# Polydimethylsiloxane–Urea–Urethane Copolymers with 1,4-Benzenedimethanol as Chain Extender

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*Received July 16, 1993*•

ABSTRACT: An investigation of polyurethanes and polyureas containing unusual diols directed toward the formation of minimally adhesive surfaces is reported. A two-step polymerization method was used to prepare dimethylsiloxane–urea–urethane copolymers with 1,4-benzenedimethanol as the chain extender. First, the reaction between isophorone diiisocyanate and benzenedimethanol was carried out in bulk at elevated temperatures without a catalyst. In the second stage, the reaction between aminopropyl end-capped dimethylsiloxane oligomers and diisocyanate intermediates was carried out in tetrahydrofuran solution at room temperature. Copolymers with chain extenders were found to be superior to those without chain extenders in thermal and mechanical properties. The improvements are due to the additional interactions between urea and urethane linkages. These interactions occur in both soft and hard segment domains.

## Introduction

We have begun an investigation of poly(urethane–ureas) containing unusual diols directed at the formation of minimally adhesive surfaces. Our goal is to discern the compositional and morphological features which create a surface minimally attractive to the settlement of marine organisms, an area pioneered by Griffith et al.[1]

Initially, polyurethanes based on a series of fluorinated diols and hexamethylene diisocyanate were investigated and their bulk and surface properties determined.[2] Analysis of contact angle and angle resolved ESCA data[3] revealed that surface composition and properties were those expected on the basis of bulk composition. In order to achieve surface phase separation of the low surface energy portion of the polymer, longer chain length diols have been sought. In addition to low surface energy, we believe that a low $T_g$ for the surface phase is desirable for minimizing mechanical locking of a prospective adherent to the surface. With the dual criteria of surface energy and morphology in mind, we have prepared and characterized a series of poly(dimethylsiloxane) containing poly(urethane–ureas) and have examined the effects of chain extenders on properties. A separate paper addresses the surface characterization of these polymers.[4]

Synthesis of siloxane–urea–urethane copolymers through step-growth polymerization has been explored previously,[5-8] and a summary of work performed before 1988 can be found in a review by Yilgör and McGrath.[9] We used a "hard segment first" two-step polymerization procedure, which allows the separate characterization of the hard segments. Control over the molecular weight distribution of the hard segments therefore is possible. Our approach is similar to the one used by Harrell[10] in which polyurethanes with well defined hard segments were derived from piperazine, butanediol, and poly(tetramethylene oxide), but in contrast to that effort there is no intricate synthesis involved in our scheme.

## Experimental Section

**Materials.** Isophorone diisocyanate (IPDI, **1**, 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane, a mixture of isomers), and 1,4-benzenedimethanol (BDM), **2**, were purchased from Aldrich Chemicals. 3-Aminopropyl end-capped dimethylsiloxane oligomers, $H_2N(CH_2)_3(Si(CH_3)_2O)_nSi(CH_3)_2(CH_2)_3NH_2$, with different average molecular weights were kindly provided by Dr. İ. Yilgör of Goldschmidt Chemical Corp., Hopewell, VA. The nominal molecular weights of tegomer A-Si 2120, **4a**, tegomer A-Si 2320, **4b**, and tegomer A-Si 2920, **4c**, were 1000 ($n$ = 11), 2400 ($n$ = 30) and 10 000 ($n$ = 133), respectively. In addition, aminopropyl end-capped PDMS oligomer Hüls PS 513 (viscosity 2000 cs, MW ≅ 27 000, $n$ = 363) was employed. All chemicals were used as received.

**Polymerization.** The two-step polymerization is shown in Scheme I. In a typical run, measured amounts of IPDI and BDM were introduced into a dried three-necked flask. The molar ratio of IPDI to BDM varied between 1.5 and 2. At room temperature, IPDI is a viscous liquid while BDM is a powder. The contents of the flask were stirred and heated under nitrogen. At 105 °C BDM started melting, and by 118 °C the contents were transparent. The reactants were kept at 118 °C for 2 h, at which point an IR spectrum was taken to ascertain the formation of the diisocyanate intermediate **3**. The intermediate was cooled to room temperature, resulting in a colorless, transparent solid. This material was dissolved in tetrahydrofuran (THF) and a measured amount of tegomer A-Si was added dropwise to the solution.[11] After addition of tegomer (so that the molar ratio of isocyanate to the sum of amino and hydroxyl groups was 1) the total reactants amounted to about 15% by weight of the solution. The second stage of the reaction was carried out at room temperature for 2 h and then at 50 °C for 15 h to ensure complete reaction. The product was poured into a glass petri dish, and solvent was removed by drying in the hood for 5–8 h and then in a vacuum oven at 60 °C for at least 1 day.

**Scheme I**

$$\underset{\mathbf{1}}{(x+1)\text{IPDI}} + \underset{\mathbf{2}}{(x)\text{BDM}} \xrightarrow{105\text{–}115\ ^\circ\text{C}} \underset{\mathbf{3}}{\text{IPDI-(BDM-IPDI)}_x} \quad (1)$$

$$\text{IPDI-(BMD-IPDI)}_x + \text{Tegomer A-Si} \xrightarrow{\text{THF, 50 °C}} \text{PDMS–urea–urethane copolymer} \quad (2)$$

Polymers without chain extender were prepared in THF solution

• Abstract published in *Advance ACS Abstracts*, October 15, 1993.

0024-9297/93/2226-7029$04.00/0 

using only the second step of Scheme I.

**Characterization. IR Spectroscopy.** FTIR spectra were collected using a Perkin-Elmer 1800 FTIR spectrometer. Samples were coated on KBr plates for measurement.

