

## 비닐단량체를 함유한 새로운 실리콘의 합성과 수성 Polyurethane-Veova/Vinyl Acetate 하이브리드 에멀전 공중합체 내에서 사용

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## Synthesis of Novel Silicone Containing Vinylic Monomer and Its Uses in the Waterborne Polyurethane-Veova/Vinyl Acetate Hybrid Emulsion Copolymers

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**Abstract:** A novel silicone (Si) containing vinylic monomer, *N*-(3-(triethoxysilyl)propyl) methacrylamide (TESPMA), based on 3-aminopropyltriethoxysilane (APTES) and methacryloyl chloride (MCl) has been synthesized for formulation of waterborne polyurethane (WPU). Two types of vinyl group containing Si, methacryloxypropyltriethoxysilane (MPTES) and triethoxyvinylsilane (TEVS), have been used as coupling reagents for comparison of the effects of Si kinds with TESPMA on the WPU. A series of new siliconized WPU, vinyl acetate/vinyl ester of versatic acid (VAc-Veova), TESPMA, MPTES and TEVS hybrid latexes have been successfully prepared by emulsion polymerization in the presence of WPU dispersion.

**Keywords:** *N*-(3-(triethoxysilyl)propyl) methacrylamide, silicones, polyurethanes, polymer synthesis and characterization, glass transition, coatings.

### Introduction

Waterborne polyurethane (WPU) materials have a wide application because of their excellent properties including good mechanical properties, abrasion, and chemical resistance.<sup>1-3</sup> However, poor water resistance and thermal stability limit their applications in some fields. On the other hand, siloxane materials have high thermal and oxidative stability, weatherability, low surface energy and a wide service temperature range (glass transition temperature ( $T_g$ , -123 °C)), but lower mechanical property and abrasion resistance.<sup>4</sup> It is possible to prepare polyurethane/silicone/acrylic (PU/Si/A) or polyurethane/silicone/vinyl acetate (PU/Si/VAc) copolymers which would have better thermo and water resistance than polyurethane (PU), while the mechanical and abrasion characteristics are little damaged.<sup>5</sup> Landfester and coworkers<sup>6</sup> have explored different synthetic pathways to synthesize siloxane-modified polyurethane/acrylic (PU/A) hybrid latexes with small particle sizes narrowly distributed and using the specific

advantages of the miniemulsion approach. It was demonstrated by Youssef *et al.*<sup>7</sup> that the introduction of functional silane improves some physical and chemical properties, i.e. very low surface energy, excellent gas and moisture permeability, good heat stability, low temperature flexibility and biocompatibility. Jung *et al.*<sup>8</sup> illustrated that high siloxane content PU/A hybrid nanocomposite film show a decrease of tensile strength, elastic modulus and  $T_g$  an increase in water resistance as well as friction resistance. Webster *et al.*<sup>9</sup> showed PU/A hybrid coatings went from a hydrophilic surface to a hydrophobic surface when the siloxane was incorporated into the polyurethane formulation. Zhang and coworkers<sup>10</sup> pointed out that the Si modified PU/A emulsion resin can improve the physical and chemical properties of the building paints. According to Wu *et al.*<sup>11</sup> modification with organosilicone is one of the ideal methods available for improving the hydrophobicity of the surfaces of thermoplastic PUs coats. Zhang<sup>12</sup> and Lee *et al.*<sup>13</sup> indicated that the chain structure and the particle size of siloxane modified PU/A hybrid emulsion were confirmed by FTIR and TEM analysis. Additionally, the emulsion particle size was uniform and around

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45 nm, which ensures better performance of the formed film. The obtained PU/Si/A proved to possess higher contact angle and better water resistance when siloxane content was higher than 6.5% and also the mechanical property has great change when siloxane content is above 6.5%. Finally, Larock *et al.*<sup>14</sup> showed that the acrylics play an important role in enhancing the thermal stability of the PU/Si/A hybrid latexes. The improved thermal stability of the hybrid latexes can be explained by the occurrence of extensive grafting, cross-linking, and interpenetration.

