

# Synthesis and Thermal Properties of Polyurethane–Polysiloxane Crosslinked Polymer Networks

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**ABSTRACT:** Polysiloxane–polyurethane crosslinked polymer networks (PSI–PU) were synthesized in solution by polymerization of oligosiloxanes containing  $\gamma$ -hydroxy propyl groups with polymethane polyphenyl polyisocyanate. Polyether-based polyurethane and polyester-based polyurethane were also prepared by a “one-shot” method. Their thermal properties were studied by thermogravimetric analysis. It was observed that the thermal stability of PSI–PU was better than that of polyether-based polyurethane and polyester-based

polyurethane, and an inert atmosphere had no effect on decomposition of polyurethanes below 350°C. It was found that polyurethane–polysiloxane crosslinked polymer networks decomposed slower in oxygen than in nitrogen in the temperature range of 350–550°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 310–315, 2003

**Key words:** polysiloxanes; polyurethanes; networks; crosslinking; thermal properties

## INTRODUCTION

Polyurethane block copolymers, polyether-based polyurethane (PET–PU), and polyester-based polyurethane (PES–PU) have found a variety of applications in industry as cellular materials, elastomers, coatings, and sealants. These polymers are known for their excellent abrasion and tear resistance, high load-bearing capability, and design flexibility. The thermal stability of urethanes depends on the type of isocyanates and polyols used in their preparation.

Polydimethylsiloxane (PDMS) has many desirable features, such as low-temperature flexibility based on a low glass-transition temperature ( $\sim -123^\circ\text{C}$ ), and high thermal and oxidative stability, for example. A variety of applications of the polysiloxanes results from their stability at elevated temperatures and unusual flexibility. However, PDMS has two shortcomings: very weak mechanical characteristics and incompatibility with almost all organic polymers. In blends, they tend to migrate to the surface of the materials.<sup>1–5</sup> A convenient method used to overcome these drawbacks that can widen the applications of polysiloxanes seems to be incorporation into copolymer structures by the usual classification methods of random, alternating block and graft, including networks and interpenetrating networks. The synthesis of polysiloxane-containing polymers has been of substantial interest

because of their desirable thermal, mechanical, chemical, electrical, and surface properties.

PSI–PU copolymers have gained increasing attention, and thus much effort has been made to synthesize copolymers composed of some hard segments and PDMS as a portion of the soft segments.<sup>6–16</sup> Segmented polyurethane copolymers containing PDMS as soft-segment component are considered as possible candidates for biomedical materials.<sup>6,7,17</sup> Kazama and coworkers<sup>18</sup> prepared polyurethane–polysiloxane graft copolymers using uniform-size polysiloxanes with a diol end group as the macromonomer. McGrath et al.<sup>19,20</sup> studied the kinetics of model poly(urethane–siloxane) formation reactions, which reacted between 4,4-diphenylmethane diisocyanate (MDI) and 1,3-bis(4-hydroxybutyl)tetramethyl disiloxane, and reported the electron spectroscopy for chemical analysis (ESCA) studies on polydimethylsiloxane–urethane copolymers. Yu et al.<sup>21,22</sup> synthesized PDMS–PU segmented copolymers and related zwitterionomers of these copolymers, and studied the effect of the degree of ionization on the physical properties. Liu et al.<sup>23</sup> investigated the preparation, kinetics, and morphological structures of poly(siloxane–urethane) block copolymers. Stanciu et al.<sup>24,25</sup> studied the thermal stability and tensile properties of linear PSI–PU elastomers. In all systems mentioned,  $\alpha,\omega$ -bis(functional)polydimethylsiloxanes were used to synthesize linear copolymers.

Stanciu et al.<sup>26,27</sup> also synthesized poly(ester–siloxane)urethane networks. In such systems, polysiloxanes were introduced by poly(dimethylsiloxane) diol as a part of the soft segments. Chemical crosslinks were introduced by means of a low molecular mass

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polyol (diglycerin maleate tetrol). Ebdon et al.<sup>28</sup> carried out the synthesis and characterization of PSI-PU interpenetrating polymer networks (IPNs).

