

# Preparation and Characterization of Aqueous Polyurethane Dispersions with Well-Defined Soft Segments

Qunchao Zhang, Jiankun Hu, Shuling Gong

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

Received 4 August 2010; accepted 4 January 2011

DOI 10.1002/app.34095

Published online 7 July 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Novel aqueous polyurethane (PU) hybrid dispersions were successfully prepared with 5–15 mol % functionalized hexamethylene diisocyanate trimer modified by *N*-(*n*-butyl)-3-aminopropyltriethoxysilane and dihydroxypropyl-terminated siloxane oligomers (TS). The results of the differential scanning calorimetry and X-ray diffraction tests show that the degree of segment order was reduced by the introduction of TS. The hybrid polymer films with TS introduced into the PU backbone displayed excellent water and xylene resistance. Atomic force microscopy showed that the films had a smooth surface. It

was noticeable that the tensile strength ( $\sigma_b$ ) and Young's modulus of the films increased simultaneously when TS was incorporated into PU;  $\sigma_b$  of the PU15 film with 15 mol % TS was much higher than that of the neat PU0 film, and the breaking elongation of the film with 10 mol % TS was clearly higher than that of the other films. The results indicate that an appropriate content of TS significantly improved the properties of the aqueous PU hybrids. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3064–3070, 2011

**Key words:** coatings; polysiloxanes; polyurethanes

## INTRODUCTION

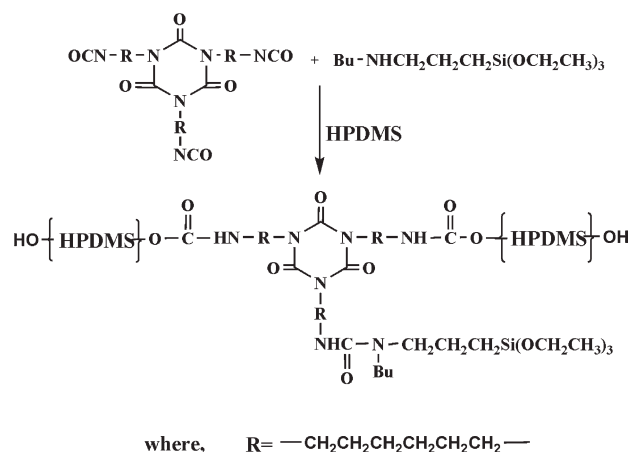
Waterborne polyurethane dispersions (PUDs), which usually include a cationic, anionic, or poly(ethylene oxide) nonionic dispersing center in its molecular chain, can be applied to coatings, printings, inks, and so on. PUDs have excellent elasticity, wear resistance, and flexibility and easy processing and low contamination.<sup>1,2</sup> However, PUDs films have some disadvantages, such as a low strength, water resistance, and surface hydrophilicity.<sup>1</sup> These properties could be improved with different mixing compositions of soft segments.<sup>3</sup>

Polydimethylsiloxane (PDMS) has unique properties, such as a low surface energy, good thermal stability, and excellent flexibility mainly because of their structure, which is composed of inorganic Si—O bonds and organic grafted CH<sub>3</sub> groups.<sup>4,5</sup> However, their mechanical properties are usually poor, especially with low-molecular-weight PDMS. Combinations of polyurethane (PU) and siloxane would have a better heat resistance and lower temperature flexibility than PU and better mechanical properties and abrasion characteristics than polysiloxane.<sup>6</sup> Therefore, the possibility of combining the advantages of polysiloxane and PU has attracted many investigations for a long time.

To enhance the properties of water resistance, surface hydrophilicity and mechanical strength for

PUDs,<sup>7</sup> several methods have been developed for the synthesis of PUDs through the application of functional organosiloxane moieties.<sup>8</sup> These reports have mainly focused on the design of the segmented or blocked polysiloxane chains or functional cross-linked siloxane moieties into the PU molecular backbone. It had been proven that poly(dimethylsiloxane)diol can be used for the synthesis of PDMS and PU and improve the physical characteristics of polymers, such as the water resistance and mechanical strength of block hybrids;<sup>9–13</sup> however, the hydrolysis rate of the products was much too high because of the presence of Si—O—C bonds in the backbone, which limits their applications. In comparison with Si—O—C bonds, Si—C—N and —NH—CO—NH— bonds were much more stable; therefore, the introduction of primary amine-terminated siloxane oligomers in segmented PU has become a positive method.<sup>3,14,15</sup> Nevertheless, the primary amino groups existing in the PU backbone would like to form partial crosslinking among PU molecular chains; this results in poor dispersion stability.<sup>16</sup> Thus, the utilization of secondary amino-terminated siloxane oligomers or hydroxylalkyl-terminated siloxane oligomers into the PU system could be a better choice,<sup>17–19</sup> but the excess siloxane oligomers, which are only blocked into PU system as chain extenders, results in a very weak mechanical strength and serious incompatibility,<sup>2</sup> whereas crosslinking trifunctional silane or silane-modified inorganic silica or clay could also be introduced into the PU system to form PU/silica or clay-hybrid composites.<sup>20–23</sup> Although the mechanical properties and water resistance were enhanced, stable properties were difficult to improve with trifunctional

Correspondence to: S. Gong (gongsl@whu.edu.cn).



