APPENDIX A

SYNTHESIS OF POLYDIMETHYLSILOXANE BASED SEGMETNED POLYURETHANE AND POLYUREA COPOLYMERS

Polydimethylsiloxane (PDMS) oligomers with $<M_n>$ ranging from 900 to 7000 g/mol and which were α,ω-aminopropyl, α,ω-N-methylaminopropyl and α,ω-hydroxyhexyl terminated were obtained from Th. Goldschmidt AG in Essen, Germany. The $<M_n>$ of amine-terminated oligomers were determined by the titration of the end groups with hydrochloric acid. The $<M_n>$ of hydroxyhexyl terminated PDMS oligomers were determined by ^{1}H-NMR spectroscopy. Bis(4-isocyanatocyclohexyl) methane (HMDI) with a purity of greater than 99.5% was supplied by Bayer AG. Reagent grade ethylene glycol (EG), propylene glycol (PG), 1,4-butanediol (BD), ethylene diamine (EDA) and 1,6-diaminohexane (HMDA) were purchased from Aldrich and used as received. 2-methyl-1,5-diaminopentane (Dytek) was kindly supplied by Du Pont. Chromatographic grade reaction solvents, methyl ethyl ketone (MEK), tetrahydrofuran (THF), dimethylformamide (DMF) and isopropanol (IPA) were obtained form Carlo Erba and were used without further purification. Dibutyltindilaurate (DBTDL) catalyst was obtained from Witco. The chemical structure of the precursors and the repeat unit of the segmented copolymers are presented in Scheme 4.2.

All copolymers were prepared by using the two-step prepolymer method. Reactions were carried out in three-neck, round bottom flasks equipped with overhead stirrer, nitrogen inlet, and addition funnel. During the preparation of the silicone-urethane copolymers, calculated amounts of HMDI and hydroxy-terminated PDMS were introduced into the reactor, stirred and heated. When the mixture reached 80ºC, 1 drop of 1 wt % DBTDL solution in toluene was added as a catalyst. Prepolymer formation was monitored by FT-IR spectroscopy, following the disappearance of the broad O-H stretching peak and formation of the N-H peak near 3450 and 3300 cm^{-1} respectively. For chain extension, a stoichiometric amount of chain extender (EG, PG or BD) was added into the reactor together with MEK, as the reaction solvent and the reaction was continued at 70ºC until the complete disappearance

of the isocyanate peak at 2270 cm^{-1} in FT-IR. Reaction mixtures were homogeneous and clear throughout the polymerizations.

Silicone-urea copolymers were produced at room temperature. Prepolymer was obtained by the drop-wise addition of a solution of the PDMS oligomer in THF into a reactor containing HMDI (also dissolved in THF). After the prepolymer was obtained, the system was diluted with DMF or IPA to increase the polarity of the solvent before the chain extension step. During chain extension, a stoichiometric amount of diamine (EDA, HMDA or Dytek) was dissolved either in DMF or IPA and added drop-wise into the reactor, through an addition funnel. The complete disappearance of the strong isocyanate peak at 2270 cm^{-1} via FT-IR was used to determine the completion of the chain extension reaction.

APPENDIX B

CALCULATION OF THE ELECTRON DENSITY CONTRAST RATIO IN SELECTED PDMS BASED SEGMENTED POLYURETHANE AND POLYUREACOPOLYMRS

The electron density of a component i is calculated using the formula:

$$\rho_i = (\rho \, x \, n)/M \tag{B1}$$

where ρ is the mass density of component i in g/cm^3, M the molecular weight, and n the total number of electrons present in that chemical structure. For an ideal two-phase system with sharp phase boundaries the electron density contrast is given by [Ref. 46 in Chapter 4]

