses showed that the incorporation of a secondary chain extender disrupted the hard segment order in all cases. The highest disruption was observed with HFPD, while the silicon-based chain extenders gave less disruption, particularly in Series A. Further, the silicon chain extenders improved the compatibility of the PDMS soft segment phase with the hard segment, whereas with HFPD and HQHE, this was not observed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2979–2989, 1999

Key words: aliphatic polyurethane elastomers; siloxane macrodiol; silicon chain extenders; synthesis; thermal and mechanical properties; morphology

INTRODUCTION

Polyurethane elastomers are linear alternating block copolymers of soft and hard segments de-

rived from a macrodiol, and a diisocyanate-chain extender combination, respectively. These polymers typically exhibit a two-phase morphology due to the incompatibility of the soft and hard segments. The excellent mechanical properties of polyurethanes, such as high tensile strength and toughness, are primarily due to the two-phase microstructure resulting from this phase separation.^{1–2} The structure and the molecular weight of the macrodiol significantly influence the phase

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Table I Chain Extender Structures and Abbreviations

Secondary Chain Extenders	Structure	Abbreviation
1,3-bis(4-hydroxybutyl)tetramethyldisiloxane		BHTD
1,3-bis(3-hydroxypropyl)tetramethyldisiloxane		BPTD
1,3-bis(3-hydroxypropyl)tetramethyldisilylethylene		HTDE
Hydroxyquinonebis(2-hydroxyethyl)ether		HQHE
2,2,3,3,4,4-Hexafluoro-1,5-pentanediol	$\text{HO}-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-\text{OH}$	HFPD

separation behavior of polyurethanes and, consequently, their properties. Most previous studies^{1–6} on structure–property relationships of polyurethanes have been focused on polyether, polyester, and polycarbonate macrodiols. There has been some recent interest on polyurethanes based on nonpolar macrodiols, such as polydimethylsiloxane (PDMS),⁷ polyisobutylene,⁸ and polybutadiene⁹ macrodiols. Typically, polyurethanes based on nonpolar macrodiols are highly phase separated (poor interfacial adhesion) and, consequently, have poor mechanical properties.¹⁰

However, recent studies^{11–14} in our laboratory have demonstrated that polyurethanes with good mechanical properties can be prepared from nonpolar macrodiols, such as PDMS by incorporating a small amount of the polyether macrodiol poly(hexamethylene oxide) (PHMO). It was postulated that the polyether–macrodiol segment when present at a low level primarily concentrates in the interfacial region between hard and soft domains. A low level of the polyether macrodiol (~20 wt % of the macrodiol) improves the compatibility of the two segments to a controlled extent, resulting in polyurethanes with enhanced mechanical properties. Further studies¹⁴ have shown that silicon-based chain extenders when combined with conventional chain extenders, such as 1,4-butanediol, and PDMS–PHMO macrodiols, can lead to materials with low flexural

modulus and that retain good mechanical properties and biostability.

As part of our efforts to develop polyurethanes with low flexural modulus and degradation resistance, we have studied the effect of chain extender structure on properties and morphology of polyurethanes based on the aliphatic diisocyanate H₁₂MDI. Typically, polyurethanes based on H₁₂MDI (a configurational isomeric mixture of cis–cis, cis–trans, trans–trans) are transparent with good flexibility and set but generally have poor biostability.^{15–18} It is envisaged that by the incorporation of PDMS-based soft segments, the degradation resistance of H₁₂MDI based polyurethanes could be improved. Further, the use of chain extender mixtures would allow one to control the level of phase mixing to overcome any incompatibility associated with PDMS macrodiol. The inherent light-stability of aliphatic polyurethanes,¹⁹ combined with improvement in biostability and flexibility, might make such materials highly desirable for medical implant applications.

In this investigation, the structure of the chain extender component of the polyurethane was varied by using a mixture of 1,4-butanediol (BDO, primary chain extender) and a secondary chain extender. Five secondary chain extenders (see Table I), 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (BHTD), 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane (BPTD), hydroxyquinonebis(2-hydroxy-

ethyl)ether (HQHE), 1,3-bis(3-hydroxypropyl)tetramethyldisilylethylene (HTDE) and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (HFPD), were explored in two composition ratios. The two chain extender compositions were 80 : 20 (Series A) and 60 : 40 (Series B) molar ratios of the primary and secondary chain extenders. All polyurethanes were H₁₂MDI-based with a constant weight fraction (50%) of an 80/20 (*w/w*) mixture of PDMS and PHMO.