**Scheme 1** Synthesis of the model TS.

silane, silane-modified inorganic silica, or clay (>2.5%). Hence, improving the properties of silicon-modified PUDs and expanding the application of various silicon-modified PUDs are still a challenge.

In this work, we incorporated *N*-(*n*-butyl)-3-aminopropyltriethoxysilane (BAPTS) and dihydroxypropyl-terminated siloxane oligomer (TS) modified hexamethylene isocyanate trimer into PUDs by the typical acetone process (Schemes 1 and 2). With the isocyanate trimer, trifunctional silane and PDMSs were simultaneously introduced to the PU backbone; this process offered a novel self-designing approach and allowed us to obtain excellent properties. The structure and properties of the resultant materials were investigated by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), atomic force microscopy (AFM), differential scanning calorimetry (DSC), and mechanical and swelling tests. With three active ethoxy groups in the side chain and polysiloxane segments in the backbone, the effects of the hydrolysis and condensation of TS, associated with polysiloxane domains being formed, on the properties are discussed. In contrast to the previous reports of blocking certain dosages of polysiloxane, silane, or nanomaterials into the PU matrix to simply increase the elongation or tensile strength ( $\sigma_b$ ),<sup>7-23</sup> the appropriate loading of TS enhanced the elongation and  $\sigma_b$  at one time. The mechanism of simultaneous reinforcement and flexibility was also explored.

## EXPERIMENTAL

### Materials

Hexamethylene diisocyanate (HDI), HDI trimer (Desmodur N-3900), dimethylol propionic acid (DMPA), and poly(tetramethylene oxide glycol) [PTMO; number-average molecular weight ( $M_n$ ) = 2000] were obtained from Bayer Material Science (Pittsburgh, PA). Dihydroxypropyl-terminated poly-

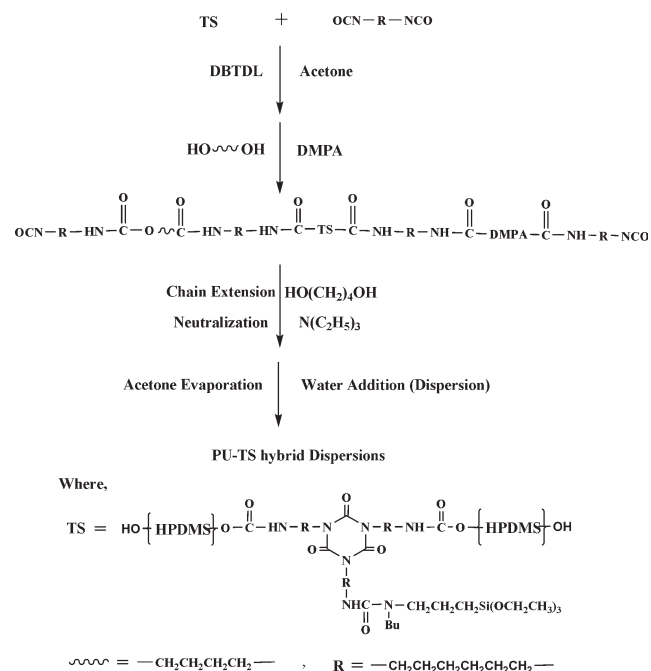
dimethylsiloxane (HPDMS;  $M_n = 990$ ) was donated by Siltech Corp. (Ontario, Canada). BAPTS was provided by Hubei Diamond Advanced Material of Chemical, Inc. (Hubei, China). Dibutyltindilaurate (DBTDL), triethylamine, 1,4-butanediol (BD), and acetone were received from Shanghai Regent Chemical Co. (China).

### Typical synthesis of TS

BAPTS (27.9 g, 0.10 mol) and HDI trimer (53.8 g,  $-NCO = 0.30$  by mol) were added separately to anhydrous acetone (122.0 g, 2.10 mol) in a 500-mL, round-bottom flask at 0°C over a period of 2 h with stirring. The stirring was continued at room temperature when the theoretical NCO value was reached (the isocyanate content was monitored during the reaction with the standard dibutylamine back-titration method<sup>21</sup>); then, HPDMS (198.0 g, 0.20 mol) was added dropwise to the mixture. The reaction was carried out for 48 h. The targeted products (TS) were obtained, as shown in Scheme 1.