In the present work, the PSI-PU crosslinked polymer networks were prepared by a reaction between multifunctional oligosiloxane polyols (functionality  $\sim 10$ ) and polymethane polyphenyl polyisocyanate (PAPI) (functionality  $> 3$ ). The thermal properties of this polymer network are reported. For the sake of comparison, PET-PU and PES-PU were also investigated.

## EXPERIMENTAL

### Materials

Adipic acid (AA), phthalic anhydride (PA; Chemistry Plant of Shanghai Chemical Agent Station), ethylene glycol (EG), propanediol-1,2 (1,2-PDO; Shandong Chemical Engineering College), and trihydroxymethylpropane (TMP; Shandong Academy of Science) are all chemical agents. Polyether N-307 (Jinling Petrochemical Corp. Ltd., China) and PAPI ( $-NCO\%$ , 30–31%; BASF Company Ltd. Korea) are industrial chemicals and were used without further treatment. Trimethyl(2-propenyloxy)silane and oligosiloxanes containing Si—H bonds were synthesized in our laboratory. The oligosiloxanes were vacuum distilled at a pressure  $< 3$  mmHg and a temperature of  $165^\circ\text{C}$  to remove cyclic siloxanes. The number-average molecular weight of the oligosiloxanes was 3398 determined by GPC and the bulk viscosity was 20.5 mPas ( $20^\circ\text{C}$ ).

### Measurements

IR spectra were recorded on a Nicolet FTIR 20SX spectrometer (Nicolet Instruments, Madison, WI) by using films for liquids and KBr pellets for solids. The bulk viscosity values were measured by using an NDJ-79 rotation viscometer (Tongji University).

The GPC analysis of polydimethylsiloxanes containing Si—H groups was done by using a system consisting of a Waters 515 pump, two Waters styragel columns (HT3, HT4), and a Waters 2410 refractive index detector (Waters Chromatography Division/Millipore, Milford, MA) and shipped in toluene. The system was calibrated using narrow molecular weight polystyrene standards.

Thermogravimetric analyses (TGA) were carried out using a Rheometric Scientific TGA1500 (Piscataway, NJ) to investigate the thermal properties of samples. The samples were heated from ambient temperature to  $700^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  in an inert atmosphere of nitrogen or oxygen.

### Synthesis of polyester polyols

Polyester polyols were prepared by reacting EG, 1,2-PDO, and TMP with AA and PA at a fixed hydroxyl to

carboxyl ratio of 2.4. The molar ratio of PA to AA is 2 : 3. To allow crystallization of the polyester polyols, 1,2-PDO was used. Aromatic rings were introduced in the polyol chains by using PA. The polyesterification reaction was carried out in a 500-mL round-bottom glass reactor having a stirring assembly, a thermometer, a nitrogen gas inlet tube, and a distillation condenser. The reactants were gradually heated from ambient temperature to  $140^\circ\text{C}$  for about 1.5 h and then from 140 to  $180^\circ\text{C}$  for 1.5 h. The reaction mixture was held at  $180^\circ\text{C}$  for 3.0 h, and subsequently slowly heated to  $200^\circ\text{C}$ . The reaction proceeded at atmospheric pressure, followed by distilling under reduced pressure to remove the water formed in the reaction. The extent of the reaction was controlled by the product's acid value. The reaction was over when the acid value was less than 1.0 mg KOH/g. The hydroxyl value of the polyester polyols ( $M_n = 2000$ ) was 247.0 mg KOH/g and the bulk viscosity was 3100.0 mPas ( $25^\circ\text{C}$ ). The theoretical functionality was around 9.