EXPERIMENTAL

Materials

The isomeric composition of the commercial sample of H₁₂MDI used in this study was 13.5% *trans-trans*, 84.6% *cis-trans*, and 2.0% *cis-cis*, as determined by gas chromatography–mass spectroscopy (GC–MS). Poly(hexamethylene oxide) was synthesized by the acid-catalyzed condensation polymerization of 1,6-hexanediol.²⁰ The BDO was dried over molecular sieves (3 Å) and distilled under vacuum, and the middle fraction was used for polymerization; whereas BHTD and BPTD (Silar Laboratories), HQHE (Aldrich), and HFPD (Fluorochem) were used as received. HTDE was synthesized from allyl alcohol and tetramethyldisilylethylene using a hydrosilylation reaction. α,ω -Bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS) was obtained from Shin Etsu (Japan). Both PDMS and PHMO were dried thoroughly under a vacuum of 0.1 torr at 105°C for at least 12 h prior to synthesis. The catalyst dibutyltin dilaurate (Eastman Kodak) was used as received.

Synthesis of Polyurethane Elastomers

The polyurethane elastomers were synthesized by a one-step bulk polymerization method. All glassware was dried in an oven at 105°C. A typical one-step bulk polymerization procedure was performed as follows.

The predried macrodiols, PDMS (40.0 g, MW 940.3) and PHMO (10 g, MW 696.1), BDO (4.43 g), BHTD (9.13 g), and catalyst dibutyltin dilaurate (0.006 g, 0.01 wt % of total solids) were placed in a 250-mL polypropylene beaker and degassed at 80°C in an oven under a vacuum of 2 torr for 1.5 h. H₁₂MDI (36.4347 g, MW 262.35) was weighed into a wet-tared 50-mL polypropylene beaker and quickly poured into the macrodiol mixture while

rapidly stirring with a stainless steel spatula under a nitrogen blanket. After mixing for 1 min, the viscous polymer was poured onto a Teflon-coated metal pan and cured for 12 h in an oven at 100°C under dry nitrogen.

All polyurethanes were designated as PU-XXXX-YY, where XXXX is the secondary chain extender abbreviation and YY is its molar percentage in the chain extender mixture, with the exception of the control material based on BDO alone. It was labelled as PU–BDO. For example, PU–BHTD-20 denotes a polyurethane prepared from PDMS–PHMO (80 : 20 *w/w*), H₁₂MDI and an 80 : 20 molar mixture of BDO and of 1,3-bis(4-hydroxybutyl)tetramethyl-disiloxane (BHTD). The polyurethanes based on the 80 : 20 and 60 : 40 molar ratios of the chain extenders are referred to as Series A and Series B, respectively. As a group, BHTD, BPTD, and HTDE were referred as silicon chain extenders for simplicity.

Size-Exclusion Chromatography

Size exclusion chromatography (SEC) of polyurethanes was carried out on a Waters 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 (10⁵, 10³, and 500 Å). The system was equipped with a refractive index detector and was calibrated with narrow distribution polystyrene standards. Results are expressed, therefore, as polystyrene-equivalent molecular weights.

Sample Preparation

After drying for 15 h at 60°C *in vacuo* (0.1 torr), polyurethane samples were compression-moulded into flat sheets at temperatures between 200 and 250°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. All samples were inspected under cross-polarizers to confirm the absence of internal stress. Dumbbells were stored under ambient conditions for at least 2 weeks 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

Table II Molecular Weights of Polyurethanes

Sample Code	\bar{M}_n	\bar{M}_w	Polydispersity \bar{M}_w/\bar{M}_n
Control:			
PU-BDO	68,300	96,800	1.42
Series A:			
PU-BHTD-20	64,830	173,040	2.66
PU-HTDE-20	64,820	151,480	2.33
PU-BPTD-20	55,950	123,660	2.21
PU-HQHE-20	91,460	162,250	1.77
PU-HFPD-20	122,100	193,800	1.58
Series B:			
PU-BPHD-40	57,260	139,900	2.44
PU-HTDE-40	57,530	138,400	2.40
PU-BPTD-40	60,900	133,950	2.19
PU-HQHE-40	92,360	379,400	4.10
PU-HFPD-40	84,070	155,840	1.85

kN load cell was used and the crosshead speed was 500 mm/min. The results reported are the mean values for five replicates. Hardness measurements were carried out using a Shore A durometer.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analysis over the temperature range -150 to 250°C were performed using a Mettler DSC 30 calorimeter linked to a Mettler TC 10A thermal analysis processor. The experiments were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. Sample weights were 20–25 mg. The samples were dried at 65°C for 48 h under vacuum (0.1 torr) prior to analysis.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) was carried out on a Rheometric Scientific Mark IV instrument. The samples with dimensions $10 \times 1.6 \times 45$ mm were mounted on a dual cantilever with a 5-mm free length frame. The analysis frequency was 14 Hz, and the heating rate was $2^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

All polyurethanes were clear and transparent, as expected from commercial H_{12} MDI, which is a mixture of configurational isomers. Table II lists the molecular weights of the two series of poly-

urethanes and the control polyurethane based on BDO as the chain extender. The number-average molecular weight varied between 55,950 and 122,100 with various chain extender combinations. The structure and the amount of the secondary chain extender had a significant effect on the polyurethane molecular weight and polydispersity. The secondary chain extenders, HQHE and HFPD, produced polyurethanes with higher molecular weights than those from silicon chain extenders. Generally, the polydispersities of the mixed chain-extender-based polyurethanes were higher than the control. With the exception of BHTD, the others showed an increase in polydispersity when the amount of the secondary chain extender was increased. However, this did not have a significant effect on the molecular weight; the exception was HFPD, for which the molecular weight was lower for the polyurethane with 40 mol % secondary chain extender.