### Synthesis of the representative PU-TS hybrid dispersion (PU10)

PU10 was prepared as follows. In a 500-mL, round-bottom flask equipped with a nitrogen bubbler, 28.6 g of TS (0.027 hydroxyl equiv) was dissolved in 125 g of acetone, and 17.4 g of HDI (0.207 isocyanate equiv) was added dropwise with magnetic stirring at ambient temperature. After 20 min, two drops of DBTDL were added. After 10 min, the flask was



**Scheme 2** Preparation of waterborne PU-TS hybrid dispersions.

TABLE I  
Composition of the PU-TS Hybrids

Sample	TS weight (mol)			HDI	PTMO-2000 ( $M_n = 2000$ )	DMPA	BD
	HDI trimer	BAPTS	HPDMS ( $M_n = 990$ )				
PU0				15.9 (0.190)	71.0 (0.071)	3.1 (0.046)	2.4 (0.053)
PU5	2.5 (0.005)	1.4 (0.005)	9.9 (0.010)	16.5 (0.196)	66.2 (0.066)	3.1 (0.046)	2.4 (0.053)
PU10	5.1 (0.010)	2.8 (0.010)	19.8 (0.020)	17.4 (0.207)	60.0 (0.060)	3.1 (0.046)	2.6 (0.057)
PU15	7.8 (0.016)	4.2 (0.016)	30.0 (0.032)	17.4 (0.207)	51.0 (0.051)	3.1 (0.046)	2.6 (0.057)

The data in parentheses represents the molar equivalent of those compound.

fitted with a mechanical stirrer, a thermocouple-controlled heating mantel, and a condenser with a nitrogen bubbler. PTMO (60.0 g, 0.06 hydroxyl equiv) and DMPA (3.1 g, 0.046 hydroxyl equiv, and 0.023 acid equiv) were charged into the flask, and stirring was continued while the temperature was raised to 58°C. When the theoretical NCO value was reached, the prepolymer was chain-extended with BD (2.6 g, 0.057 hydroxyl equiv), and the reaction continued for 2 h to complete the polymerization, yielding the desired PU/TS hybrid copolymer. Lastly, the copolymer was neutralized by the addition of 2.3 g of triethylamine (0.023 equiv) and stirred for 30 min while the temperature was maintained at 58°C. The formation of the dispersion was accomplished by the slow addition of 212 g of water to the neutralized acetone solution of the PU polymers at 50°C over 2 h with an agitation speed of 1300 rpm. After 2 h of stirring, the reaction mixture was transferred to a rotary evaporator, and the acetone was removed to afford free organic solvent dispersions with 30 wt % solids, shown in Scheme 2.

The series of other PU-TS hybrid (HDI-based) dispersions were synthesized by the addition of 5 and 15 mol % TS. Pure PU was also prepared for comparison with the PU-TS hybrid dispersions. The composition for the preparation of the PU-TS hybrid is given in Table I.

### Characterization

The IR spectrum was recorded with an FTIR spectrometer (Perkin Elmer, SanJose, USA). Analyses were performed in transmission mode in the range 4000–600  $\text{cm}^{-1}$  at room temperature. Each of the test dispersion samples was coated on KBr disks.

The particle size and distribution of the waterborne PUD were measured with a Zetasizer Nano ZS (Malvern Instruments, Ltd., Worcestershire, United Kingdom). The viscosity of the dispersion was measured with a Brookfield LVDV-II viscometer (Middleboro, MA) at 25°C. The dispersions in sealed bottles were kept at room temperature to examine the storage stability.

XRD profiles were recorded on Bruker D8 X-ray diffractometer (Bruker Co., Bremen, Germany) with

a Cu K $\alpha$  radiation source ( $\lambda = 0.154$  nm) at 40 kV and 40 mA with a scan rate of 5°/min. The diffraction angle  $2\theta$  ranged from 8 to 50°.

DSC analysis was carried out on a DSC-204 instrument (Netzsch, Bavarian, Germany) under a nitrogen atmosphere at a heating rate of 10°C/min from –80 to 200°C.

AFM imaging was conducted with a PicoScan atomic force microscope (Molecular Imaging Devices Co., Jialifon, US). Freshly prepared samples were mounted on an AFM stage and imaged under magnetic alternating current (MAC) mode in air (relative humidity = 40–50%, temperature  $\approx 25^\circ\text{C}$ ) with MAC-lever type II probes (spring constant = 2.8 N/m, resonant frequency  $\approx 75$  kHz, Molecular Imaging). Scan rates were about 1.5 line/s. The images were rastered at  $256 \times 256$  pixels, unfiltered, and flattened when needed.

