

Effect of Polydimethylsiloxane Macrodiol Molecular Weight on Properties and Morphology of Polyurethane and Polyurethaneurea

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ABSTRACT: Two series of polyurethanes and polyurethaneureas were prepared using a two-step bulk-solution polymerization procedure. Each series consisted of three polymers based on three molecular weights of α,ω -bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS): 940, 1913, and 2955. The soft segment in all cases was an 80:20 mixture of PDMS and poly(hexamethylene oxide) (MW 700), and the hard segment was based on 4,4'-methylenediphenyl diisocyanate and mixed chain extenders (40 wt %). In the polyurethane (PU) series the chain extender was a 60:40 (mol) mixture of BDO and 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD), whereas in the polyurethaneurea (PUU) series it was a 60:40 (mol) mixture of BHTD and 1,2-ethylenediamine. The polymerization was carried out by preparing a prepolymer using a bulk polymerization procedure followed by chain extension in a solution of *N,N*-dimethylacetamide. Polymers were characterized by size-exclusion chromatography, tensile testing, differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA). The number-average molecular weights of the polymers in the PU series were in the range of 114,300–124,500, whereas they were in the 78,400–103,300 range for the PUU series. Polymers with good clarity and

mechanical properties were obtained with PDMS-940 and PDMS-1913, but those obtained from PDMS-2955, despite having good tensile strength, had a low percentage of elongation, high modulus, and poor clarity. DSC and DMTA results indicated that regardless of the PDMS molecular weight, the siloxane segments existed as a highly phase-separated state. This poor compatibility was consistent with the low solubility of PDMS compared to that of the hard-segment-forming components. The polymers in the polyurethane series exhibited multiple melting endotherms, attributed to the melting of ordered domains from different hard segments. The combined heats of fusion were similar for the materials in the PU series. In contrast, the polymers in the PUU series showed a hard-segment order that was significantly less defined, with the heat of fusion approximately a third to a half that of the materials in the polyurethane series. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1565–1573, 2003

Key words: polydimethylsiloxane macrodiol; polyurethane; polyurethaneurea; poly(hexamethylene oxide); synthesis; morphology; thermoplastic

INTRODUCTION

The incorporation of siloxane segments as part of the polyurethane structure significantly improves its biostability. Siloxane can be incorporated as part of both the soft and hard segments of polyurethane without significantly compromising the excellent mechanical properties of polyurethane.^{1–5} The synthesis of siloxane-based polyurethane with good mechanical properties requires a second macrodiol to act as a compatibilizer to overcome the typical incompatibility problems associated with nonpolar macrodiols.^{6–8} Polyether macrodiols such as poly(hexamethylene oxide) (PHMO) or polycarbonate macrodiols are good compatibilizing macrodiols.^{1–2,5} Similarly, chain ex-

tenders such as 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD) are useful in incorporating siloxane segments as part of the hard segment when added in combination with conventional diol chain extenders such as 1,4-butanediol (BDO). In preparing siloxane-based polyurethanes, α,ω -bis(6-hydroxyethoxypropyl) poly(dimethylsiloxane) (PDMS) with a molecular weight of about 1000 has been the most widely used siloxane macrodiol. This macrodiol has ethoxypropyl end groups, which may also contribute both to its improved compatibility with the hard segment and its improved mechanical properties. The influence of the amount of the comacrodiol as well as the effect of the chain extender composition on polyurethane properties and morphology has been investigated.^{10–12} However, no previous article has reported a detailed study of the effect of PDMS molecular weight on polyurethane properties and morphology.

The aim of this study was to understand the effect of PDMS molecular weight on the properties and mor-

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phology of both polyurethane and polyurethaneurea. PDMS macrodiols with molecular weights of 940, 1913, and 2955 were selected for this study. These molecular weights were chosen because they are representative of the typical useful range of molecular weights in polyurethane synthesis as well as having considerably different values for the solubility parameter. All polymers were prepared by two-step bulk-solution polymerization because bulk polymerization with higher-molecular-weight PDMS produces highly phase-separated materials.² The soft segment in all cases was an 80:20 mixture of PDMS and PHMO and the hard segment based on 4,4'-methylenediphenyl diisocyanate (MDI) and mixed chain extenders was kept constant at 40 weight percent. In the polyurethane (PU) series the chain extender was a 60:40 mixture of BDO and BHTD, whereas in the polyurethaneurea (PUU) series it was a 60:40 mixture of BHTD and 1,2-ethylenediamine (EDA).