$$(\rho_1 - \rho_2)^2 \tag{B2}$$

When the above formula is applied to segmented copolymer systems where the two components (hard phase and soft phase respectively) are covalently bonded to each other, it must be recognized that the effect on the electron densities of the copolymer environment at the sites where these components are covalently linked is not taken into account by eq. (B2). Furthermore, since eq. (B2) assumes an ideal two-phase system with sharp phase boundaries, the possibility of an interface is also ignored. The issue of whether the end groups of the PDMS SS (hexyl for urethanes and propyl for ureas) should be considered a part of the SS or the HS is also open to discussion [Refs. 31 and 45 in Chapter 4]. Despite these limitations, as long as eq. (B2) is applied consistently, a qualitative comparison of equivalent siloxane based polyurethane and polyurea systems can be made using the following ratio,

$$\frac{(\rho_1 - \rho_2)^2_{urethane}}{(\rho_1 - \rho_2)^2_{urea}} \tag{B3}$$

Example (Electron Density Contrast Ratio of PDMS7.0k-BG-30 to PDMS-7.0k-EDA-25): The computation of the electron density contrast in the urethane sample PDMS7.0k-BG-30 is demonstrated below. For the purposes of this computation the hexyl functional end group of the PDMS oligomer (see Scheme 4.2) is considered to be a part of the SS.

Molecular weight of the SS = 6974 g/mol

Number of electrons in this chemical unit = 3768

Mass density of α,ω-hydroxyhexyl terminated PDMS = 0.98 g /cm^3

Hence, ρ_l = 0.53 mol-elec/cm^3 = 0.319 elec/Å^3

      The electron density of the HS, using the above procedure, is 0.335 elec/Å^3. Thus, from eq. (B2) the electron density contrast in PDMS7.0k-BG-30 is *2.56 x 10^{-4} (elec/Å^3)^2*. Similarly, the electron density contrast in PDMS-7.0k-EDA-25 is *3.6 x 10^{-5} (elec/Å^3)^2*. Therefore, the contrast ratio in the two samples (urethane: PDMS-7.0k-BG-30 and urea: PDMS-7.0k-EDA-25) under the restrictions placed by the assumptions stated above is *7.1*.

SYNTHESIS OF POLYDIMETHYLSILOXANE BASED SEGMETNED POLYUREA COPOLYMERS CONTAINING POLYPROPYLENE OXIDE CO-SOFT SEGMENT AS THE GRADIENT COMPONENT

The α,ω-Aminopropyl terminated PDMS oligomers with $<M_n>$ of 3,200 g/mol and α,ω-N-methylaminopropyl terminated PDMS oligomers with $<M_n>$ of 7,000 g/mol were obtained from Wacker Chemie and Th. Goldschmidt AG, respectively. Amine terminated PPO oligomers with $<M_n>$ of 450 and 2000 g/mol were obtained from Huntsman Chemical Corp. The $<M_n>$ of amine-terminated oligomers were determined by titration of the end groups with standard hydrochloric acid. Bis(4-isocyanatocyclohexyl)methane (HMDI) with a of greater than 99.5 % purity was supplied by Bayer AG whereas Du Pont provided 2-methyl-1,5-diaminopentane (Dytek A) (Scheme C1). Reagent grade isopropanol (IPA) purchased form Carlo Erba was used as the reaction solvent without further purification.

$$OCN-\text{(cyclohexyl)}-CH_2-\text{(cyclohexyl)}-NCO$$

Bis(4-isocyanatocyclohexyl)methane

$$H_2N-CH_2-CH(CH_3)-(CH_2)_3-NH_2$$
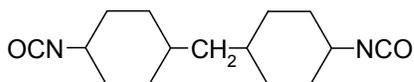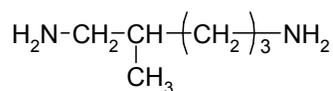
1,5-diaminopentane