$\sigma_b$ , the elongation at break ( $\xi_b$ ), and the Young's modulus ( $E$ ) of the dispersion-cast films were measured on a CMT6503 universal testing machine (SANS, Shenzhen, China) at a crosshead rate of 200 mm/min according to GB13022-91. The tested specimens were 10 mm wide, whereas the distance between testing marks was 30 mm.

The water and xylene resistance of the films ( $40 \times 20$  mm<sup>2</sup> in size) was measured by immersion of preweighed films in deionized water or xylene, respectively, for 24 h at room temperature. After the residual solvent was wiped from the film surface with filter paper, the weight of the swollen film was measured immediately. The swelling (solvent uptake) was expressed as the weight percentage of solvent in the swollen film:

$$\text{Swelling}(\%) = (W_s - W_d)/W_d \times 100\%$$

where  $W_s$  is the weight of the swollen film and  $W_d$  is the weight of the dry film.

## RESULTS AND DISCUSSION

### Infrared spectroscopy

A series of PU-TS hybrid dispersions was synthesized on the basis of the HDI trimer modified by

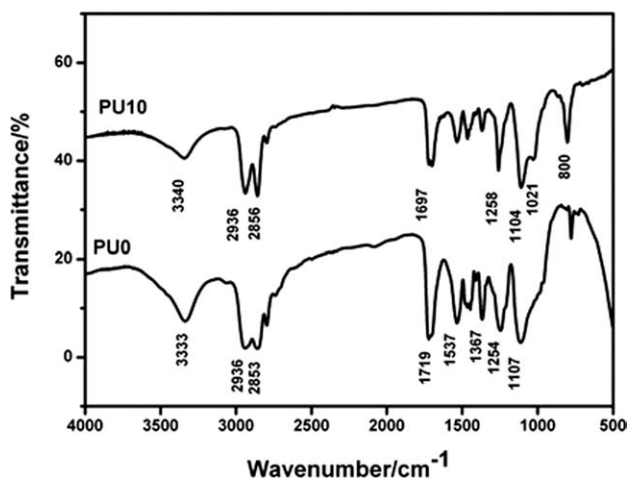


Figure 1 IR spectra of the PU0 and PU10.

BAPTS and HPDMS. Stable dispersions were obtained by the addition of 5, 10, and 15 mol % TS to PU. The representative FTIR spectra of the PU-TS dispersions are shown in Figure 1. The absorption bands around  $3340\text{ cm}^{-1}$  (N-H stretching) and  $1530\text{ cm}^{-1}$  (N-H bending) and strong absorptions at  $1719\text{ cm}^{-1}$  (free C=O stretching of urethane and carboxylic groups) and  $1210\text{--}1240\text{ cm}^{-1}$  (stretching vibration of N-CO-O) confirmed the formation of the urethane linkage. The peaks at  $2938$ ,  $2857$ , and  $2800\text{ cm}^{-1}$  ( $\text{CH}_2$  and  $\text{CH}_3$  stretching vibration);  $1105\text{ cm}^{-1}$  (C-O-C stretching vibration of PTMO and Si-O-Si asymmetric stretching vibration);  $1258\text{ cm}^{-1}$  ( $\text{CH}_3$  in Si- $\text{CH}_3$  symmetric bending),  $1072$  and  $1021\text{ cm}^{-1}$  (Si-O stretching); and  $800\text{ cm}^{-1}$  (Si-C stretching) could be clearly observed in the spectra; this indicated that siloxane groups were successfully introduced into the PU-TS hybrid dispersions.

#### Particle size and viscosity of the PU-TS hybrid dispersions

The particle size and viscosity of the PU-TS hybrid dispersions (30 wt % solid contents) are presented in Table II. The particle size of all of the PU-TS dispersions was larger than that of the pure PU0, and with the increase in TS content, the average particle size increased with PU15 having the largest size. This result shows that the particle size of the PU-TS hybrid dispersions was affected by silylation in the acetone process, and this may have been due to the large amounts of TS for the acetone process. Moreover, the complete hydrolysis and condensation of the silane groups, being in the side chain of PU, occurred, and hence, the corresponding trend of  $\text{PU15} > \text{PU10} > \text{PU5} > \text{PU0}$ ,<sup>24</sup> with a constant content of the type of isocyanate, concentration of polymer, ionic concentration, degree of neutralization, and chain extension.