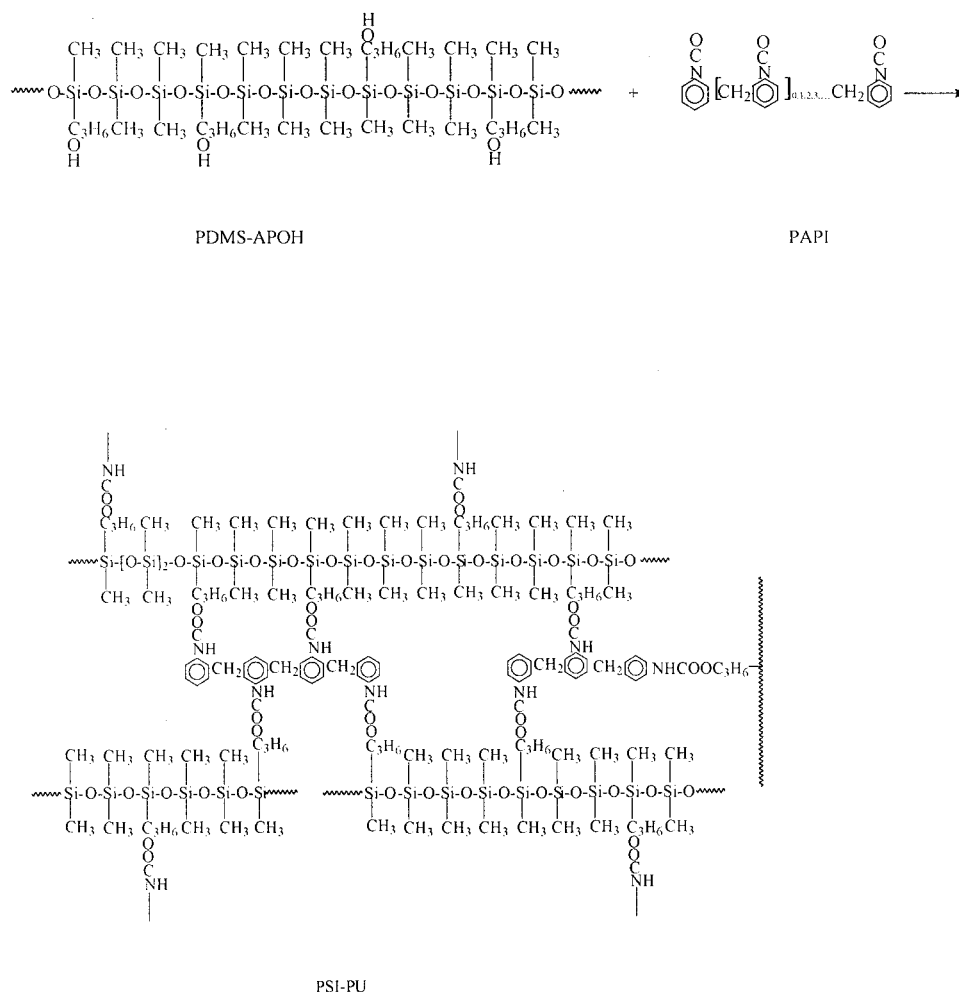
### Synthesis of oligosiloxanes containing $\gamma$ -hydroxy propyl groups (PDMS-APOH)

Oligosiloxanes containing  $\gamma$ -hydroxy propyl groups were prepared by the following procedure: 40.0 g of oligosiloxanes containing 0.48% (mol/g) Si—H groups, 34.0 g of trimethyl(2-propenyloxy)silane, and 0.1 mL of 0.1M chloroplatinic acid in isopropanol was heated under reflux for 8 h. The IR spectrum showed that the Si—H peak at  $2154\text{ cm}^{-1}$  disappeared. The residue was evaporated to remove nonreactants and gave oligosiloxanes containing  $\gamma$ -trimethylsiloxy propyl (PDMS-APOSiMe<sub>3</sub>). Methanol and acetic acid were added to PDMS-APOSiMe<sub>3</sub> and the mixture was refluxed for 1 h more to effect the alcoholysis of the  $-\text{SiMe}_3$  groups. The residue was evaporated and gave 50.8 g of PDMS-APOH. The bulk viscosity was 1450.0 mPas ( $20^\circ\text{C}$ ).

IR ( $\text{cm}^{-1}$ )  $\nu$  (OH), 3317;  $\nu$  (Si—Me), 1259, 842;  $\nu$  (Si—O—Si), 1024–1091;  $\nu$  (Si—CH<sub>2</sub>), 1412, 800. No peak at 2100–2250 (Si—H).