Scheme C1

All polymerization reactions were carried out in IPA at room temperature in a three-neck round bottom flask equipped with an overhead stirrer, nitrogen inlet, and an addition funnel. As shown in Reaction Scheme 5.1, polymers were prepared using a three-step procedure. Calculated amount of HMDI was weighed into the reaction flask and dissolved in IPA. Calculated amounts of amine terminated PDMS and PPO oligomers were separately

weighed into the Erlenmeyer flasks and dissolved in IPA. These solutions were *sequentially* introduced into the addition funnel and added drop-wise into the reactor containing the HMDI solution, under strong agitation, to prepare the prepolymer. Finally, stoichiometric amount of diamine chain extender was dissolved in IPA and added drop-wise into the reactor, through the addition funnel. Progress and completion of the reactions was monitored by FT-IR spectroscopy, following the disappearance of the strong isocyanate peak at 2270 cm^{-1} and formation of urea (N-H) and (C=O) carbonyl peaks around 3300 and 1700 cm^{-1} respectively. Reaction mixtures were homogeneous and clear throughout; no precipitation was observed.

APPENDIX D

SYNTHESIS OF SEGMENTED POLYURETHANE AND POLYUREA COPOLYMERS WITH A SINGLE DIISOCYANATE MOLECULE AS THE HARD SEGMENT

The materials 1,4-phenylene diisocyanate (*p*PDI) and 1,3-phenylene diisocyanate (*m*PDI) 1,6-hexamethylene diisocyanate (HDI) were purchased from Aldrich. mPDI was used as received, while *p*PDI was sublimed under vacuum at 70°C. The purity of the diisocyanates were determined by reacting them with a known excess of dibutylamine (DBA) solution in toluene and then back titrating the excess DBA with standard hydrochloric acid in isopropanol (IPA) using bromophenol blue indicator to yellow end point. The purities of both diisocyanates were better than 99.5 %. α,ω-Aminopropyl terminated poly(tetramethylene oxide) (PTMO) with $<M_n>$ 1100 g/mol was purchased from Aldrich. Poly(tetramethylene oxide)glycol, with $<M_n>$ 975 g/mol was kindly provided by DuPont. $<M_n>$ value for amine terminated PTMO was determined by the titration of the end groups with standard hydrochloric acid in tetrahydrofuran (THF) using bromophenol blue indicator to yellow end point. Reagent grade reaction solvents, IPA, THF, and dimethylformamide (DMF) were purchased from Aldrich and used as received. Dibutyltin dilaurate catalyst (T-12) was also purchased from Aldrich.

Equimolar amounts of diisocyanate and poly(tetramethylene oxide)glycol were weighed into a three-neck round bottom Pyrex reaction flask, which was fitted with an overhead stirrer and nitrogen inlet. The reactants were dissolved in DMF to form a 50 % solution by weight and stirred at room temperature until a homogeneous mixture was obtained. Reaction mixtures containing the aromatic diisocyanates, *p*PDI and *m*PDI, were heated to 60°C and maintained at that temperature until completion of the reaction. Reaction mixtures were further diluted with DMF when the viscosity increased due to the growth in the overall polymer MW.

Polyurea copolymers based *p*PDI or *m*PDI were prepared in solution at room temperature and at 0°C respectively. The reaction set-up consisted of a three-neck, round

bottom Pyrex reaction flask, fitted with an overhead stirrer, nitrogen inlet and an addition funnel. A particular diisocyanate was weighed into the reaction flask and dissolved in DMF. Amine terminated PTMO was weighed into an Erlenmeyer flask and also dissolved in DMF and introduced into the addition funnel. The concentrations of both the diisocyanate and PTMO solutions were ca.20 wt %. Polymerization was conducted by the drop wise addition of PTMO solution onto the diisocyanate solution in the reaction flask. As the viscosity of the reaction mixture increased they were further diluted with the reaction solvent.

The completion of a given reaction was determined by monitoring the disappearance of the isocyanate absorption peak around 2270 cm^{-1} with a FT-IR spectrophotometer.

Polymer films, *ca.*1 mm thick were obtained by pouring the solutions into Teflon molds, which were covered with a glass Petri dish to slow down the solvent evaporation. The molds were then placed directly into a 60°C oven. After evaporation of the solvent the glass cover was removed and molds were placed in a vacuum oven at 60°C for complete drying, which was monitored gravimetrically, until constant weight was achieved. The resulting films were then removed from the Teflon molds and stored under vacuum at room temperature until needed for testing.