EXPERIMENTAL

Materials

α,ω -Bis(6-hydroxyethoxypropyl) poly(dimethylsiloxane) (PDMS; X-22-160AS, KF-6001, KF-6002) was obtained from Shin-Etsu, Tokyo, Japan. Poly(hexamethylene oxide) (PHMO) was synthesized using a method reported previously.¹³ 1,4-Butanediol (BDO; GAF) was distilled under vacuum, and the middle fraction was used for polymerization. The silicon chain extender 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD) was obtained from Silar Laboratories and degassed at room temperature under a vacuum of 0.1 torr for about 6 h to remove cyclic impurities. 1,2-Ethylenediamine (Aldrich) was used as received. 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'-Methylenediphenyl diisocyanate (MDI, Suprasec MPR™ from Orica) and anhydrous *N,N*-dimethylacetamide (DMAc, Aldrich) were used as received.

Hydroxyl number

The hydroxyl number of the macrodiols was determined by the phthalic anhydride reflux method in accordance with ASTM Standard D 2849.

Synthesis of polyurethane elastomers

Poly(ether urethane) was synthesized by a two-step solution (DMAc) polymerization procedure (20 wt % solid content) without catalyst. A typical two-step solution polymerization procedure used for the synthesis of both PUU and PU is described below.

Preparation of PUU-940

A mixture of 40 g of PDMS (MW 940) and 10 g PHMO (MW 700) was degassed at 80°C for 2 h under a vacuum of 0.1 torr. Molten MDI (26.53) was weighed into a three-neck, round-bottom flask equipped with a mechanical stirrer, a dropping funnel, and a nitrogen inlet. The flask was then heated in an oil bath at 70°C. Then 50 g of the degassed macrodiol mixture was added through a dropping funnel over a period of 45 min. After the addition was completed, the reaction mixture was heated at the same temperature for 2 h with stirring under nitrogen. To the above prepolymer, 5.14 g of BHTD was quickly added, and it was reacted for another 30 min at 70°C. The flask was then cooled to a subambient temperature (0°C), and anhydrous dimethylacetamide (DMAc) was added through a syringe to get a clear solution. Ethylenediamine (1.66 g) in 50 mL of DMAc was added dropwise into the cooled prepolymer with slow stirring. Once this addition was completed, the reaction mixture turned into a gel-like mass. Stirring was stopped at this stage, and the polymer mass was heated to 90°C for about 3 h. The temperature of the reaction mixture was then lowered to 70°C, and stirring continued to allow the polymer to dissolve. When the polymer solution became clear, after about 12 h of stirring, it was then transferred to a screw-cap glass bottle under a nitrogen atmosphere and stored at ambient temperature.

Preparation of PU-940

A mixture of 40 g of PDMS (MW 940) and 10 g of PHMO (MW 700) was degassed at 80°C for 2 h under a vacuum of 0.1 torr. Molten MDI (26.03) was weighed into a three-neck, round-bottom flask equipped with a mechanical stirrer, a dropping funnel and a nitrogen inlet. The flask was then heated in an oil bath at 70°C. Then 50 g of the degassed macrodiol mixture was added through a dropping funnel over a period of 45 min. Once this addition was completed, the reaction mixture was heated at 70°C for 2 h with stirring under nitrogen. Then 4.92 g of BHTD was quickly added to the prepolymer and was reacted for another 30 min at the above temperature. The flask was then cooled to ambient temperature (25°C–30°C), and anhydrous dimethylacetamide (DMAc) was added through a syringe to get a clear solution. BDO (2.39 g) in DMAc was added quickly at room temperature, and the polymer mixture was heated to 90°C for 3 h. The polymer solution was then transferred to a screw-cap glass bottle under a nitrogen atmosphere and stored in ambient conditions.

In all cases, clear and gel-free PU and PUU solutions containing 20% solids were obtained except for PU-2955 and PUU-2955 prepared with a content of 10%

solids. All PU and PUU solutions were filtered through a 0.45- μm polypropylene filter bag. In this article polyurethane and polyurethaneurea are denoted according to the molecular weight of the PDMS; for example, PU-940 and PUU-940 are, respectively, a polyurethane and a polyurethaneurea, both prepared from PDMS with an MW of 940.

Size-exclusion chromatography

Size-exclusion chromatography of PU and PUU 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. Therefore, in this article results are expressed as polystyrene-equivalent molecular weights.

Sample preparation (solvent casting)

Polyurethane film samples about 0.5–1 mm thick were cast on Petri dishes using a 10%–20% concentrated polyurethaneurea solution to test the tensile properties. The film was dried by evaporating the polymer solution at 50°C in a nitrogen circulating oven for 24 h. The dried film was then placed in water for an hour before peeling the film off from the Petri dishes. The film was then dried under a nitrogen atmosphere at the above temperature and was further dried under vacuum at 0.1 torr for another 24 h. An inspection of all the samples under cross-polarizers to determine if internal stress was present showed that all samples were stress free and exhibited no birefringence. Dumbbells were stored in ambient conditions for at least 1 week before the 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 results reported here are the median values of five replicates. Tear strength was measured according to ASTM Standard D 624 at a crosshead speed of 200 mm/min, and the results reported are the median values for three replicates.