The observed broadness in molecular weight distribution reflects a difference in reactivity of the hydroxyls of the mixed chain extenders. Since all of the chain extenders used had primary hydroxyl groups, the difference may be largely due to compatibility differences with H_{12} MDI and macrodiols.

Among the secondary chain extenders, HFPD produced polyurethanes with the narrowest polydispersity, attributed to its symmetrical structure with no substituent groups in the chain. The highest polydispersity was observed for PU-HQHE-40, presumably due to poor miscibility with other components, especially at the 40 mol % level. In this case, during the initial mixing of reactants to polymerize, the mixture stayed cloudy for over 2 min, indicating that HQHE had poor miscibility with other reactants. In all the other cases, the reaction mixture turned clear within a few seconds of initial mixing.

Mechanical Properties

Series A

The tensile properties, Shore hardness, and flexural modulus of Series A polyurethanes, along with those of the control polyurethane PU-BDO, are shown in Table III. The control polyurethane exhibited the highest Young's modulus and flexural modulus of all polyurethanes investigated. The polyurethanes based on mixed chain extenders were more elastomeric than PU-BDO as with higher elongations at break. However, the UTS

Table III Mechanical Properties of Series A Polyurethanes

Sample	Elongation at Break (%)	UTS (MPa)	YM (MPa)	Stress at 100% Elongation (MPa)	Flexural Modulus (MPa)	Shore A Hardness
PU-BDO	255 ± 25	23.8 ± 0.9	127 ± 11	18.2 ± 0.3	151 ± 9.3	92
PU-BHTD-20	352 ± 10	17.4 ± 9.5	41.2 ± 6.0	8.70 ± 0.2	38.5 ± 1.2	87
PU-HTDE-20	343 ± 19	14.9 ± 1.0	46.2 ± 2.4	8.70 ± 0.1	40.1 ± 1.3	84
PU-BPTD-20	339 ± 9	20.8 ± 7.2	51.8 ± 5.1	9.3 ± 0.1	43.8 ± 6.5	90
PU-HQHE-20	294 ± 19	22.6 ± 1.3	102 ± 20	13.3 ± 0.3	112 ± 2.0	94
PU-HFPD-20	351 ± 16	19.9 ± 0.9	89.3 ± 11	10.6 ± 0.5	68.6 ± 0.5	93

were lower than the control in all cases; and, in general, the decrease in UTS for silicon-based chain extenders (BHTD, HTDE, and BPTD) was significantly higher than those of HQHE and HFPD-based polyurethanes. The most notable differences were observed for Young's modulus and flexural modulus. All mixed chain extender-based polyurethanes were softer (low Shore hardness) and more flexible than the control material. Further, the silicon chain extenders made the polyurethanes significantly softer than either HQHE or HFPD-based polyurethanes. Of the three silicon chain-extender-based polyurethanes, PU-BPTD-40 was the least flexible (Table III), while PU-BHTD-40 was the most flexible. The Shore hardness measurements were consistent with this effect.

Series B

The properties of the Series B polyurethanes are shown in Table IV. The observed trend here was very similar to that seen with the Series A materials. As expected, increasing the secondary chain extender concentration decreased the Shore hardness and flexural modulus. In both series, the

silicon chain extenders produced materials with the lowest flexural modulus and Shore hardness, whereas HQEE and HFPD produced less flexible polyurethanes. Increasing the secondary chain extender proportion from 20 to 40 mol % (see Tables III and IV) resulted in a decrease in UTS in all cases, except for PU-HQHE and PU-HTDE. The latter showed no change in UTS, while the former showed an increase.

These results indicated that by incorporating a secondary chain extender, aliphatic polyurethanes with increased flexibility and good elasticity could be prepared, while retaining good ultimate tensile strength. Of the five chain extenders investigated, the silicon chain extenders generally produced polyurethanes with the lowest flexural modulus. It is postulated that the silicon chain extenders increase the size of the interfacial region and strengthen the otherwise weak interactions of the nonpolar PDMS-rich soft segment and the hard segment.