The viscosity of the PU-TS hybrid dispersions decreased with increasing TS content, except for PU15. The highest viscosity corresponded to PU15, containing 15 mol % TS, which could be attributed to the creation of more hydrogen bonds between the silanol groups.<sup>25</sup> The PU-TS hybrid dispersions with higher TS contents (PU5 and PU10) exhibited lower viscosities than the pure PU0, mainly because of the change of interaction forces between the polymer latex particles caused by the difference in the structure and polarity of organosiloxane and PU.<sup>25</sup> Furthermore, these changes were also due to the high concentration of TS, which led to extensive crosslinking from the hydrolysis of the silane groups, and the polymer chains possessed covalent crosslinks, which prevented free motion of the chains. Thus, this restricted motion might have resulted in the reduction of the viscosity.<sup>24</sup>

The stability of the PU-TS dispersions depended on the pH, solid content, particle size, and viscosity of the dispersions. As no precipitation was observed in all of the PU-TS hybrid dispersions, these were stable for over 6 months of storage at room temperature.

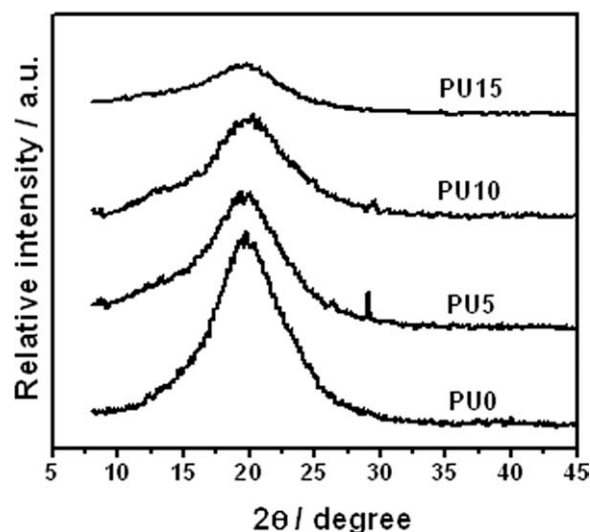
#### XRD studies of the PU-TS hybrid films

Figure 2 shows the XRD profiles of the PU-TS hybrid films with various TS contents. The X-ray pattern for the pure PU0 showed a rather broad amorphous halo centered at  $2\theta = 20.0^\circ$ ; this was due to short-range ordering in the hard-segment domains.<sup>26</sup> All of the PU-TS hybrid dispersions inherited the amorphous nature of the pure PU0, which was shown as a diffuse peak located at  $2\theta = 20^\circ$ ; this indicated that small ordered domains were still present in the TS-modified PU matrix.<sup>27</sup> For PU5 and PU10, two small diffraction peaks occurred at  $26.5$  and  $29^\circ$  which appeared to be spurious; similar results were obtained by Paik Sung.<sup>26</sup> However, the relative intensity of the broad diffuse scattering peak was weaker in TS-modified PU; this showed that the ordered domains decreased in size with increasing TS content, and the PU-TS hybrid films were almost amorphous, which implied that soft-segment/hard-segment phase mixings could have disturbed the hard-segment crystallization.<sup>24,25</sup>

TABLE II  
Particle Size and Viscosity of the PU-TS Hybrid Dispersions

Sample	Average particle size (nm)	Viscosity (cp)
PU0	822	47
PU5	1085	19
PU10	1843	28
PU15	2554	61