**NMR Spectroscopy.** All NMR spectra were acquired on a Bruker AMX 400 spectrometer operating at 400.13 MHz for $^1H$ acquisition and 100.62 MHz for $^{13}C$ acquisition. Solutions of tegomers and of polymers were prepared in $CDCl_3$ (Cambridge Isotope Laboratories) and the residual protonated solvent or the solvent carbon nucleus was used as the secondary reference to TMS. An inverse probe was used for all of the work presented herein. Standard Bruker microprograms were used for HMQC,[12] HMBC,[13] and TOCSY[14] data collection. For $^1H/^{13}C$ correlations, spectral widths were 20 000 Hz (F1) and 4000 Hz (F2), while delays were 3.7 and 62.5 ms, corresponding to short and long range coupling constants of 135 and 8 Hz, respectively. Data sets (256 or 512 × 2k) were acquired and multiplied by a shifted sine-bell squared function prior to Fourier transformation. Transforms were zero-filled out to 2K, multiplied by a shifted sine-bell squared function and transformed in the second dimension.

**Viscometry.** Inherent viscosity was determined with a Cannon-Fenske type (No. 50) viscometer immersed in a water bath controlled at 25 °C. Solutions in tetrahydrofuran (THF), concentration 0.5 g/dL, were used.

**Gel Permeation Chromatography (GPC).** Molecular weight was determined by GPC. The equipment consisted of a Hewlett-Packard Series 1050 pump and two Altex $\mu$ Spherogel columns (size $10^3$ and $10^4$ Å, respectively) connected in series. The solvent was THF. Polymer contents in the effluent of the columns were detected with a Wyatt/Optilab 903 interferometric refractometer, and the average molecular weights were determined using polystyrene standards as references. As previous workers have noted, polymers containing high weight fractions of poly(dimethylsiloxane) segments have low specific refractive increments ($dn/dc$) in THF solution.[15] High concentrations (about 2–3 wt %) were therefore used to enhance the signals. The resulting chromatograms were smoothed by the method of Fourier transform convolution.[16]

**Mechanical Tests.** Stress–strain tests were performed in an Instron Universal Testing instrument (Model 4206). Standard type V specimens as specified in ASTM Standards, Method D-638, were used. Dynamic mechanical properties were evaluated with a Rheovibron dynamic viscoelastomer. Strips 5 mm wide and 15–20 mm long were utilized.

## Results and Discussion

The preparation of copolymers of aminopropyl end-capped dimethylsiloxane oligomers and isophorone diisocyanate with 1,4-benzenedimethanol as the chain extender has been carried out according to Scheme I. This strategy is similar to the one used by Pascault and coworkers to prepare alkoxysilane terminated macromers.[17] This "hard segment first" method allows the separate characterization of the hard block. Furthermore, some unusual features were discovered about some of the siloxane macromonomers. Before describing polymer synthesis and characterization, sections are provided on characterization of the hard segment 3 and of the tegomers.

**Diisocyanate Intermediate 3.** As noted above, the "hard segment first" method allows the independent characterization of hard segments incorporated in the final copolymer, with e.g. GPC and DSC. In Figure 1, the molecular weight distribution of products from a reaction between 3 mol of IPDI and 2 mol of BDM is shown. The GPC trace can be fitted with the sum of three Gaussian distribution curves. On the basis of knowledge of the molecular weights of possible products and the positions of the prominent peaks in the GPC trace, a linear relationship between the logarithm of molecular weight and elution time was established. The peak represented by curve A is assigned to the species IPDI-BDM-IPDI-BDM-IPDI, curve B to IPDI-BDM-IPDI, and curve C to BDM-IPDI-BDM. The ratio of the intensities of the curves indicates that more than 85% of the molecules in the mixture are of the target "3:2" composition.

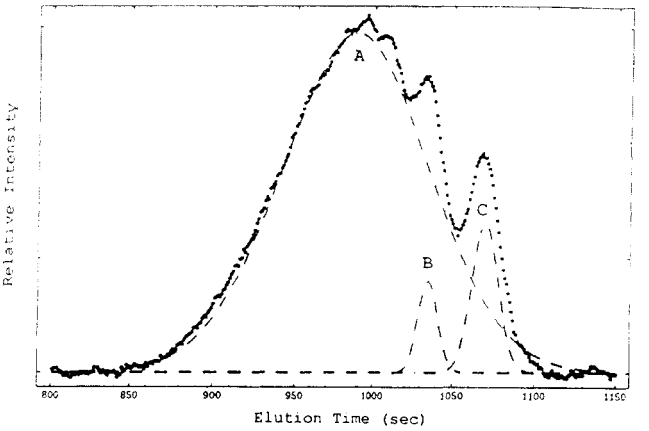


**Figure 1.** GPC trace for the products from a reaction between 3 mol of IPDI and 2 mol of BDM. The trace can be fitted with the sum of three Gaussian distribution curves. Curve A is assigned to the species IPDI-BDM-IPDI-BDM-IPDI, curve B to IPDI-BDM-IPDI, and curve C to BDM-IPDI-BDM.

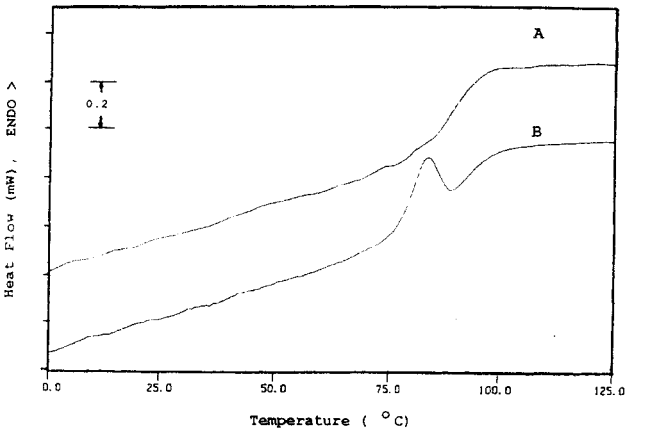


**Figure 2.** DSC trace for the same products described in the caption of Figure 1. Curves: (A) a fresh sample; (B) a sample after aging at room temperature for 7 days.

The DSC trace for the same mixture is shown in Figure 2. The glass transition temperature for a fresh sample is about 90 °C (Figure 2A). Time dependent changes in this transition were observed. For example, after aging at room temperature for 7 days, an additional peak appeared at 84 °C (Figure 2B). These changes were found to be thermally reversible, and physical aging apparently occurred in this sample.[18] No transitions were observed at higher temperatures.