Thermal analysis

Differential scanning calorimetry (DSC) analysis over a temperature range of -150°C – 220°C was performed using a Mettler Toledo DSC 821^e. The experiments were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. The samples, which weighed between 20

and 25 mg, were dried at 65°C for 48 h under vacuum (0.1 torr) prior to analysis. Dynamic mechanical thermal analysis was performed on a Rheometric DMTA IV dynamic thermal mechanical analyzer equipped with a bending head and reducing force option. The analysis was carried out only on predried as-molded materials at a heating rate of 2°C at a 14 Hz frequency setting.

RESULTS AND DISCUSSION

Polymer synthesis

The modified solution polymerization procedure in which the solvent DMAc was added during the chain extension stage was always successful in yielding a clear and transparent polymer, except for PU-2955 and PUU-2955, whose solutions were opaque and contained a small fraction of gel, which was filtered off before preparing the films for characterization by solvent casting. This difference in solution clarity may always be related to poor solubility from the relatively higher molecular weight of the PDMS. The molecular weights of the polymers synthesized in the PU and PUU series ranged from 114,300 to 124,500 and 78,400 to 103,300, respectively, whereas their respective polydispersities were 1.89–1.98 and 1.35–1.61 (Table I). The molecular weights observed are typical of what is normally achieved with this class of polymers and should not have significantly affected their mechanical properties.¹²

The films cast from polymers in each series showed different degrees of transparency, as measured using a Gardner UX10 Hazemeter with a PG5500 digital photometer attachment. The results are summarized in Figure 1. In both series the highest-molecular-weight

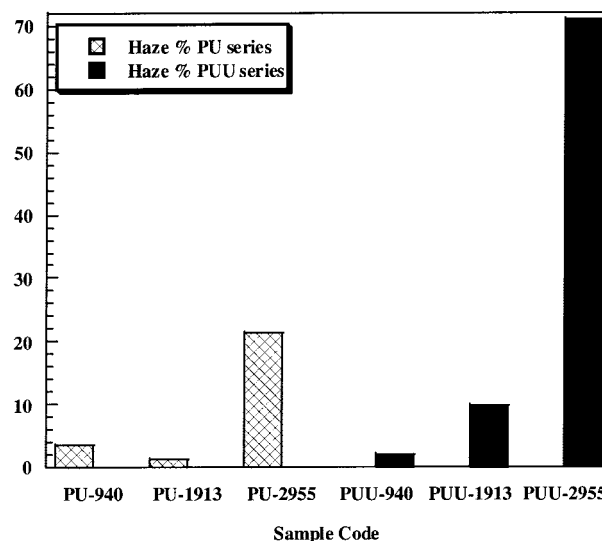


Figure 1 Haze measurements of PUs and PUUs of about 0.5 mm solvent cast films.

TABLE I
Molecular Weights (by SEC) of Polyurethanes
and Polyurethaneureas

Sample	\bar{M}_n	\bar{M}_w	PD
PU-940	121,700	230,800	1.89
PU-1913	114,300	227,300	1.98
PU-2955	124,500	243,200	1.95
PUU-940	100,800	136,900	1.35
PUU-1913	103,300	147,000	1.42
PUU-2955	78,400	126,400	1.61

PDMS produced the least transparent film, and the difference between the materials from the two lower-molecular-weight PDMSs was not very significant. Because polymer was formulated with constant hard-segment weight percent in this study, increasing the PDMS molecular weight resulted in longer hard segments, which led to larger hard domains as well as increased phase separation. This effect may have caused the light to scatter, resulting in poor clarity.

The modified solution polymerization procedure described in this study provides a way of employing higher-molecular-weight PDMS to synthesize polyurethane and polyurethaneurea with good mechanical properties. We have previously shown² that the bulk polymerization method is not very successful for making polyurethane with PDMS macrodiols that have a molecular weight greater than 1000. This is because PDMS is relatively incompatible with hard-segment components, which can be rationalized by the calculated solubility parameters shown in Table II. Two-step bulk-solution polymerization overcomes this incompatibility, perhaps by preventing the formation of longer hard-segment blocks, but with PDMS-2955 the incompatibility effect was still dominant.