**Figure 2** XRD patterns of the PU-TS hybrids with various TS contents.

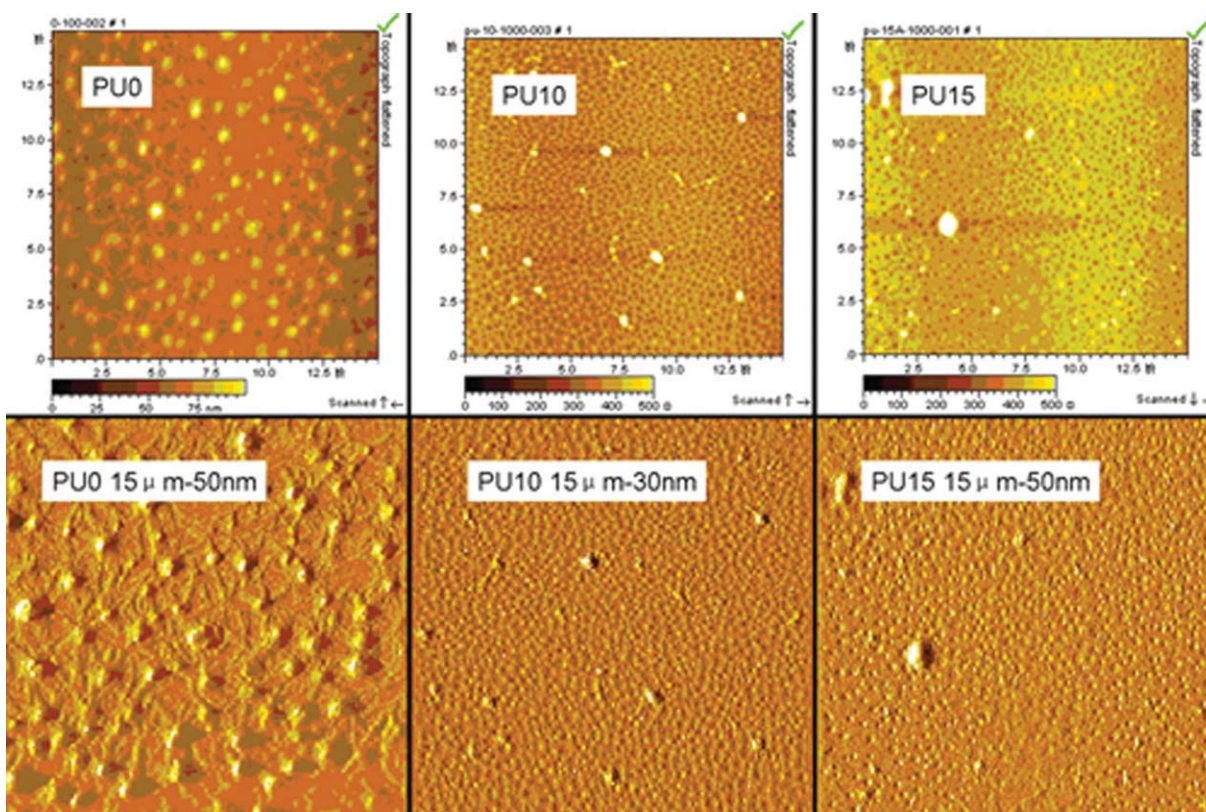
#### AFM study

AFM measurements were performed to identify the surface morphology of the cured films. The AFM image of the neat PUDs (PU0) film showed the presence of some regular domains distributed in the reticular formation; these domains had an average diameter of  $0.376 \mu\text{m}$  and a height of about  $26.5 \text{ nm}$ ,

higher than the surrounding area ( $5.2 \pm 1.0 \text{ nm}$ ). These domains were composed of hard segments with a tendency to crystallize, whereas the surrounding area consisted of soft segments. Tapping-mode AFM studies showed that the TS-modified PU films had more smooth surfaces, in contrast to that of PU0. With increasing TS content, the surface became smoother, especially for PU10 and PU15, as illustrated in Figure 3. The microstructure of the PU10 surface showed many regular protruding nodes distributed uniformly in the network; the domain size was smaller with a more uniform size distribution than that of PU0. However, PU15 with higher cross-linking siloxane had a different surface microstructure; no significantly raised nodes were observed. Because polysiloxanes have a much lower surface energy than PU, the siloxanes should stratify on the surface during film formation and complete hydrolysis and condensation of the silane groups to result in a PU coating with a smooth, low-surface-energy siloxane outer layer with a tough PU sublayer.<sup>28,29</sup>

#### Thermal transition behavior of the PU-TS hybrid films

DSC provides information on the transition temperatures, such as the glass-transition temperature and melting temperature ( $T_m$ ), and on the degree of



**Figure 3** Tapping-mode AFM height images of PU0, PU10, and PU15 (up) and tapping-mode AFM phase images of PU0, PU10, and PU15 (bottom). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

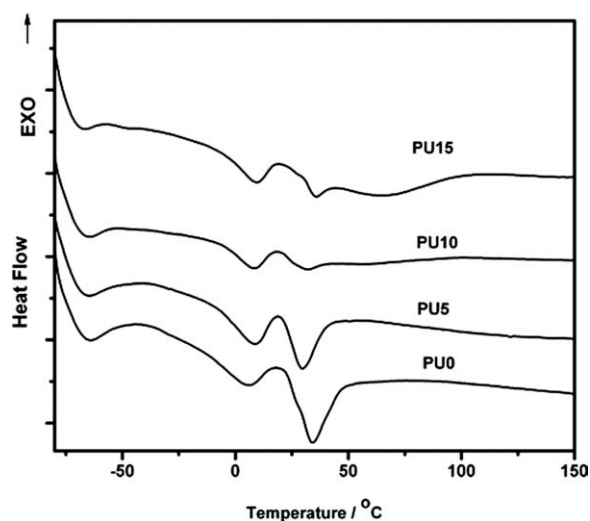


Figure 4 DSC thermograms of the PU-TS films.