Polyurethane Morphology

DSC was used to investigate the effect of the structure of the secondary chain extender on poly-

Table IV Mechanical Properties of Series B Polyurethanes

Sample	Elongation at Break (%)	UTS (MPa)	YM (MPa)	Stress at 100% Elongation (MPa)	Flexural Modulus (MPa)	Shore A Hardness
PU-BDO	255 ± 25	23.8 ± 0.9	127 ± 11	18.2 ± 0.3	151 ± 9.3	92
PU-BHTD-40	424 ± 21	15.9 ± 1.4	18.4 ± 2.0	5.1 ± 0.2	10.7 ± 2.9	72
PU-HTDE-40	384 ± 9.3	22.0 ± 0.3	22.2 ± 3.6	6.1 ± 0.1	12.7 ± 0.5	76
PU-BPTD-40	385 ± 30	15.0 ± 0.1	19.1 ± 2.7	5.2 ± 0.2	17.8 ± 0.2	78
PU-HQHE-40	279 ± 13	22.8 ± 0.7	92.5 ± 19	13.1 ± 0.4	122 ± 9.2	91
PU-HFPD-40	368 ± 33	14.3 ± 1.2	69.5 ± 4.8	8.2 ± 0.3	49.0 ± 5.5	90

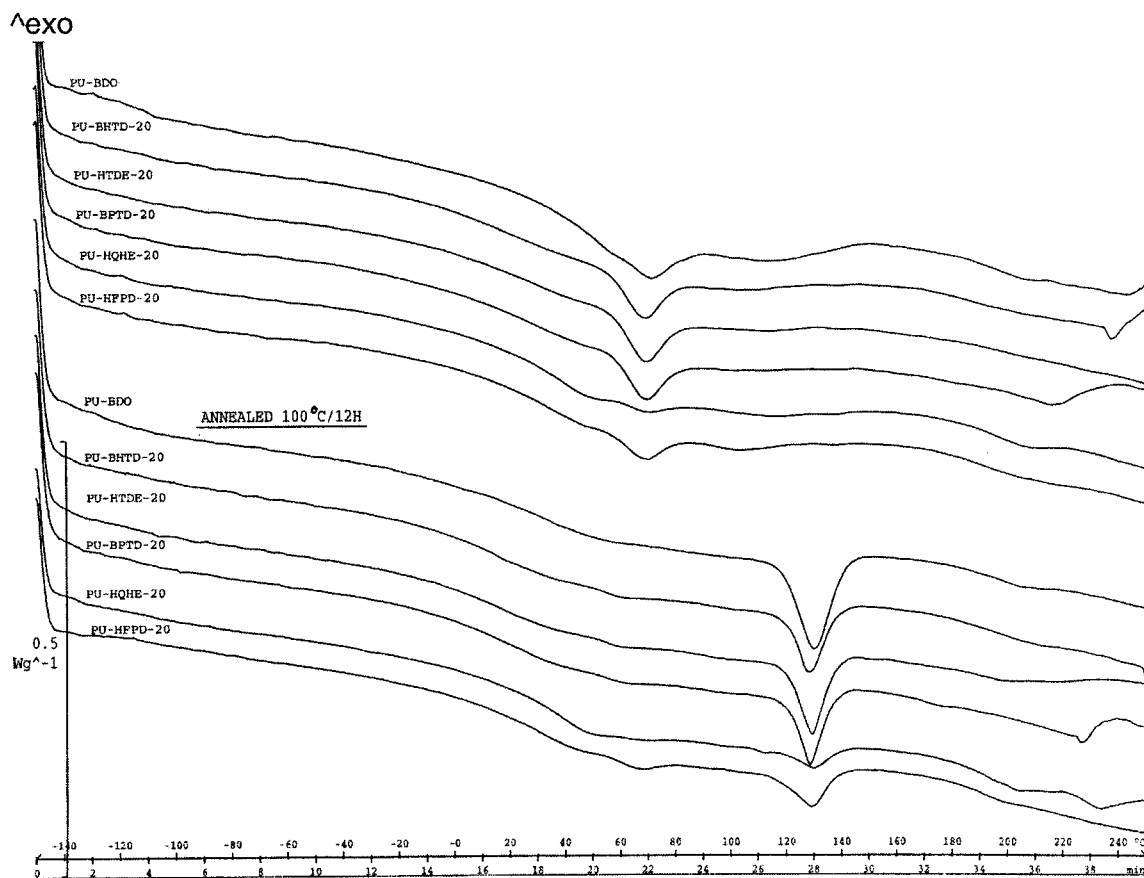


Figure 1 DSC thermograms of Series A polyurethanes.

urethane morphology. Figures 1 and 2 show the DSC thermograms of compression-moulded polyurethanes in Series A and B. All samples were analyzed in as-moulded and annealed states. H_{12} MDI-based polyurethanes typically exhibit very little hard segment crystallinity because of the presence of a mixture of three isomers.^{15–18,19} Figure 1 shows the DSC thermograms of as moulded Series A polyurethanes. The thermal transitions for PU-BDO appeared in the temperature range of 0 to 140°C. This broad transition appeared to be resulting from overlapping of a number of transitions, which are largely associated with ordered and amorphous hard segment domains based on the three isomers of H_{12} MDI and the glass transition of PHMO. Within this broad transition, a peak that appeared as a melting endotherm was observed, centered around 70°C. This endotherm in similar systems reported^{16,17,19} in the literature has been attributed to annealing effects. The DSC thermograms of the three silicon chain extender-based polyurethanes showed similar thermal transitions in the 0 to