### Synthesis of PET-PU and PES-PU

PET-PU was prepared from PAPI and polyether, and PES-PU was prepared from PAPI and polyester by a "one-shot" technique, as described below. Polyether polyols or polyester polyols, catalyst (0.01 wt % triethylenediamine), and a chain extender (if required) were charged into a 150-mL three-neck, round-bottom flask, equipped with a mechanical stirrer and vacuum inlet. This mixture was degassed with stirring for 30 min under vacuum. After the stirring was stopped and the vacuum broken, PAPI was added to give a 20% excess over the requisite amount. The mixture was stirred vigorously and vacuum was reapplied. After about



Scheme 1

50 s the reacting mixture was poured into a mold of polytetrafluoroethylene. Finally, the sample was allowed to cure and age at ambient temperature at least 2 weeks before tests were carried out.

#### Synthesis of PSI-PU crosslinked polymer networks

To 7.6 g of PAPI in 25.0 mL tetrahydrofuran (THF), 10.0 g of PDMS-APOH containing 2,4,6-tris[(dimethylamino)-methyl]phenol (DMP-30) in 25.0 mL THF was added and the solution was mechanically stirred under nitrogen at ambient temperature for about 1 h. It was then poured into a mold of polytetrafluoroethylene. Because of short gelation time of the reaction mixture, prompt operation was required. The solvent was evaporated in vacuum, leaving pale yellow polymer network materials. The IR spectrum showed that the  $\text{-NCO}$  peak at  $2270\text{ cm}^{-1}$  disappeared.

#### Synthesis of PSI-PU containing hydroxy-terminated groups

The procedure for the preparation of PSI-PU containing hydroxy-terminated groups was the same as the

synthesis of PSI-PU, except the stoichiometric amounts of PAPI and PDMS-APOH were 3.8 and 11.0 g, respectively. The IR spectrum showed the  $\text{-OH}$  peak at  $3319\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

PSI-PU is composed of crosslinked polymer networks formed by the reaction of oligosiloxanes containing hydroxy propyl groups with polymeric isocyanates. Excess isocyanates will react with the active hydrogens of the urethane linkages to form allophanates and they may also be trimerized to form polyisocyanurate structures. The crosslinked polymer networks

TABLE I  
PSI-PU Physical Properties

Theoretical concentration of urethane groups (mol/kg)	Hardness (Shore D)	Tensile strength (MPa)
2.1	75	21.7

<sup>a</sup> The crosslinking degree is greater because of excess PAPI.

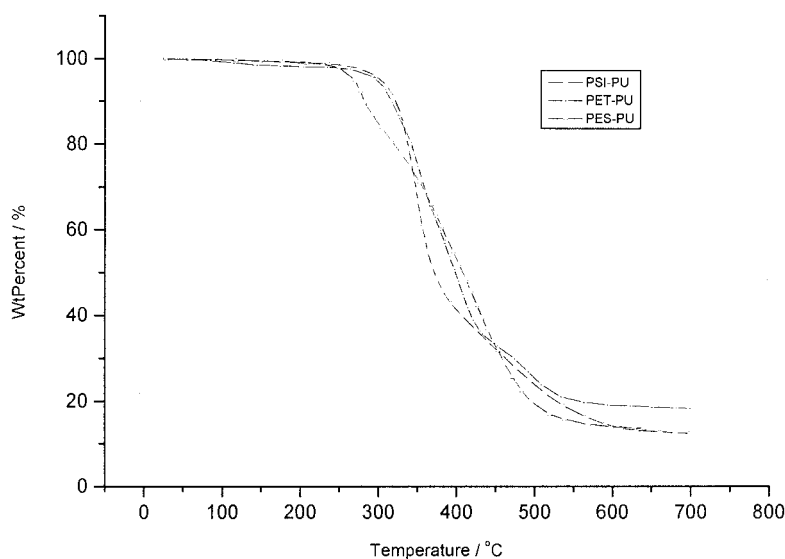


Figure 1 TGA curves of PSI-PU, PET-PU, and PES-PU,  $N_2$ .

in this study were synthesized by a reaction described in Scheme 1. PSI-PU physical properties are shown in Table I.