Mechanical properties

The tensile properties of the polymers in the PU and PUU series are shown in Table III. The effect of PDMS molecular weight was most significant on the percent of elongation and modulus. The elongation at break decreased with increasing macrodiol molecular weight, whereas the modulus increased. This is illus-

TABLE II
Calculated Solubility Parameters

Compound	Solubility Parameter [δ (cal/mL) ^{1/2}]
PDMS-1000	6.7 ± 0.2
PDMS-2000	6.1 ± 0.1
PDMS-3000	5.5 ± 0.2
PHMO-700	9.3 ± 0.1
MDI	9.9 ± 0.1
(MDI-BDO) _t	12.2–12.7 ^a

The parameters were calculated using the MSI amorphous cell package with the PCFF2 force field. ^aFrom Tonelli et al.¹⁶

trated graphically in Figures 2 and 3. The ultimate tensile strength was very similar for all materials in both series, with the exception of PU-2955. Polyurethaneurea exhibited higher tear strength than polyurethane, presumably because of the stronger hydrogen-bonding interactions from the urea linkages. Generally, polyurethaneurea was less elastomeric than polyurethane, as shown by its higher modulus as well as lower elongation at break. In both series tear strength decreased with increasing PDMS molecular weight.

In both series the observed difference in tensile properties could be attributed to the structural difference resulting from increasing PDMS molecular weight. It is unlikely that the molecular weight of the polymers affected these properties because observed molecular weight are generally well above the molecular weight for there to be a significant reduction in the values of mechanical properties. For polyurethane it has been reported that above a molecular weight of 50,000, the mechanical properties were not changed significantly.¹⁴ In this study the polymers in both series were prepared with a constant weight percent (40 wt %) of hard segments, and, accordingly, increasing the PDMS molecular weight resulted in longer hard segments. On average PU-940, PU-1913, and PU-2955 would have 1.8, 2.7, and 3.3 MDI units, respectively, in the hard segment. This would have the effect of correspondingly larger hard domains and associated morphological differences, resulting in materials with increased modulus and low elasticity.

TABLE III
Tensile Properties of Polyurethanes and Polyurethaneureas

Sample	Elongation (%)	UTS (MPa)	YM (MPa)	Stress 100% (MPa)	Tear S (N/mm)
PU-940	492 ± 10	21 ± 2	7 ± 1	5 ± .02	55 ± 4
PU-1913	439 ± 11	22 ± 1	15 ± 4	7 ± .2	59 ± 3
PU-2955	233 ± 48	17 ± 2	86 ± 15	11 ± .3	46 ± 2
PUU-940	379 ± 22	23 ± 2	26 ± 2	11 ± .1	81 ± 5
PUU-1913	391 ± 26	21 ± 2	39 ± 4	12 ± .5	63 ± 5
PUU-2955	168 ± 11	21 ± 1	63 ± 5	15 ± .3	55 ± 2

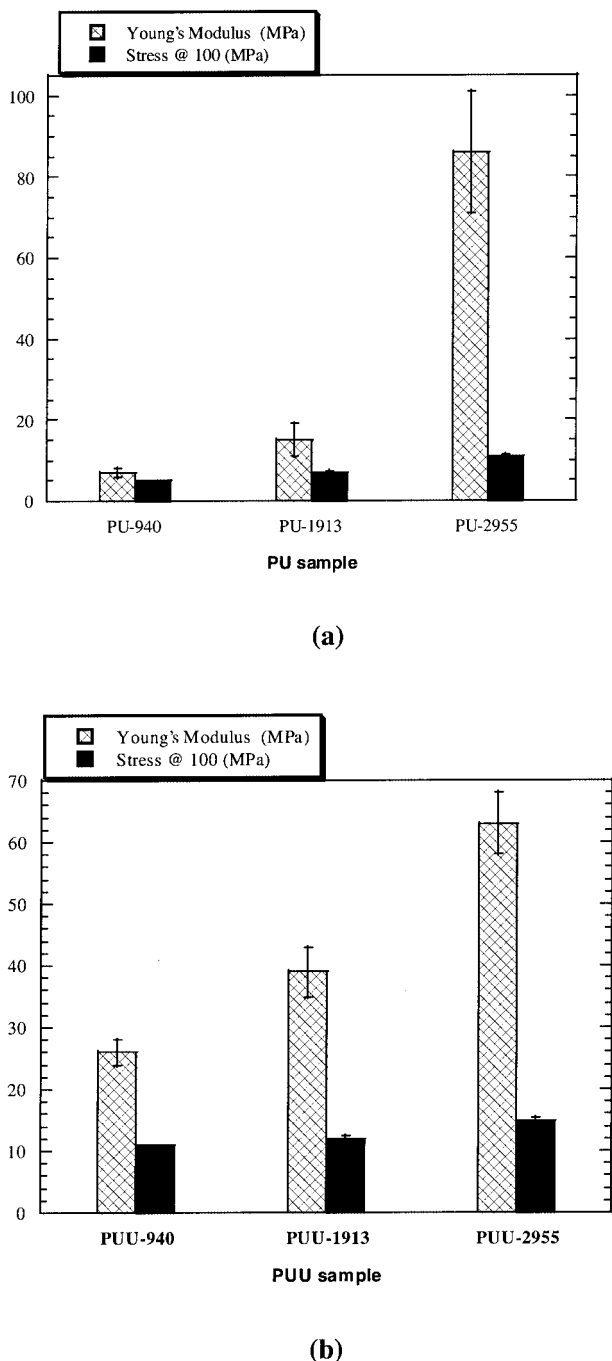


Figure 2 A comparison of Young's modulus and stress at 100% for: (a) polyurethane series; (b) polyurethaneurea series.