**Tegomer Characterization.** Assignment and determination of relative intensities of the peaks due to the dimethylsilyl and the propylamine end group protons were important in confirming GPC determined macromonomer molecular weights. In the assignmemts below, the commercial designations for these macromonomers are utilized. Peak assignment was straightforward. Thus, for tegomer A-Si, 2320 (Figure 3B): $SiCH_3$, 0.07 ppm (s); $SiCH_2CH_2CH_2NH_2$, 0.53 ppm (apparent triplet); $SiCH_2CH_2CH_2NH_2$, 1.45 ppm (multiplet); $SiCH_2CH_2CH_2NH_2$, 2.65 ppm (triplet). The $NH_2$ peak changed in position and intensity due to varying trace amounts of water with which rapid exchange occurred. Typically, the observed signal was at 1.5–1.8 ppm (s).

In Figure 3B, additional peaks are observed for tegomer A-Si, 2320: 0.97 ppm (doublet) and 2.5 and 2.9 ppm (doubled doublets). These peaks were also seen in 1K

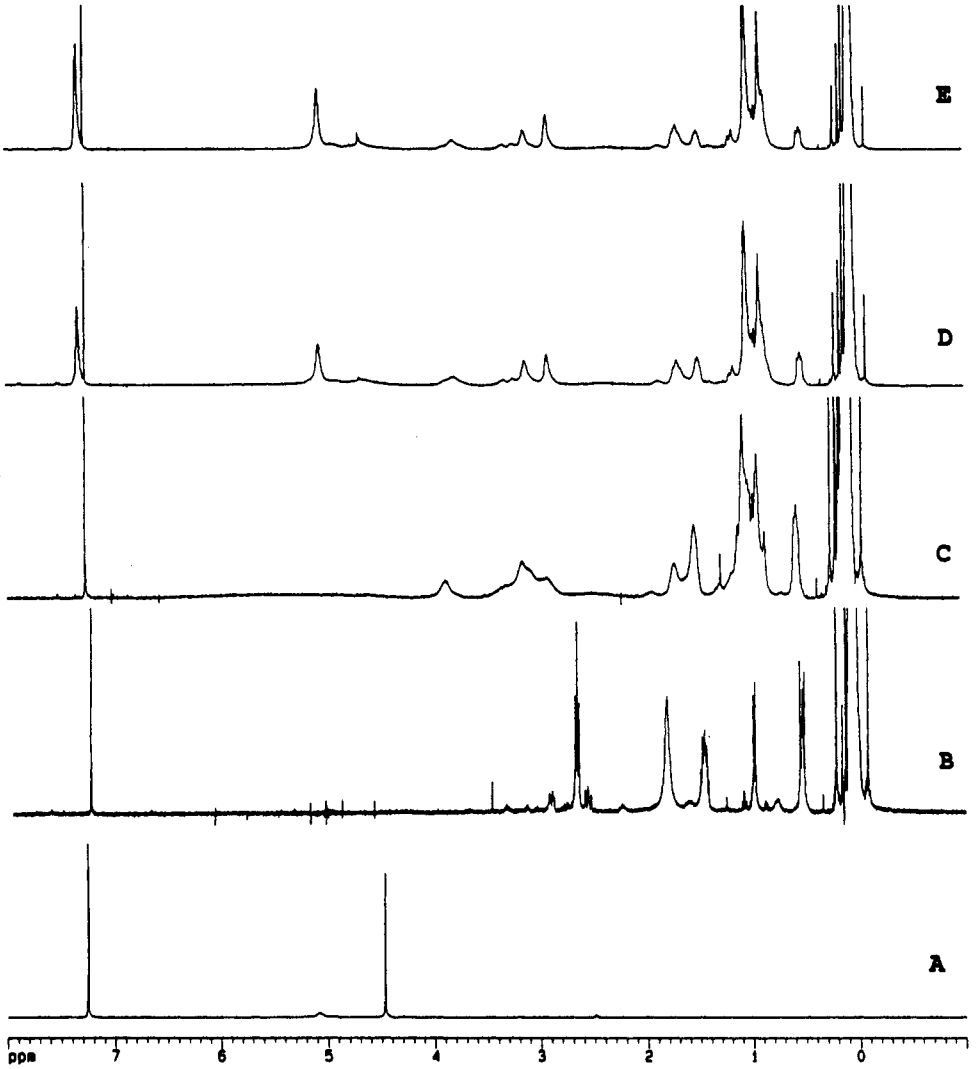


**Figure 3.** Polymer $^1$H NMR spectra for (A) benzene dimethanol, (B) tegomer A-Si 2320, **4b**, (C) PDMS2.4K-IP-B0, (D) PDMS2.4K-IP-B1, and (E) PDMS2.4K-IP-B2.