Thermal decomposition of polyurethane has been studied in detail in a number of previous investigations.<sup>29–35</sup> The results show that degradation of polyurethane copolymers starts in the hard segments in the first degradation step (250–400°C). A radical breakdown and isocyanates suffer degradation in the second step (beyond 400°C). Thermogravimetry (TG) was used to study the thermal stability of these polymer networks. The TG curve of the networks at the heating rate of 10°C/min is shown in Figure 1. The polymer networks decomposed in two stages. The first occurred from 280 to 380°C and accounted for the

loss of about 55.0% of the networks' weight. The remainder of the networks decomposed in the second stage from 380 to 650°C. The hard segments decomposed in the first stage. After the initial decomposition, the low thermal stability of oligosiloxanes containing hydroxy groups, which came from the first degradation stage, decomposed rapidly in the temperature range of 280–380°C. The principal decomposed products were probably cyclic oligomers. As seen in Figure 2, the degradation reaches a maximum rate at 349°C. A comparison of thermal stability of PDMS-OH, PSI-PU containing hydroxyl-terminated groups, and PSI-PU is shown in Figure 3. The TG curves reveal the effect of hydroxyl groups of the oligosiloxane chains on thermal stability. It is believed to depo-

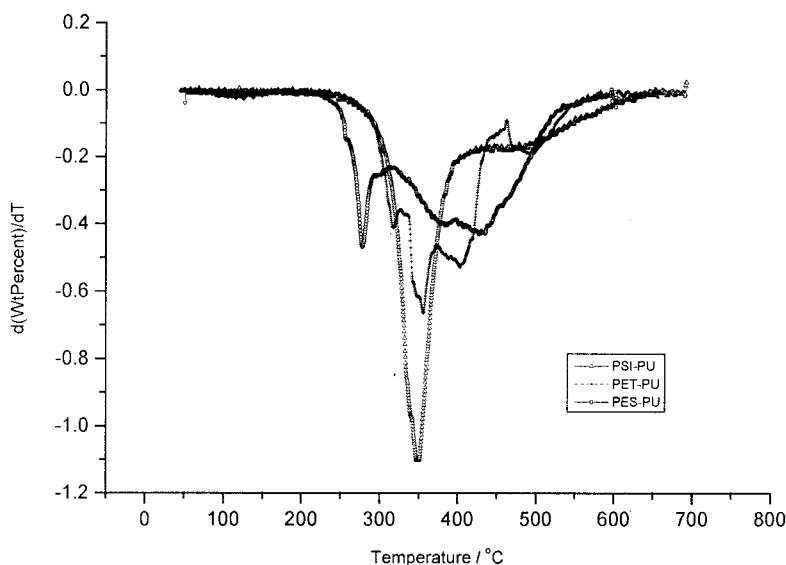
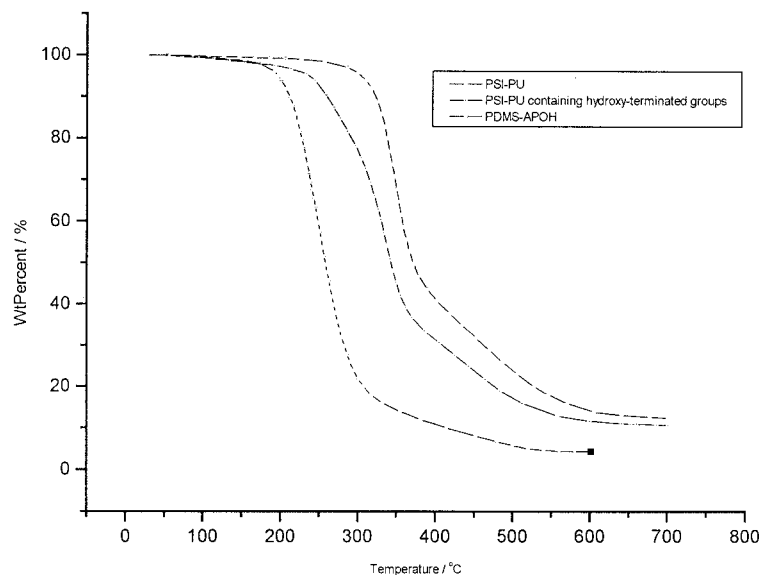


Figure 2 DTG curves of PSI-PU, PET-PU, and PES-PU,  $N_2$ .