Morphology

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used to study the effect of PDMS molecular weight on polyurethane morphology. All tests were performed on test specimens obtained from solvent cast films.

The DSC thermograms of the polymers in the PU and PUU series are shown in Figure 4(a,b), respec-

tively. The major thermal transition temperatures are summarized in Tables IV and V.

Polymers in the PU series showed two main glass-transition temperatures due to soft segments. The low glass-transition temperature (T_g) was assigned to the PDMS segments. It is interesting to compare these transition temperatures with those observed for the corresponding pure macrodiols (see Fig. 5 and Table IV). If the soft segments in the polyurethane were phase-mixed, the T_g would be expected to shift to higher temperatures. The observed results clearly illustrate that PDMS existed as a highly phase-separated state in these materials, and it appears that this was independent of PDMS molecular weight. The second glass transition, assigned to segments derived predominantly from PDMS end groups (ethoxypropyl) and PHMO, shifted to higher temperatures with increasing PDMS molecular weight. This is perhaps a reflection of the decreasing ethoxypropyl end group concentration with increasing PDMS molecular weight. It should be noted that because of these components were a small percentage of the weight, the thermal transitions were relatively weak, and unambiguous assignment was difficult. The glass-transition temperature of the PHMO macrodiol was -35°C .¹⁵ In all samples the combined transition was higher than this temperature, perhaps indicating that ethoxypropyl, PHMO, and maybe some hard-segment components were phase-mixed and formed interfacial regions.

The polymers in the PUU series exhibited similar thermal transitions for the soft segments, and a similar trend in change in transition temperatures with increasing PDMS molecular weight was observed. The

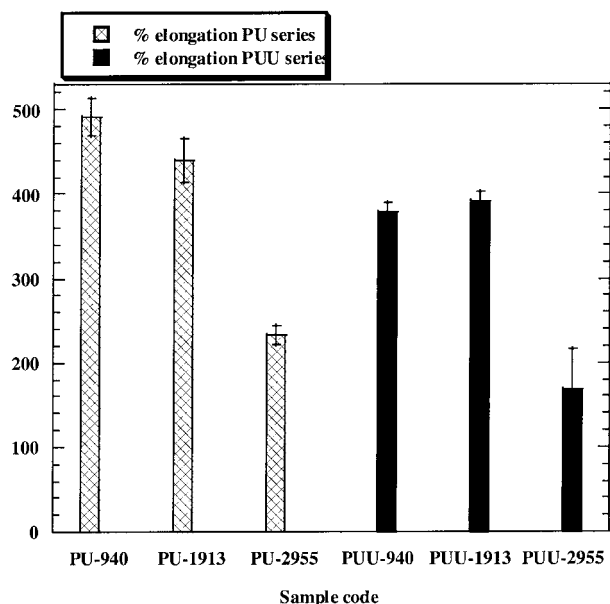


Figure 3 A comparison of percent elongation of polyurethane and polyurethaneurea series.