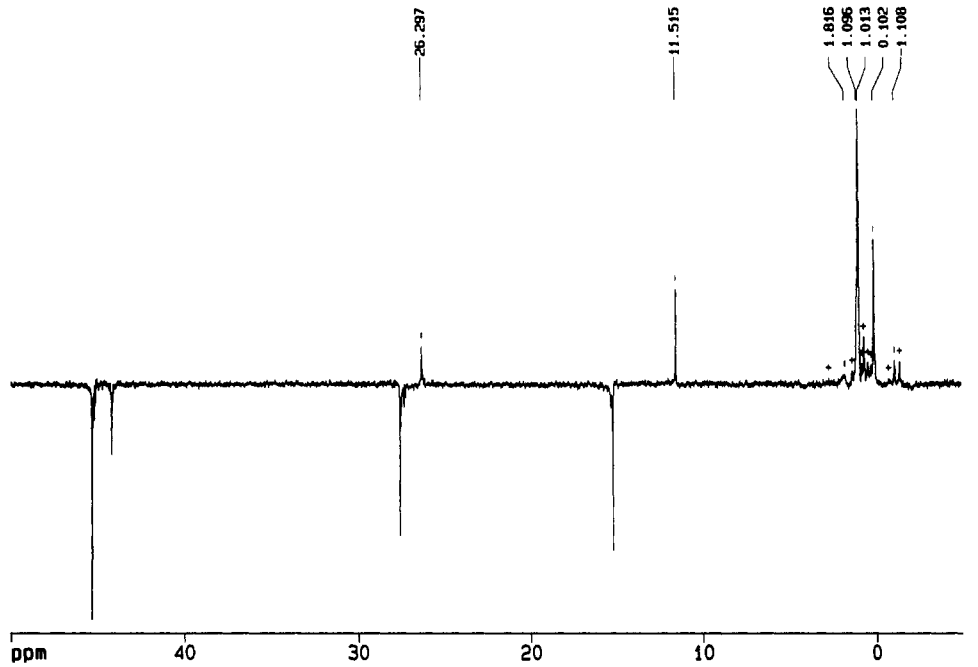


**Figure 4.** $^1$H GASPE spectrum of tegomer A-Si 2120, **4a**.

and 10K tegomer samples from Goldschmidt Chemical Co. A careful investigation of tegomer A-Si 2120 was carried out to determine the identity of any additional materials present. The 1K macromonomer was chosen for detailed analysis as, when spectra for 1K, 2.4K, and 10K tegomers were examined, extraneous peaks were of

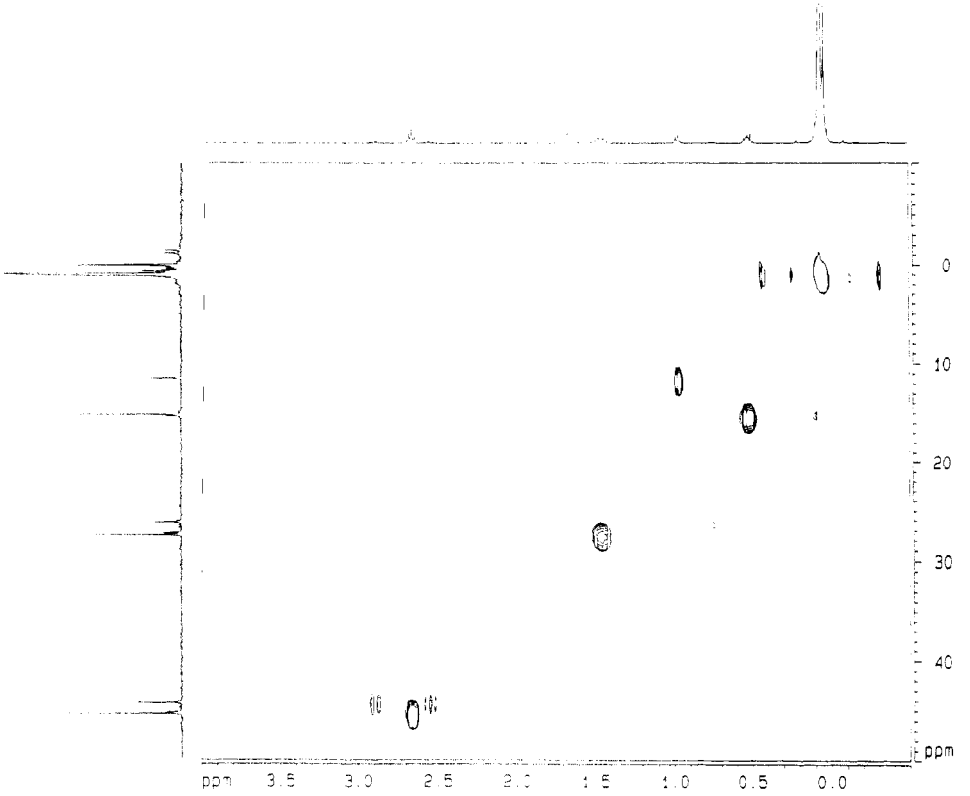


**Figure 5.** $^1H$ HMQC spectrum of tegomer A-Si 2120, **4a**.

**Table I. Short and Long Range $^1H/^{13}C$ Correlations for Tegomer 2120**

| $^1H$ frequency[a] | one-bond $^{13}C$ | two- or three-bound $^{13}C$ |
|---|---|---|
| 0.53 | 15.22 | 27.58, 45.35 |
| 0.75 | 26.31 | 11.51, 44.24 |
| 0.97 | 11.51 | 26.31, 44.24 |
| 1.45 | 27.58 | 15.22, 45.35 |
| 1.66 | | |
| 2.65 | 45.35 | 15.22, 27.58 |
| 2.89, 2.66 | 44.24 | 11.51, 26.31 |

[a] Frequencies in ppm relative to TMS secondary reference standard (0 ppm).

the greatest intensity for the 1K tegomer relative to the intense $(CH_3)_2Si$ peak. The $^{13}C$ gated spin echo (GASPE) spectrum for the 1K tegomer is shown in Figure 4. Peaks expected for the *n*-propyl terminated poly(dimethylsiloxane) are seen at 15.22, 27.58, and 45.35 ppm and are confirmed as $CH_2$'s by down position. In addition, peaks at 11.51 (up), 26.31 (up), and 44.24 (down) ppm, were assigned as methyl, methine, and methylene carbons, respectively, on the basis of the GASPE attached proton test. This sample was then subjected to 2-dimensional experiments. HMBC (heteronuclear multiple bond correlations) and HMQC (heteronuclear multiple quantum correlations) yielded long and short range $^1H/^{13}C$ correlations. The so-called inverse 2-dimensional correlation techniques are applicable to moderately high molecular weight polymers as long as the proton resonances are not extremely broadened. These techniques allow identification of all one-bond correlations and many two- and three-bond correlations. The HMQC spectrum is displayed in Figure 5, and the short and long range connectivity results are in Table I. The HMBC results (Figure 5) contain artifacts in the F1 dimension which are at the F1 transmitter frequency. In addition, the strong $Si-CH_3$ resonance leads to striping near 0 ppm in F2. The TOCSY (total correlation spectroscopy) results displayed in Figure 6 were run in order to establish all proton–proton connectivities. All results, including chemical shifts and coupling patterns, indicate that the "impurity" is a 2-amino-1-methylethyl end group.