140°C temperature range, except that the most prominent endotherm (centered at 68°C) was sharper than that of the control. The other two materials, PU-HQHE-20 and PU-HFPD-20, exhibited the least-ordered hard segment of the series. The assignment of various transitions with any certainty was difficult due to the structural complexity of these polyurethanes. Since annealing at moderate temperatures²¹ typically improves hard segment ordering without changes to chemical structure, the polyurethanes were annealed at 100°C for 12 h and analyzed by DSC. Figure 1 shows the DSC thermograms of the annealed Series A polyurethanes. Annealing significantly changed the DSC profile of all of the polyurethanes. The most notable feature was the appearance of a sharp melting endotherm around 130°C and the disappearance of the endotherm at 70°C. This type of melting endotherm, which appears to be 20 to 50°C above the annealing temperatures, has been described as due to local rearrangement of hard domains in other polyurethanes.¹⁷ Considering that the diisocyanate is

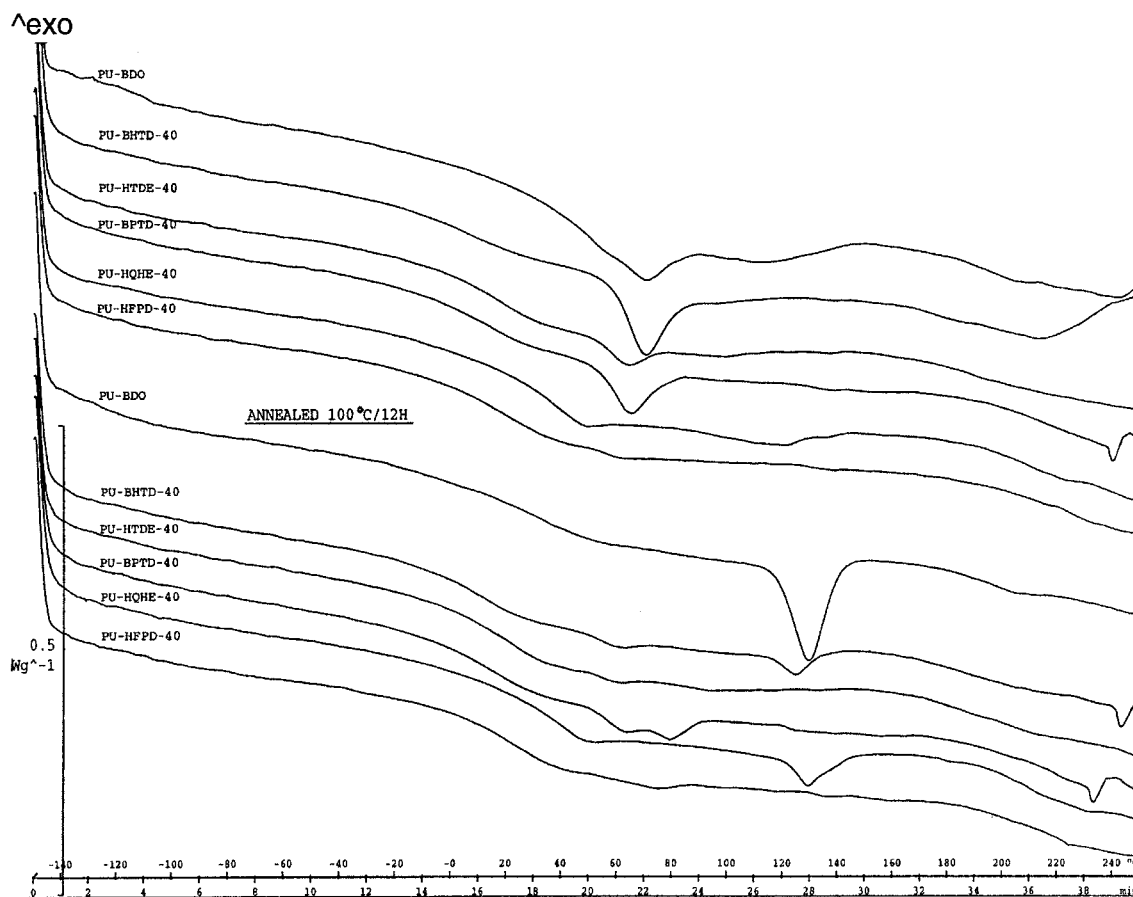


Figure 2 DSC thermograms of Series B polyurethanes.

rich in *cis*-*trans* isomer (85%), this endotherm can be assigned to melting of domains associated with $[(c-t\text{-H}_{12}\text{MDI})_2\text{-BDO}]_x$ -type hard segments. In the as-moulded state, this transition appeared at a lower temperature due to mixing with hard segments involving the other isomers. The thermograms of the three silicon chain-extender-based polyurethanes were similar to that of the control material, except for the presence of what appeared to be a second glass transition, presumably associated with the hard segments based on the silicon chain extenders. In these cases, the silicon chain-extender-based hard segments appeared to exist in separate phase from the BDO-based hard segments. The other two materials, PU-HQHE-20 and PU-HFPD-20, showed a relatively weak melting endotherm at 130°C and exhibited the least-ordered hard segments of the series. In these two cases, the respective secondary chain-extender-based hard segments appeared to be more compatible with the BDO-based hard segment. The observed low ΔH (see

Table V) for the transition at 129°C in these two materials compared to the other materials supported this argument.