phase separation. Figure 4 shows the DSC curves of the series of aqueous PU-TS hybrid films. The glass-transition temperature of the soft-segment phase ranged from  $-64$  to  $-67^{\circ}\text{C}$  and decreased slightly with increasing TS content; this demonstrated an increased degree of microphase separation in the system.<sup>30</sup> PU0 showed two apparent melting endotherms at  $5.9$  and  $34.2^{\circ}\text{C}$ , which corresponded to  $T_m$  of the microcrystallite or crystal.<sup>30</sup> Although all of the TS-modified PU films also showed two  $T_m$ 's,  $T_{m1}$  was slightly higher than that of PU0 in the range  $9.3 \pm 0.4^{\circ}\text{C}$ , and  $T_{m2}$  decreased by  $2$ – $4^{\circ}\text{C}$  at lower TS contents, in which the enthalpy was decreased. This indicated that the addition of TS affected the crystal structure of the polymer and resulted in a lower crystallinity or lower degree of segment order;<sup>26</sup> and the DSC results were consistent with the results by XRD.

### Mechanical properties of the PU-TS films

The influences of TS content on the mechanical properties of the PU-TS hybrid films, including  $\sigma_b$ ,  $\xi_b$ , and  $E$ , are shown in Table III. Compared with neat PU0, the PU-TS hybrid films showed different enhancements in  $\sigma_b$ ,  $\xi_b$ , and  $E$ , depending on the TS content. When the TS content was higher, at 5 and 10 mol %, the simultaneous enhancements in  $\sigma_b$ ,  $\xi_b$ ,

and  $E$  might have been due to the position of the silane being in the side chain of PU rather than in the backbone. This was because when the polysiloxane networks formed from the hydrolysis–condensation of silane effectively accumulated on the polymer surface, a greater phase separation occurred, which increased the values of  $\sigma_b$ ,  $\xi_b$ , and  $E$ .<sup>16</sup> However, with the addition of 15 mol % TS,  $\sigma_b$  and  $E$  were enhanced, but  $\xi_b$  was lowered. These effects could be attributed to the self-crosslinking networks of the functional alkoxy silane present in the side chain by the hydrolysis–condensation mechanism; this resulted in the film being tougher, even though the siloxane units reduced the close packing and order of the hard segments.<sup>24</sup> Therefore, introducing the silane with crosslinking function in side chain would increase the strength of the film.

The PU-TS hybrid films were superior because (1)  $\xi_b$  was enhanced from 380% for PU0 to 850% for PU10 and (2) PU-TS containing 15 mol % TS had a higher  $E$  and enhanced  $\sigma_b$  over the PUDs film. Thus, the introduction of an appropriate content of TS ensured excellent mechanical properties of the polymers.

### Swelling in water and xylene

As shown in Table III, the PU-TS hybrid films displayed different swelling properties in water and xylene. The PU-TS samples exhibited much lower swelling percentages than that of the pure PU0 film, which decreased with increasing TS content because the siloxane networks formed in PU-TS hybrid films migrated to the surface and prevented the solvent molecules, either water or xylene, from entering the bulk.<sup>3</sup> In addition, another obvious change was that all of the PU-TS hybrid films showed a lower water uptake and higher xylene swelling; this was attributed mainly to the nature of bonding, the bond length, and the crosslinkages.<sup>24</sup> The siloxane bonds were flexible and highly hydrophobic, so the water uptake of the PU-TS hybrid films was much lower than that of the pure PU0 film. Meanwhile, the higher xylene swelling of pure PU0 film and lower xylene swelling of the PU-TS hybrid films were ascribed to the toughness of the urethane bonds and the flexibility of the siloxane bonds.

TABLE III  
Mechanical and Swelling Properties of PU0  
and the PU-TS Hybrid Films

Film sample	$\sigma_b$ (MPa)	$E$ (MPa)	$\xi_b$ (%)	Water uptake (%)	Swelling in xylene (%)
PU0	5.4	9.2	380	9.6	1298
PU5	5.8	9.4	635	3.5	137
PU10	9.2	12.4	850	3.1	98
PU15	16.6	22	570	2.3	72

### CONCLUSIONS

A series of aqueous PU-TS hybrid dispersions with well-defined TS units were successfully synthesized. The results from DSC and XRD indicated that the degree of the segment order was reduced by the introduction of TS. AFM images showed that with increasing content of TS, the surface of PU-TS became smoother than that of PU0. From tensile

tests, it was found that  $\sigma_b$  and  $E$  of the PU-TS hybrid films were higher than those of the neat PU0 film. The introduction of TS for aqueous PUDs produced excellent water and xylene resistance and produced a lower viscosity, which could have great potential for applications in coatings, inks, and so on. The aqueous PU hybrid dispersions modified by TS provided a novel method for the modification and exploitation of polymers containing silicon.