The 2-amino-1-methylethyl end group was most likely introduced early in the synthesis stage in the preparation of the disiloxane "end-blocker". The disiloxane was presumably synthesized via hydrosilation (probably addition of allylamine to hydrodimethyldisiloxane, usually catalyzed by chloroplatinic acid). In this reaction, Si may add to the 3- or 2-carbon position. Addition to the 3-carbon gives the (3-aminopropyl)dimethyldisiloxane, while addition to the 2-carbon gives (2-amino-1-methylethyl)-dimethyldisiloxane. The mixture of end groups would then be carried along into the tegomers which are made by catalyzed equilibration reactions.[9] Our review of the literature revealed surprisingly few quantitative studies of isomeric products from Pt-catalyzed allyl addition. Significant 2-addition was observed in the hydrosilation of allyl carbonates,[19,20] and the patent literature suggests that formation of straight chain and branched aminopropylsiloxanes has also been observed in the reaction of triethoxysilane with allylamine.[21]

Integrated $^1H$ spectra for $SiCH(CH_3)CH_2NH_2$ vs $SiCH_2CH_2CH_2NH_2$ revealed the relative amounts of these two end groups. In the respective tegomers, % $SiCH_2CH_2CH_2NH_2$ is as follows: 72%, tegomer A-Si 2120; 73%, tegomer A-Si 2320; 76%, tegomer A-Si 2920. Interestingly, the presence of $SiCH(CH_3)CH_2NH_2$ end groups could not be detected in the aminopropyl end-capped PDMS oligomer Hüls PS 513.

Molecular weights (amu) determined by NMR are as follows: tegomer A-Si 2120, $0.93 \times 10^3$; tegomer A-Si 2320, $2.55 \times 10^3$; tegomer A-Si 2920, $10.7 \times 10^3$; Hüls PS 513, $20.7 \times 10^3$. The same properties determined with GPC: tegomer A-Si 2120, $M_w = 0.91 \times 10^3$, $M_n = 0.49 \times 10^3$; tegomer A-Si 2320, $M_w = 2.60 \times 10^3$, $M_n = 0.89 \times 10^3$; tegomer A-Si 2920, $M_w = 17.3 \times 10^3$, $M_n = 6.20 \times 10^3$; Hüls PS 513, $M_w = 27.8 \times 10^3$, $M_n = 19.8 \times 10^3$.

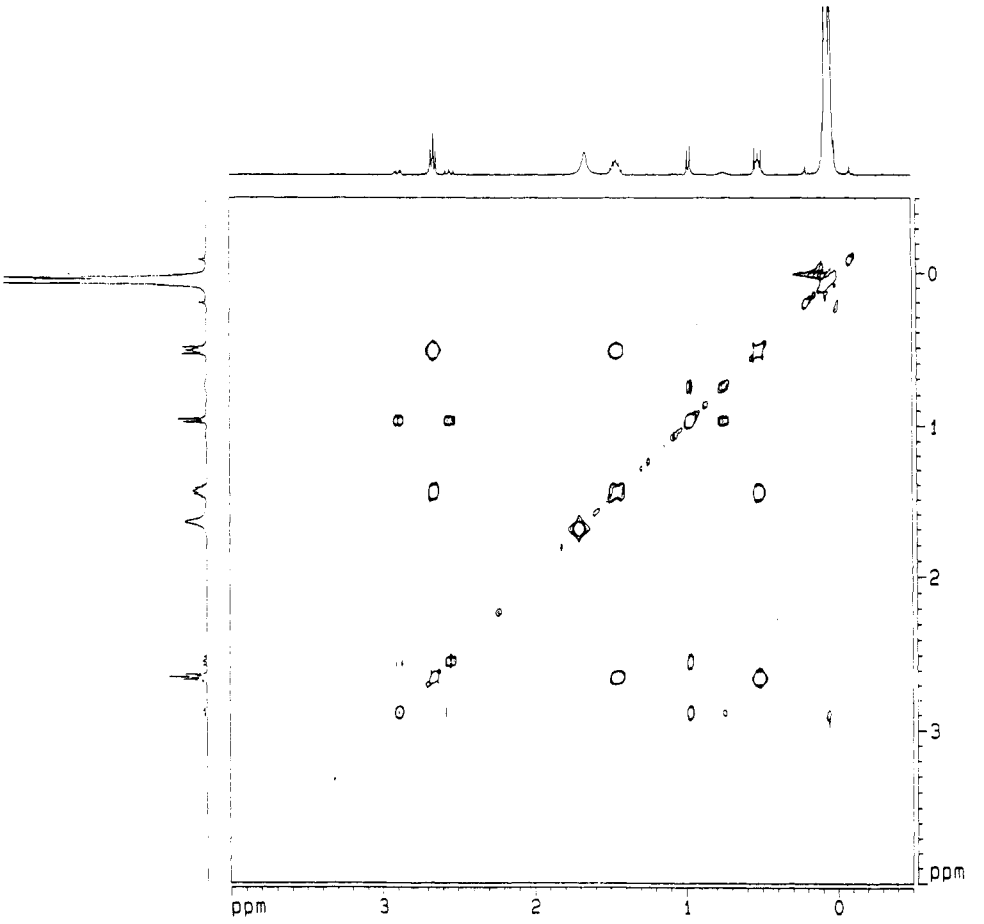


**Figure 6.** $^1$H TOCSY spectrum of tegomer A-Si 2120, **4a**.

**Table II. PDMS–Urea–Urethane Copolymers**

| designation | MW of olig[a] | reactants ratio S:I:E[b] | $M^c$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| PDMS1K-IP-B0 | 1000 | 1:1:0 | 16 700 | 12 000 | 1.4 |
| PDMS1K-IP-B0.5 | 1000 | 2:3:1 | 17 600 | 11 800 | 1.5 |
| PDMS2.4K-IP-B0 | 2400 | 1:1:0 | 65 000 | 30 700 | 2.1 |
| PDMS2.4K-IP-B1 | 2400 | 1:2:1 | 76 500 | 27 700 | 2.8 |
| PDMS2.4K-IP-B2 | 2400 | 1:3:2 | 42 700 | 19 100 | 2.2 |
| PDMS10K-IP-B0 | 10000 | 1:1:0 | 109 000 | 54 500 | 2.0 |
| PDMS10K-IP-B2 | 10000 | 1:3:2 | 81 200 | 29 200 | 2.8 |
| PDMS27K-IP-B2 | 27000 | 1:3:2 | 198 000 | 149 000 | 1.3 |

[a] olig: amino end-capped siloxane oligomers, molecular weights provided by the supplier. [b] S, siloxane oligomer; I, isophorone diisocyanate; E, benzenedimethanol. [c] Polymer molecular weights determined by GPC.