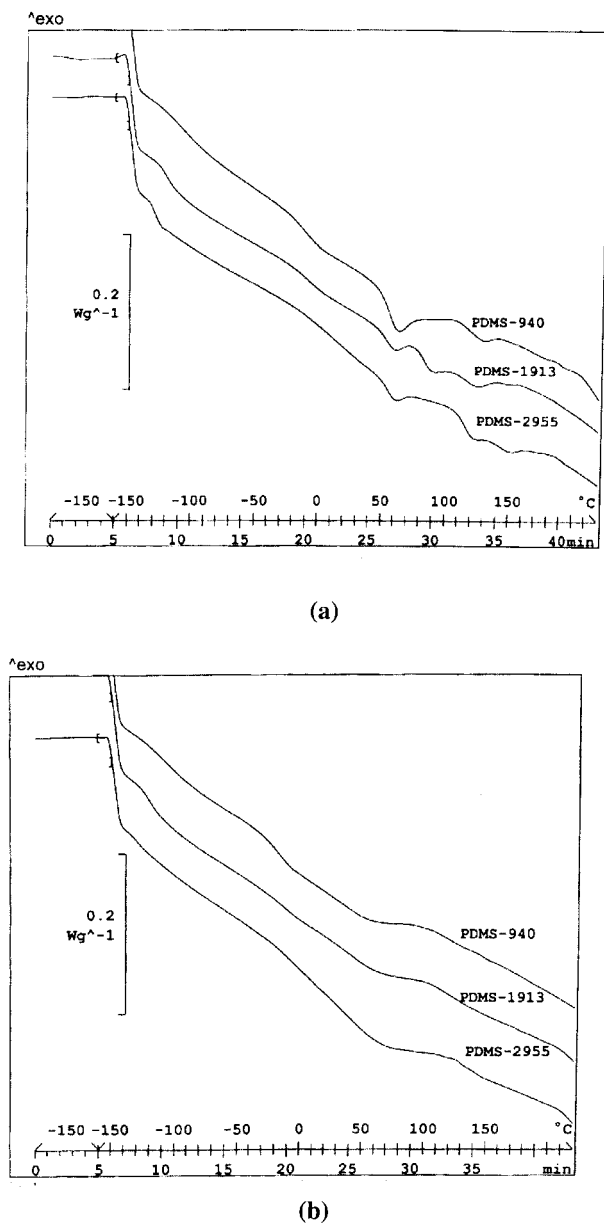


Figure 4 DSC thermograms of (a) PU series, (b) PUU series.

results therefore clearly indicate that the siloxane segments in these materials, regardless of whether they were urethanes or ureas, existed largely as phase-separated domains. The combined glass transition from the PHMO and ethoxypropyl end groups of PDMS appeared at similar temperatures for materials in both series. Further, the heat capacity change was comparable for materials, with a similar PDMS molecular weight in both series.

The thermal transitions resulting from the hard segments of the polymers in the two series were significantly different. In the PU series multiple melting endotherms were observed and the number of these peaks increased with increasing PDMS molecular

weight. It is common for polyurethanes to exhibit multiple melting peaks, which are generally attributed to melting of the domains formed by the ordering of hard segments of different lengths. In the current series this was more complicated because two structurally different chain extenders were used. Accordingly, segments such as MDI₂-BDO, MDI₃-BDO-BHTD, and MDI₂-BHTD and their corresponding longer segments could form ordered domains with different melting endotherms. Without proper model compound data it would be difficult to assign the observed melting endotherms unambiguously. PU-940 showed two melting endotherms, with peak temperatures at around 60°C and 129°C. The former was attributed to the order resulting from MDI₂-BHTD units, as reported previously,¹⁰ whereas the latter peak resulted from hard segments with mixed chain extenders of the MDI₂-BDO type. In PU1913 an additional peak, at 88°C, was observed, which perhaps could be attributed to MDI₃-BDO-BHTD segments or to longer segments. The combined heats of fusion of the polymers in the PU series were very similar (see Table V). In the PUU series the hard-segment region was much less defined, and only a very broad endotherm was observed, indicating less order than that observed for materials in the PU series [Fig. 4(b) and Table V]. The corresponding heat capacity was significantly less, about one half to one third, further confirming that the hard segments in the PUU series were less ordered. The reason for this difference is not clear, but the presence of hard segments derived from two structurally dissimilar chain extenders as well as the presence of both urethane and urea linkages may make the hard segments less ordered in these materials.

Dynamic mechanical thermal analysis

The dynamic mechanical thermal analysis (DMTA) results of the polymers supported the DSC results with respect to morphological changes as well as the corresponding differences in modulus discussed earlier. Figures 6(a) and 7(a) show the change in storage modulus with temperature for, respectively, the PU and the PUU series materials. The significantly higher modulus of PU-2955 and PUU-2955 in the temperature range of 0°C–100°C was evident, consistent with the ambient temperature modulus results reported in Table II. The other two materials, which were based on

TABLE IV
DSC Thermal Transitions of PDMS of Different Molecular Weights

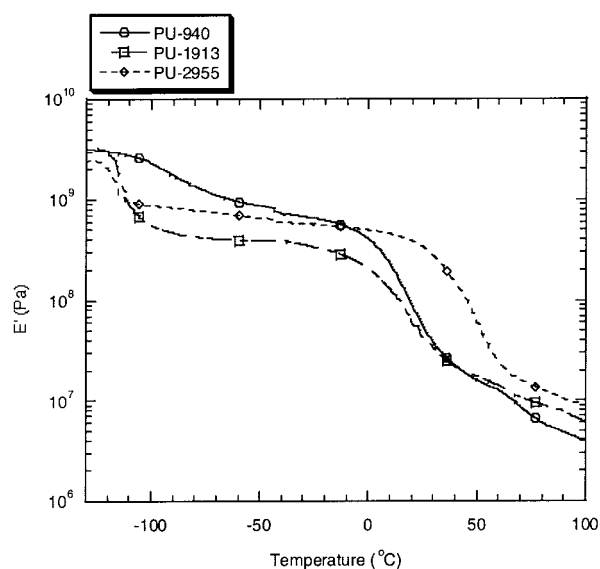
Sample codes	T_g Onset, midpoint, end set (°C)
PDMS-940	-115, -112.8, -111.1
PDMS-1913	-122.4, -120.5, -119.1
PDMS-2955	-125.5, -124.5, -122.6