## References

1. Nanda, A. K.; Wicks, D. A.; Madbouly, S. A.; Otaigbe, J. U. *J Appl Polym Sci* 2005, 98, 2514.
2. Chen, H.; Fan, Q. L.; Chen, D. Z.; Yu, X. H. *J Appl Polym Sci* 2001, 79, 295.
3. Chen, R. S.; Chang, C. J.; Chang, Y. H. *J Polym Sci Part A: Polym Chem* 2005, 43, 3482.
4. Wang, L. F.; Ji, Q.; Glass, T. E.; Ward, T. C.; McGrath, J. E.; Muggl, M.; Burns, G.; Sorathia, U. *Polymer* 2000, 41, 5083.
5. Denise, P. Q.; Maria, N. P. *Polymer* 2005, 46, 2346.
6. Iskender, I.; Ahmad, K. S.; Warren, P. S.; Dinesh, T.; Garth, L. W.; James, E. M. *Polymer* 1984, 25, 1800.
7. Mitsuhiro, S.; Masakatsu, S.; Shinichi, S.; Tomoyuki, Y.; Shunji, N. *Macromolecules* 1991, 24, 6254.
8. Piotr, K. *Prog Mater Sci* 2007, 52, 915.
9. Xiao, H.; Ping, H.; Xie, Y. W.; Yu, T. Y. *J Polym Sci Part A: Polym Chem* 1990, 29, 585.
10. Aurelian, S.; Anton, A.; Stefan, O. *Polymer* 2001, 42, 6081.
11. Li, X. R.; Fei, G. Q.; Wang, H. H. *J Appl Polym Sci* 2006, 100, 40.
12. Madec, P. J.; Marechal, E. *J Polym Sci Part A: Polym Chem* 1978, 16, 3165.
13. Pathak, S. S.; Sharma, A.; Khanna, A. S. *Prog Org Coat* 2009, 65, 206.
14. Jignesh, P. S.; Ashish, A.; Garth, L. W.; Emel, Y.; Ekin, A.; Iskender, Y.; Frederick, L. B. *Polymer* 2004, 45, 6919.
15. Emel, Y.; Iskender, Y. *Polymer* 2001, 42, 7953.
16. Fan, Q. L.; Fang, J. G.; Chen, Q. M.; Yu, X. H. *J Appl Polym Sci* 1999, 74, 2552.
17. Okkema, A. Z.; Fabrizio, D. J.; Grasel, T. G.; Cooper, S. L.; Zdrachala, R. J. *Biomaterials* 1989, 10, 23.
18. Ho, T. J.; Moon, K. J.; Byung, K. K.; Kwang, H. K. *Colloid Surf A* 2007, 302, 559.
19. Bai, C. Y.; Zhang, X. Y.; Dai, J. B.; Wang, J. H. *J Coat Technol Res* 2008, 5, 251.
20. Sankaraiah, S.; Jun, Y. L.; Sung, W. C.; Jung, H. K. *J Polym Sci Part B: Polym Phys* 2007, 45, 2747.
21. Nanda, A. K.; Wicks, D. A. *Polymer* 2006, 47, 1805.
22. Kim, C. K.; Kim, B. K.; Jeong, H. M. *Colloid Polym Sci* 1991, 269, 895.
23. Yeh, J. M.; Yao, C. T.; Hsieh, C. F.; Yang, H. C.; Wu, C. P. *Eur Polym J* 2008, 44, 2777.
24. Subramani, S.; Lee, J. M.; Cheong, I. W.; Kim, J. H. *J Appl Polym Sci* 2005, 98, 620.
25. Fei, G. Q.; Shen, Y. D.; Wang, H. H.; Shen, Y. *J Appl Polym Sci* 2006, 102, 5538.
26. Paik Sung, C. S.; Hu, C. B.; Wu, C. S. *Macromolecules* 1980, 13, 111.
27. Nada, A. K.; Wicks, D. A.; Madbouly, S. A.; Otagbe, J. U. *Macromolecules* 2006, 39, 7037.
28. Partha, M.; Dean, C. W. *Macromolecules* 2005, 38, 5857.
29. Partha, M.; Dean, C. W. *Polymer* 2006, 47, 4172.
30. Yang, D. Y.; Hu, C. P.; Ying, S. K.; Kim, J. H. *J Polym Sci Part A: Polym Chem* 2005, 43, 2606.