**Polymer Synthesis and Characterization.** A two-step polymerization method was used to prepare dimethylsiloxane–urea–urethane copolymers with 1,4-benzenedimethanol as the chain extender. Diamines or diols can be used as chain extenders, but urea linkages formed from diamines often lead to polymer insolubility.[22] Poor solubility is avoided by using diols, but this requires a two-stage preparation (Scheme I) because of the disparity in reactivity of alcohols and amines with isocyanates. To form urea and urethane linkages separately, the reaction between isophorone diisocyanate and benzenedimethanol was carried out first in bulk at 115 °C without catalyst (eq 1). Secondly, reaction between aminopropyl end-capped dimethylsiloxane oligomers and diisocyanate intermediates was effected in THF at room temperature (eq 2).

Since the capability to form films is an important requirement for coating materials, we have focused on those compositions that form flexible films. Table II contains a summary of the compositions of copolymers prepared. All of the copolymers were colorless and optically clear. Compositional designations are as follows: first, the segmental average molecular weight of the siloxane oligomer is given; the two letters following the first hyphen identify IPDI as "IP"; the letter after the second hyphen represents BDM, the chain extender, "B"; and the next number shows the molar ratio of chain extender to siloxane oligomer. Thus, polymer PDMS2.4K-IP-B0 is made of 1 mol of tegomer A-Si 2320 (MW ≈ 2400) and 1 mol of IPDI with no BDM chain extender.

**Infrared Spectra.** IR spectra obtained in a typical polymerization run for the preparation of PDMS2.4K-IP-B2 are shown in Figure 7. The spectrum of intermediate **3** (Figure 7C) confirms the formation of urethane linkages as well as the isocyanate end-caps: the –OH peak for **2** at 3234 cm$^{-1}$ disappears, the –NCO peak for **1** at 2260 cm$^{-1}$ decreases, and the –NH– peak at 3320 cm$^{-1}$ and the urea –(C=O)– peak at 1705 cm$^{-1}$ appear. In the second reaction stage (Scheme I, eq 2), the spectrum of polymer PDMS-2.4K-IP-B2 (Figure 7E) shows the disappearance of the –NCO peak seen for **3**, and the appearance of the urea –(C=O)– peak at 1631 cm$^{-1}$,[23] and peaks due to the poly(dimethylsiloxane) segments, which are similar to those observed for tegomer A-Si 2320 (Figure 7D).

**NMR Spectra.** Representative $^1$H NMR spectra for 1,4-benzenedimethanol, PDMS2.4K, and polymers PDMS-2.4K-IP-B0 through PDMS2.4K-IP-B2 are shown in Figure 3. The absence of detectable monomer peaks in the spectra of polymers PDMS2.4K-IP-B0 through PDMS2.4K-IP-B2 indicates the polymerization reaction is complete. Thus the triplet at 2.68 ppm ($SiCH_2CH_2CH_2$-$NH_2$) for PDMS2.4K (Figure 3B) is completely absent in the spectra of the PDMS2.4K-containing polymers (Figure 3C–E). The $SiCH_2CH_2CH_2NH_2$ peak which appears at 1.83 ppm[24] in PDMS2.4K (Figure 3B) is absent in the

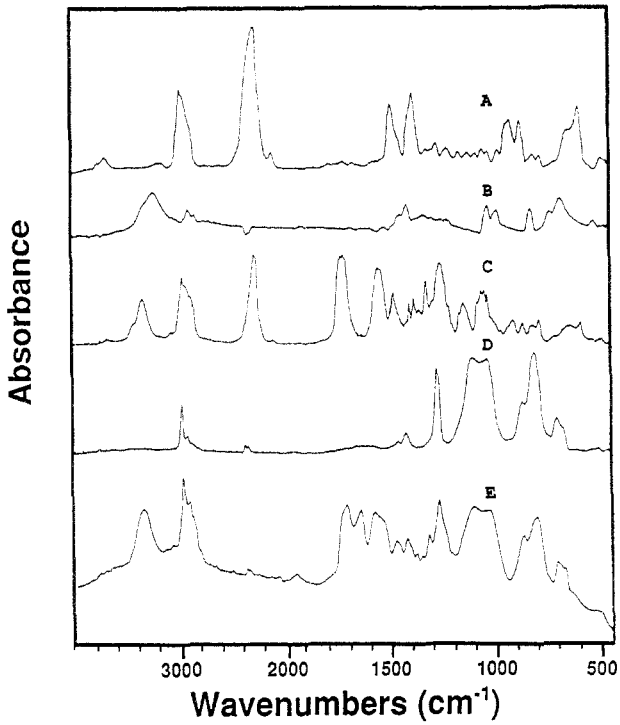


**Figure 7.** FTIR spectra: (A) isophorone diisocyanate 1; (B) benzenedimethanol, 2; (C) diisocyanate intermediate 3; (D) tegomer A-Si 2320, **4b**; (E) PDMS2.4K-IP-B2.