The other main transition common to all materials in the series was the very broad glass transition due to amorphous hard segment/interfacial regions of the polyurethanes. The very broad temperature range covered by this transition indicated that multiple glass transitions would be involved, presumably from structurally different hard and soft segments possible in these materials. The T_g of the PHMO soft segment is also expected to fall in this temperature range.

Series B was similarly analyzed by DSC in as-moulded and annealed (100°C) states (see Table VI and Fig. 2). The as-moulded polyurethanes exhibited significantly broader thermal transitions than those observed for Series A, indicative of the presence of significantly less-ordered structures. PU-HQHE-40 and PU-HFPD-40 were largely amorphous, as evidenced by the presence

Table V DSC Thermal Transitions and Melting Endotherm Heat of Fusion for Series A Polyurethanes

Polyurethane	Soft Segment PDMS T_g [Onset and End Point (°C)]	Hard Segment T_g [Onset, Mid-, & End Point (°C)] (ΔC_p , J/g * K)	Hard Segment Melting Peaks Temperature (°C) ($\Delta H/jg^{-1}$)
As-moulded:			
PU-BDO	-118.7, -103.0	40.9, 49.0, 57.1 (0.29)	70.9 (6.50)
BDO-BHTD-20	-116.1, -104.7	-1.5, 16.5, 34.7 (0.29)	67.1 (7.90)
BDO-HTDE-20	-113.8, -96.0	32.8, 42.6, 52.5 (0.28)	68.0 (7.67)
BDO-BPTD-20	-109.0, -96.0	8.6, 26.9, 45.2 (0.31)	68.7 (4.52)
BDO-HQHE-20	-117.1, -100.0	24.5, 36.6, 48.7 (0.31)	49.8 (4.75), 112.3 (1.46)
BDO-HFPD-20	-116.1, -96.43	13.4, 29.9, 46.4 (0.35)	68.9 (5.66)
Annealed (100°C):			
PU-BDO	-126.8, -106.9	-5.5, 22.4, 50.4 (0.43)	129.1 (9.26), 203.7 (0.67)
BDO-BHTD-20	-108.4, -88.7	-2.8, 13.1, 29.1 (0.33)	126.8 (6.12)
BDO-HTDE-20	-105.6, -97.3	-7.3, 11.3, 30.0 (0.33)	128.1 (5.71)
BDO-BPTD-20	-107.5, -103.2	-0.4, 23.4, 48.2 (0.46)	127.4 (5.73)
BDO-HQHE-20	-116.9, -96.9	4.7, 19.9, 35.2 (0.41)	129.2 (2.60)
BDO-HFPD-20	-106.5, -95.2	19.0, 27.1, 35.2	64.5, 128.4 (3.23)

of broad glass transitions and melting endotherms.

Figure 2 shows the DSC thermograms of Series B polyurethanes after annealing at 100°C. Similar to Series A, annealing significantly changed the DSC profile of all the materials. PU-BHTD-40 showed two melting endotherms; the first at 70°C was assigned to BHTD-based hard segment domains, while the second (130°C) was

attributed to domains rich in [(*c-t*-H₁₂MDI)_n-BDO]_x segments. This latter endotherm was absent in the other two silicon chain-extender-based materials, indicating that they are more phase-mixed than PU-BHTD. Of the five chain extenders investigated, PU-HFPD showed the least-ordered hard-segment phase. At the 40 mol % level, the polyurethane was completely amorphous. DSC does not provide sufficient evidence to indi-

Table VI DSC Thermal Transitions and Melting Endotherm Heat of Fusion for Series B Polyurethanes