TABLE V
DSC Thermal Transitions and Melting Endotherm Heats of Fusion of Polyurethanes and Polyurethaneureas

Sample	T_g (PDMS) onset, midpoint, an end set ($^{\circ}\text{C}$)	T_g (PDMS end group/comacrodiol) onset, midpoint, and end set ($^{\circ}\text{C}/\Delta C_p, j/g^*k$)	Hard-segment melting endotherm peak temperature ($^{\circ}\text{C}$)	Total heat of fusion ($\Delta H/jg^{-1}$)
PU-940	-121.1, -113.3, -97.9	-25.3, -12.0, -1.13 (0.27)	61.8, 129.0	12.2
PU-1913	-124.4, -120.7, -116.4	-14.7, -7.5, -3.1 (0.14)	59.6, 87.9, 124.5	13.6
PU-2955	-130.2, -128.1, -126.3	-16.9, -10.0, 0.67 (0.18)	59.7, 120.9, 150.9	13.8
PUU-940	-118.4, -108.1, -100.2	-23.9, -17.1, -7.5 (0.22)	44.2	4.7
PUU-1913	-126.1, -121.7, -115.6	-16.9, -10.1, -4.9 (0.13)	58.6	4.8
PUU-2955	-134.9, -133.2, -127.4	-19.8, -10.1, 2.7 (0.26)	66.0	8.6

lower-molecular-weight PDMS, showed very similar moduli in this temperature range. At temperatures below 0°C , interestingly, PU-940 showed a higher modulus than that of the other materials. PU-1913 exhibited a lower modulus in this temperature range in both series.

The plots of $\tan \delta$ versus temperature are shown in Figures 6(b) and 7(b) for the PU and PUU materials, respectively. $\tan \delta$ peak temperatures and glass-transition temperatures estimated from E' -versus-temperature plots are summarized in Table VI. As we previously observed for other systems,¹² the T_g values estimated from DMTA were higher than those determined by DSC. However, the general trend was similar. With an increase in PDMS molecular weight, the PDMS T_g shifted to lower temperatures, supporting the conclusion that PDMS remained largely as a phase-separated state. Polymers in both series showed two $\tan \delta$ peaks, typical of thermoplastic polyurethanes. The first low temperature peak was assigned to PDMS and the second, higher temperature peak to amorphous hard segment/interfacial regions largely consisting of ethoxypropyl groups and PHMO. The



(a)

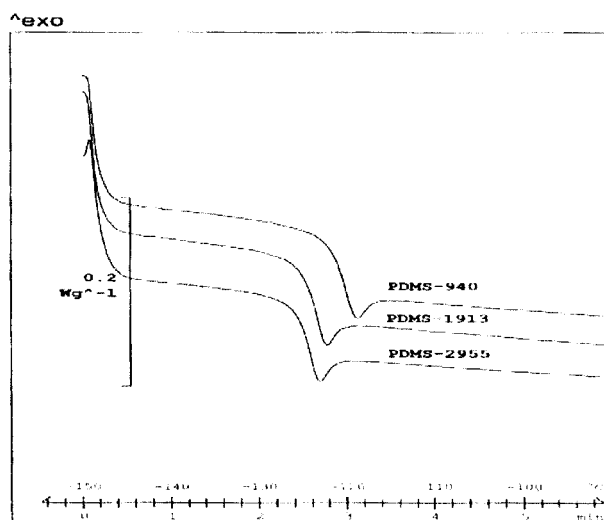
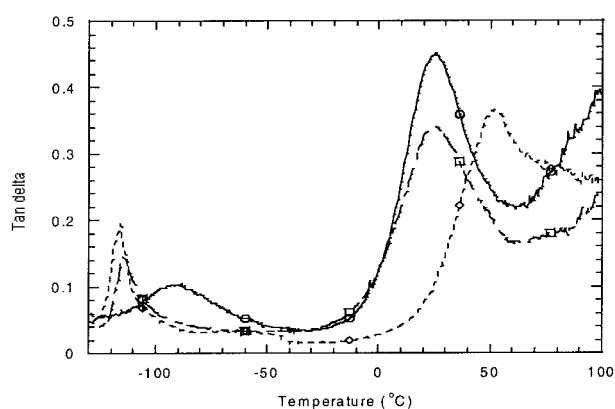
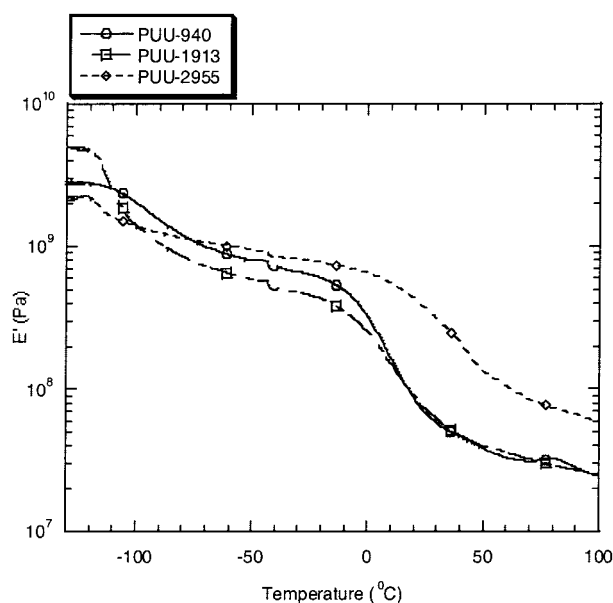