**Table III. Solution Properties of PDMS–Urea–Urethane Copolymers**

| designation | $\eta_{inh}$, dL/g | wt fraction of siloxane | swellability in hexane[a] |
|---|---|---|---|
| PDMS1K-IP-B0 | 0.10 | 0.72 | part. dissolved |
| PDMS1K-IP-B0.5 | 0.13 | 0.63 | swollen |
| PDMS2.4K-IP-B0 | 0.33 | 0.87 | dissolved |
| PDMS2.4K-IP-B1 | 0.38 | 0.77 | swollen |
| PDMS2.4K-IP-B2 | 0.25 | 0.69 | swollen |
| PDMS10K-IP-B0 | 0.59 | 0.97 | dissolved |
| PDMS10K-IP-B2 | 0.51 | 0.90 | swollen |
| PDMS27K-IP-B2 | 0.75 | 0.97 | swollen |

[a] Swollen, if the swollen pieces do not fuse; dissolved, if the swollen pieces fuse. See text for details.

spectra of the polymers, but a new broad set of peaks due to urea and urethane N*H* is observed at 4.7 ppm (Figure 3C–E).

Peak integrals were examined to confirm polymer stoichiometry, but only approximate agreement was found between expected values and those observed. For example, in Figure 3E the ratio of N*H* + $CH_2PhCH_2$ protons to $-C_6H_4-$ was 1.6 versus a calculated ratio of 2.0 for the copolymer PDMS2.4K-IP-B2. The ratio of N*H* + $CH_2PhCH_2$ to $SiCH_2CH_2CH_2NH_2$ was 5.8 (calc 5.6). The ratio of $CH_2$ + C*H* (adjacent to N in IPDI) to $SiCH_2CH_2CH_2NH_2$ is 3.4 (calc 3.1).

The presence of the 2-amino-1-methylethyl group apparently does not affect the reactivity of the 1-, 2.4-, and 10K macromonomers. Neither does the discrepancy between the nominal and actual molecular weights hinder the formation of polymers. The materials obtained are of satisfactory molecular weight and mechanical properties, as indicated by GPC data (Table II) and Instron test data (Table IV).

**Solution Behavior.** Inherent viscosities of these copolymers are listed in Table III. The trend of the inherent viscosities parallels the trend of the molecular weights as determined by GPC. All copolymers can be dissolved in THF at ambient or slightly elevated temperatures and can be swollen by hexane, a solvent for the

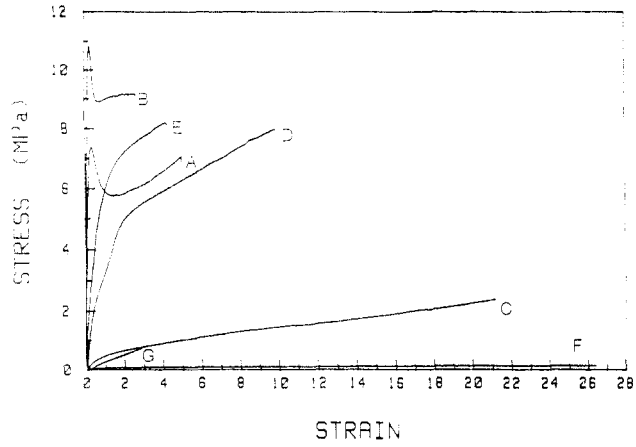


**Figure 8.** Stress–strain curves for the PDMS–urea–urethane copolymers: (A) PDMS1K-IP-B0; (B) PDMS1K-IP-B0.5; (C) PDMS2.4K-IP-B0; (D) PDMS2.4K-IP-B1; (E) PDMS2.4K-IP-B2; (F) PDMS10K-IP-B0; (G) PDMS10K-IP-B2.

**Table IV. Mechanical Properties of PDMS–Urea–Urethane Copolymers**

| designation | young's modulus (MPa) | strain at break | area under curve (MPa) |
|---|---|---|---|
| PDMS1K-IP-B0 | 42.68 | 5.0 | 31.0 |
| PDMS1K-IP-B0.5 | 70.43 | 2.7 | 24.1 |
| PDMS2.4K-IP-B0 | 1.02 | 21.2 | 30.5 |
| PDMS2.4K-IP-B1 | 6.94 | 9.8 | 57.8 |
| PDMS2.4K-IP-B2 | 12.38 | 4.2 | 28.0 |
| PDMS10K-IP-B0 | 0.03 | 26.8 | 2.82 |
| PDMS10K-IP-B2 | 0.38 | 2.8 | 1.05 |
| PDMS27K-IP-B2 | 0.18 | 6.26 | 2.08 |

siloxane oligomers. Fusion of swollen pieces of copolymers PDMS10K-IP-B0 and PDMS2.4K-IP-B0 occurred after 3 days, while swollen pieces of other copolymers remained separate. The swelling ratios were not determined; qualitatively, fusion occurred in species swelling the most. Swelling in hexane appears to be correlated with the siloxane content as well as the hydrogen bonding capabilities. The two fusible polymers, PDMS10K-IP-B0 and PDMS2.4K-IP-B0, have high weight fractions of siloxane (97 and 87%, respectively), but chain extended copolymers of comparable siloxane contents, PDMS10K-IP-B2 (90%) and PDMS27K-IP-B2 (97%) do not fuse on swelling.

**Mechanical Properties.** Stress–strain curves for the copolymers are shown in Figure 8 and the mechanical properties summarized in Table IV; the tests were performed at room temperature, and the strain rate was 1.67 $min^{-1}$. The specimens were cast from THF solutions. The average molecular weight of the siloxane segments has a dominant effect on the rigidity of the copolymers. Young's moduli for copolymers based on oligomer **4a** (MW ≈ 1000) are above 40 MPa, those for copolymers based on **4b** (MW ≈ 2400) are in the range 1–12 MPa, and the moduli for copolymers based on **4c** (MW ≈ 10,000) and Hüls PS 513 (MW ≈ 27 000) are below 0.4 MPa. The incorporation of BDM as the chain extender increases Young's modulus significantly. The addition of 2 mol of BDM/mol of siloxane oligomer in copolymers based on **4b** and **4c** results in a 10-fold increase in the modulus. On the other hand, the strain at the break of the polymers decreases with the incorporation of BDM. For copolymers based on **4a**, the break strain drops from 5.0 (500%) to 2.7 with the incorporation of 0.5 mol of BDM/mol of siloxane oligomer. In the series of copolymers based on **4b**, the strain at break decreases from over 20 to 4.2 with an increase in the content of the chain extender from 0 to 2 mol of BDM/mol of **4b**. Similarly, incorporation of BDM into copolymers based on **4c** at the ratio of 2 mol of BDM/mol of **4c** leads to a