Polyurethane	Soft Segment PDMS T_g [Onset and End Point (°C)]	Hard Segment T_g [Onset, Mid-, & End Point (°C)] (ΔC_p , J/g * K)	Hard Segment Melting Peaks Temperature (°C) ($\Delta H/jg^{-1}$)
As moulded:			
PU-BDO	-118.7, -103.0	40.9, 49.0, 57.1 (0.29)	70.9 (6.50)
BDO-BHTD-40	-110.2, -99.0	-11.7, 5.0, 21.9 (0.29)	69.6 (8.78)
BDO-HTDE-40	-113.7, -98.3	-0.19, 16.0, 32.2 (0.31)	64.0 (3.87)
BDO-BPTD-40	-108.1, -80.1	-3.4, 12.0, 27.6 (0.30)	64.6 (4.54)
BDO-HQHE-40	-114.5, -101.6	27.1, 36.6, 46.2 (0.28)	48.2 (2.51), 120.0 (2.51)
BDO-HFPD-40	-115.9, -99.5	1.1, 16.3, 31.4 (0.31)	58.07 (4.29)
Annealed (100°C):			
PU-BDO	-126.8, -106.9	-5.5, 22.4, 50.4 (0.43)	129.1 (9.26), 203.7 (0.67)
BDO-BHTD-40	-103.2, -93.4	-8.2, 9.5, 27.3 (0.39)	59.9 (0.96), 123.9 (1.46)
BDO-HTDE-40	-101.3, -87.3	-0.1, 17.1, 34.3 (0.37)	58.0 (3.46)
BDO-BPTD-40	-109.1, -93.8	-0.13, 16.2, 32.6 (0.33)	78.3 (3.92)
BDO-HQHE-40	-113.3, -104.3	16.9, 30.2, 43.4 (0.33)	128.8 (2.57)
BDO-HFPD-40	-113.1, -99.7	7.9, 21.2, 34.5 (0.30)	72.0 (3.42)

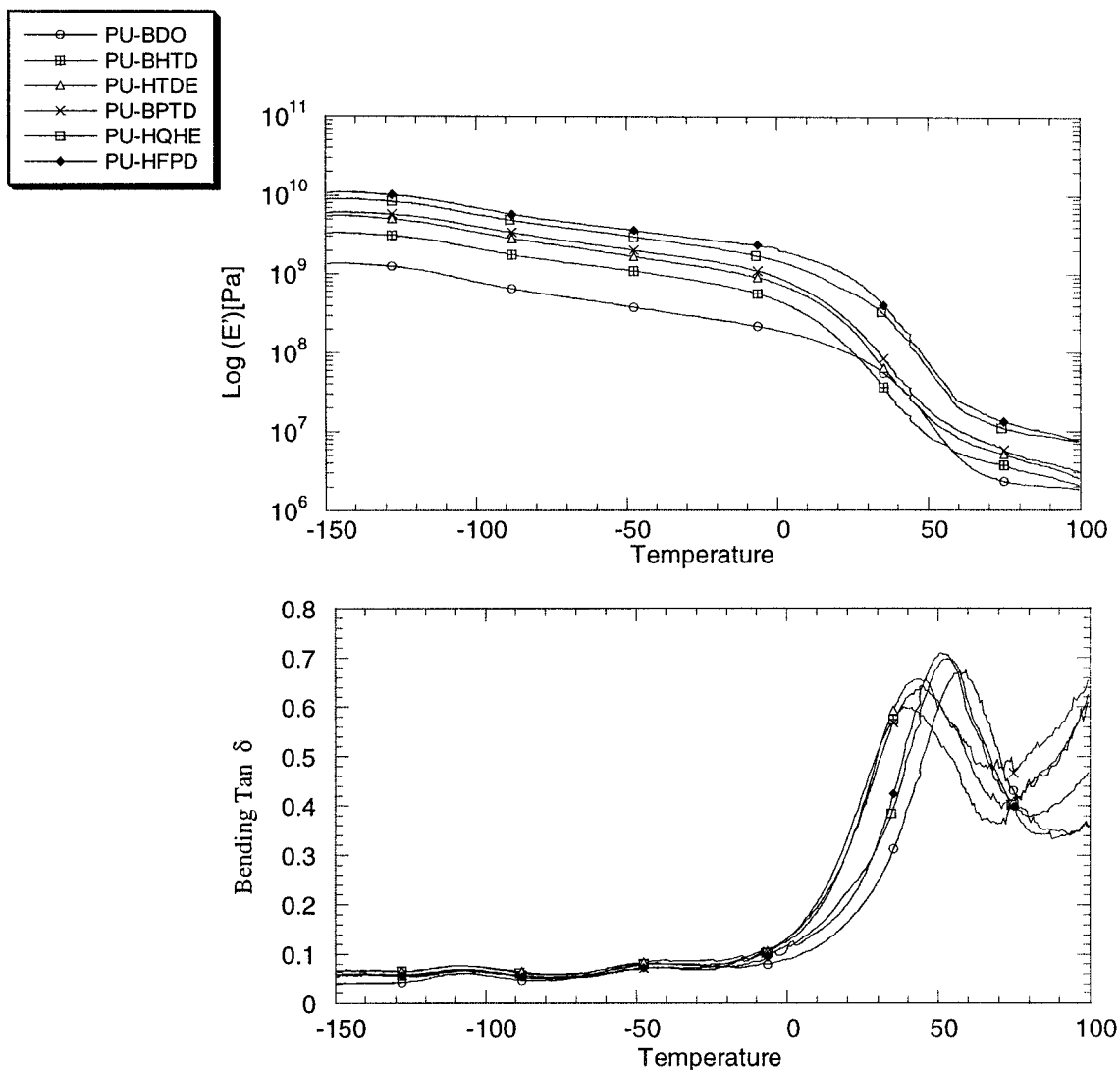


Figure 3 Dynamic mechanical spectra of Series A polyurethanes.

cate whether this is due to soft segment-hard segment phase mixing and/or due to lack of order in hard segment domains, disrupted due to mixing with HFPD-based hard segments.