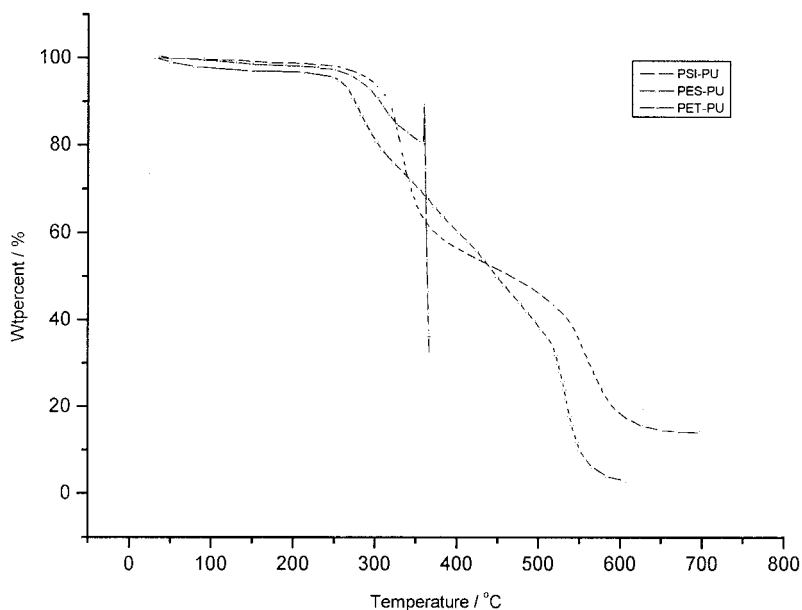
**Figure 3** TGA curves of PSI-PU, PSI-PU containing hydroxy-terminated groups, and PDMS-APOH,  $N_2$ .

lymerize by a mechanism through the hydroxy groups.<sup>36</sup> The amount of weight loss in the first stage is the same as the weight fraction of PDMS-APOH components (56.8%) in the polymer networks. This further suggests that the weight loss in the first stage was governed by the degradation of oligosiloxanes. The isocyanate sequences decomposed in the second stage. The weight loss became slow and complex. The DTG curve of PSI-PU in Figure 2 shows no peaks in the temperature range of 380–650°C.

TG curves of PET-PU and PES-PU are also shown in Figure 1. It can be observed that thermal stability of PSI-PU is better than that of either PET-PU or PES-

PU. Below 350°C, PET-PU began to decompose at a temperature slightly below that at which PSI-PU decomposed. PES-PU obtained from the aromatic polyols, of which two ester groups attached to the aromatic ring are ortho in the chains, was less thermally stable than PSI-PU and PET-PU. The PES-PU began to decompose at 240°C. It can be attributed to the structure of O-aromatic rings in the polyester polyol chains.<sup>37</sup> The presence of the structure of low thermal stability suggested the possibility of considerably decreasing the initial decomposition temperature of PES-PU.

DTG curves of PES-PU and PET-PU are also shown in Figure 2. PES-PU has two maximum rates, the



**Figure 4** TGA curves of PSI-PU, PET-PU, and PES-PU,  $O_2$ .

initial one of which is at 278°C. PET-PU has four maximum rates, the initial one of which is at 319°C. By comparing the initial maximum decomposition rate temperatures, PSI-PU shows better thermal stability than that of either PET-PU or PES-PU. The maximum rates of PES-PU and PET-PU beyond 400°C suggest that fragments of polyester or polyether suffer degradation in the second stage.

Figure 4 shows TGA traces of PSI-PU, PET-PU, and PES-PU at a heating rate of 10°C/min under oxygen. All samples were found to undergo little change in the first stage of decomposition comparison with that in Figure 1. This indicates that an atmosphere of nitrogen (inert) or oxygen had no effect on the decomposition of the hard segments in the first stage. At approximately 380°C, PET-PU burned. In the range of 500–580°C, PES-PU decomposed rapidly, different from that in nitrogen. The curve of PSI-PU displays two distinct regions of weight loss, and shows a shoulder that is quite different from that when heated under nitrogen. This illustrates that the mechanism of thermal degradation of the polymer networks is not the same in these different atmospheres.

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