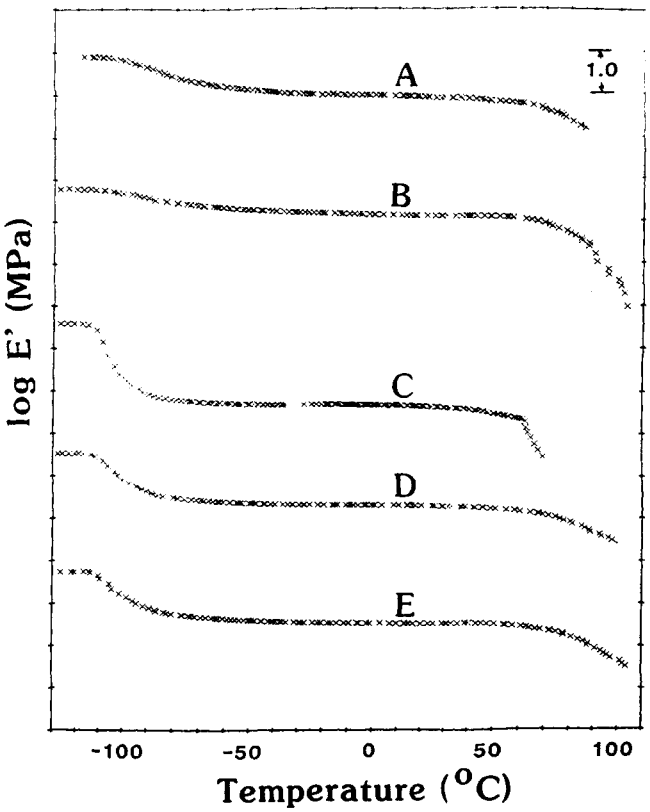


**Figure 9.** Storage modulus curves for the copolymers based on oligomers **4a** and **4b**: (A) PDMS1K-IP-B0; (B) PDMS1K-IP-B0.5; (C) PDMS2.4K-IP-B0; (D) PDMS2.4K-IP-B1; (E) PDMS-2.4K-IP-B2.

decrease in break strain from 26.8 to 2.8. Toughness of a material is proportional to the area under the stress–strain curve. By this measurement, polymers with average siloxane segmental molecular weights at 1K and 2.4K are tougher, by about 1 order of magnitude, than those with siloxane segmental molecular weights at 10K and 27K, regardless of the composition of the hard segment.

It has been recognized that many of the unique properties of the polyether or -ester based polyurethanes are due to their phase-separated structure: the hard segment (urethane or urea) rich domains provide the "solid" attributes, while the soft segment (polyether or -ester) rich domains account for the elastomeric behavior.[25] Previous work has shown that mechanical properties of PDMS urea (or urethane) copolymers also follow that pattern.[5,6,8] In the next section it is shown, on the basis of dynamic mechanical data, that phase-segregated morphologies exist in the current copolymers. In such systems, an increase in the average molecular weight of the soft segments, which increases the average distance between two hard segment domains, will cause a decrease in the rigidity of the material, while an increase in the content of chain extenders, which increases the proportion of the hard segment domain, will enhance the rigidity. The observed mechanical properties are in agreement with this reasoning. On the basis of this model the observed variation in toughness can also be explained. Materials based on **4a** are tough because of the proportionately greater contribution from the hard segment, which also leads to a high modulus. The toughness of materials based on **4b** is mainly due to the ductility of the materials facilitated by the longer soft segment. In contrast, the weakness of materials based on **4c** is probably due to failure of the long soft segment to transmit the external force to be born by the hard segment.

**Dynamic Mechanical Properties.** The storage modulus as a function of temperature for the copolymers is shown in Figure 9, where the curves have been shifted for clarity. (We were unable to obtain dynamic mechanical data on copolymers based on **4c** (MW ≈ 10 000) and Hüls PS 513 (MW ≈ 27 000) because of the extreme softness of these polymers. The lower limit for the Rheovibron viscoelastometer used for this measurement is on the order of 1 MPa.) The data indicate a two-domain morphology. The drop in modulus at temperatures of about −115 °C is due to the glass transition of the PDMS dominated soft segment domain, while the transition at temperatures between 60 and 100 °C can be attributed to the gradual melting of the hard segment domain. With diol chain extender, the glass transition region of the soft segment domain becomes broader, and the temperature at which the hard segment domain melts becomes higher.

These effects can be explained by the increased interactions between urea and urethane linkages. In both domains, the total number of urea and urethane linkages multiplies with the incorporation of chain extenders. This increase enhances the formation of intermolecular hydrogen bonding, which in turn significantly affects the material properties. In soft segment rich domains, hydrogen bonds formed among the minority area or urethane linkages would serve as diminutive physical entanglements among the constituent segments, and an increase in such hydrogen bonding would lead to a broader distribution of the molecular weights between entanglements and correspondingly a broader glass transition region. These entanglements would also reduce the drop in storage modulus through the glass transition, such reduction was observed in the dynamic mechanical measurements.

## Conclusions

A *hard-segment first* two-step polymerization was used to prepare PDMS–urea–urethane copolymers with 1,4-benzenedimethanol as the chain extender. The chain extended copolymers were found to be superior to non chain extended copolymers in thermal and mechanical properties due to the additional interactions between the urea and urethane linkages. Details of thermal and mechanical behavior were consistent with those expected of a phase-separated morphology and were shown to result from the molecular structure of the materials.

**Acknowledgment.** This research was supported in part by the Office of Naval Research. We are grateful to Dr. İ. Yilgör of Goldschmidt Chemical Corp. for a gift of the aminopropyl terminated poly(dimethylsiloxanes).

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