Figure 5 DSC thermogram of PDMSs of different molecular weights.

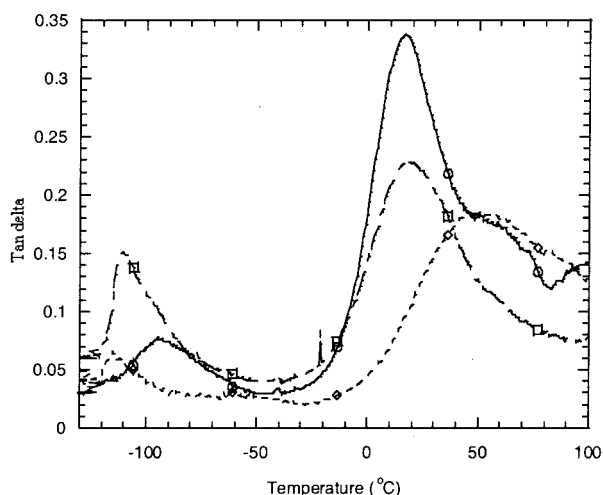


(b)

Figure 6 DMTA thermal transitions of (a) E' and (b) $\tan \delta$ versus temperature of PUs.



(a)



(b)

Figure 7 DMTA thermal transitions of (a) E' and (b) $\tan \delta$ versus temperature of PUUs.

lower temperature peaks for polymers based on PDMS molecular weights of 1913 and 2955 appeared in a very similar temperature range, but the second peak appeared in a significantly different temperature range. The higher $\tan \delta$ peak for PU-2955 and PUU-2955 may indicate that the amorphous region in these materials consists of a higher proportion of hard-segment components, perhaps single MDI linkages. This is also consistent with the observed higher modulus of these materials.

CONCLUSIONS

The results in this study demonstrated that by employing the two-step bulk-solution polymerization procedure, polyurethanes and polyurethaneureas with good mechanical properties and clarity could be prepared from PDMS whose molecular weight was in the range of 1000–2000. The materials based on PDMS-2955 were opaque and had poor elasticity, although the tensile strength was not affected significantly. The tear strength decreased with increasing macrodiol molecular weight, whereas the modulus increased.

The DSC and DMTA results indicated that regardless of PDMS molecular weight, the PDMS existed as a highly phase-separated state. This poor compatibility was consistent with the solubility of PDMS, which was low compared to that of hard-segment-forming components. The polymers in the polyurethane series exhibited multiple melting endotherms, attributed to the melting of ordered domains from different hard segments, and the combined heats of fusion of the materials in the series were similar. In contrast, the polymers in the polyurethaneurea series showed hard-segment domains that were significantly less ordered, with the heats of fusion of the materials approximately a third to a half of those in the polyurethane series. Within the polyurethaneurea series, the materials based on PDMS-2955 had the highest heat of fusion.

Further studies would be required to ascertain whether PDMS molecular weight affects the properties and morphology in the same way when hard-segment weight percent is varied.

TABLE VI
DMTA Thermal Transition Temperatures of Polyurethanes and Polyurethaneureas

Sample	Tan δ peak temperatures	T_g (PDMS) Midpoint ($^{\circ}\text{C}/\text{from } E'$)	T_g (Soft/hard interfacial regions) (Midpoint/ $^{\circ}\text{C}$ from E')
PU-940	-88.3, 25.4	-92.1	20.6
PU-1913	-102.7, 26.8	-100.1	20.2
PU-2955	-116.1, 51.5	-116.4	46.2
PUU-940	-94.9, -15.9	-93.7	15.8
PUU-1913	-109.4, 19.1	-106.8	22.2
PUU-2955	-115.4, 47.8	-113.7	29.9

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