Several samples exhibited transitions above 220°C. For example, PU-BPTD showed a transition at 230°C. Such transitions were attributed to thermal decomposition of the sample.

The onset and end temperatures of the PDMS glass transition were estimated for each polyurethane by expanding the -140 to -60 °C range of the respective DSC thermograms. The results are summarized in Tables V and VI. The onset temperature for PU-BDO appeared very close to the T_g onset of pure PDMS (-126 °C), indicating that PDMS domains exist in a phase-separated state.

With the incorporation of a secondary chain extender, the PDMS T_g onset is shifted to higher temperatures, particularly with silicon chain extenders. The shifts in temperature for PU-HQHE and PU-HFPD were insignificant, indicating that the PDMS phase in these two materials is less phase-mixed. This behavior is clearly seen with Series B materials. Interestingly, annealing of the polyurethanes causes further shifting of T_g onset to higher temperatures, which is the opposite of what is normally expected. Perhaps, this result indicates that with annealing the interfacial regions become soft-segment rich, increasing the compatibility of the PDMS phase.

Series A materials were analyzed by DMTA to obtain further evidence on morphology changes,

Table VII Transition Temperatures Determined From DMTA Results

Polyurethane	Soft Segment (PDMS) Transition (from E'') (°C)	PDMS Soft Segment Tan Δ Peak Temperature (°C)	Hard Segment Transition (from E'') (°C)	Hard Segment Tan Δ Peak Temperature (°C)
PU-BDO	-112.0	-108.8	39.3	59.3
PU-BHTD-20	-105.6	-107.5	26.0	39.0
PU-HTDE-20	-111.2	-108.3	30.0	47.2
PU-BPTD-20	-109.2	-104.8	27.0	45.9
PU-HQHE-20	-112.3	-108.8	40.7	57.2
PU-HFPD-20	-111.2	-108.9	40.5	55.0

as well as to examine transitions in the PDMS phase since this technique is more sensitive for detecting glass transitions than DSC. Figure 3 shows dynamic mechanical spectra of as-moulded Series A polyurethanes. The most prominent tan Δ peak was assigned to the amorphous hard segment/interfacial regions. This temperature showed a dependency to the secondary chain extender structure. The peak temperature shifted to lower temperatures relative to that of the control PU-BDO in all cases (see Fig. 3 and Table VII), and the three silicon chain extender-based materials showed larger shifts than the other two. Around the ambient temperature, the most flexible (lower modulus) of the series was that based on BHTD, consistent with flexural modulus results shown in Table II. The hard segment glass transitions determined (Table VII) from loss modulus curves were significantly lower for silicon chain-extender-based materials than those for the other two.

Two low-temperature transitions were observed for all materials in the series and, consistent with DSC, these transitions were very weak. The first low-temperature peak with a tan Δ maximum at -107°C is associated with glass transition of the siloxane soft segment. The origin of the intermediate transition at -42°C is not clear. However, as reported in the literature⁷ for similar polyurethanes, this peak has been tentatively assigned to the small amount of PDMS crystallinity, particularly when low heating rates are used in DMTA analysis, and/or due to the influence of the end group. However, in polyurethanes of the present study, the transition could most likely be due to the end-group segments (ethoxy-propyl), which contribute about a third of the molecular weight of the PDMS macrodiol.

T_g values calculated from loss modulus results are summarized in Table VII. Consistent with

DSC results, the T_g onset temperatures of silicon chain-extender-based materials were shifted to a higher temperature compared to the control. The other two materials showed no such shifts. These results corroborated the DSC results, indicating that the PDMS soft segment phase in silicon chain-extender-based materials exists in a relatively more phase-mixed state than in the other materials.

The DSC results indicated that the incorporation of a secondary chain extender disrupted the hard segment ordering in all cases. The highest disruption was observed with HFPD, while that from silicon chain extenders was less pronounced, particularly at the 20% level; and this difference was less significant at 40 mol %. Further, the DSC results indicated that the soft segment PDMS phase in silicon chain-extender-based polyurethanes was more phase-mixed than in PU-HQHE and PU-HFPD. This was supported by the DMTA results.

CONCLUSIONS

The results of this study concluded that by using a mixture of a conventional chain extender and a secondary chain extender, siloxane macrodiol-based polyurethane elastomers with low flexural modulus and good tensile strength could be prepared. Silicon-based chain extenders were found to be the most suitable secondary chain extenders. The chain extender composition significantly affected the polyurethane morphology; a low proportion of the secondary chain extender yields polyurethanes with good tensile properties. Further, this technique allows one to synthesize polyurethane compositions having a high level of non-polar soft segments such as PDMS.

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