In this work, we make modifications of the PU/P (VAc–Veova) hybrid emulsion by TESPMA, using the solvent-free method. We used TESPMA to incorporate the siloxane into the soft segment of PU chains and obtained a new material of TESPMA modified WPU/P (VAc–Veova). Then, two types of vinyl group containing Si, the MPTES and TEVS were used as coupling reagents for comparison of the effects of Si kinds on the WPU. The preparation technology was discussed systematically and the effect of TESPMA content on PU/Si/(VAc–Veova) was investigated.

## Experimental

**Materials and Equipment.** Reagent grade VAc (Fisher Scientific Co) was further purified by distillation in a rotary evaporator at reduced pressure of 30 mmHg to remove inhibitor. The Veova provided by Achema (Lithuania) was also distilled under vacuum and stored at 0 °C to avoid thermal polymerization. Dibutyltin dilaurate (DBTDL, Aldrich, Gillingham, UK) was analytical grade and used directly without further purification. Polypropylene glycol 1000 (PPG–1000, Korea Polyol Ltd., Korea) was dried and degassed at 65 °C under vacuum. APTES and MCl (Fluka) were used as received. Hexamethylene diisocyanate (HMDI), dimethylol propionic acid (DMPA), potassium persulfate (KPS), hydroxyethyl cellulose (HEC), sodium bicarbonate (NaHCO<sub>3</sub>), sodium chloride (NaCl), MPTES, TEVS and tetrahydrofuran (THF) were supplied by Merck, Hohenbrunn, Germany, and were used as received. Triethylamine (TEA, Junsei) was used without further purification. Double-distilled water (D.D.W) was used throughout. Fourier-transform infrared (FTIR) spectroscopy analysis was performed with a Nicolet Impact 400D Model spectrophotometer (Nicolet Impact, Madison, USA) using KBr pellets. The spectra were obtained over the wavenumber range 4000~400 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup> using an MCT detector with co-addition of 64 scans. Scanning electron micrographs were taken on a JEOL–JXA 840 A SEM (JEOL, Boston, USA). The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen

**Table 1. Recipe for Synthesis of PUD**

Ingredients	Charge (g)
PPG (M.W.: 1000)	60.00
HMDI	20.00
DMPA	1.60
TEA	1.50
D.D.W	80.00

and the application of a gold coating of approximately 300 Å with an Edwards S 150 B sputter coater. Transmission electron microscope (TEM) analysis was performed with a Hitachi H–600, Hitachi Corporation, Japan.

**Preparation of Polyurethane Dispersion (PUD).** A 500 mL, round bottom, 4-necked-flask, separable glass reactor with mechanical stirrer, thermometer, condenser and nitrogen purge was used. Basic recipe for the synthesis of PUD is presented in Table 1. Polyaddition reaction was carried out in a N<sub>2</sub> atmosphere in a constant-temperature water bath. HMDI and PPG were first charged into the reactor and heated to 80 °C under stirring, and then DBTDL was dropped into the reactor while keeping the temperature at 80 °C. The reaction proceeded over approximately 1 hr, DMPA was subsequently charged and reaction proceeded for another 4 hrs at the same temperature, upon which the theoretical NCO/OH value of 1.2. was determined by the dibutylamine back titration. This PU was then neutralized by the addition of TEA at 25 °C, followed by dispersion at high speed (1200 rpm) with D.D.W, which was added drop-wise to produce a WPUD.

**Semi-Continuous Emulsion Polymerization Using PUD.** Semi-continuous emulsion copolymerization was carried out using a 500 mL four-necked round-bottom flask equipped with a reflux condenser, a stainless-steel stirrer, a sampling device, and one feed stream. The feed stream was a solution of VAc and Veova, by adding, TESPMA, MPTES and TEVS, each one through emulsion copolymerization. Before emulsion polymerization start-up, the reaction vessel was first charged with the desired amounts of water, PUD, HEC, NaHCO<sub>3</sub>, and initiator solution ( $2.8 \times 10^{-3}$  molL<sup>-1</sup>), respectively. During polymerization, the reaction mixture was stirred at a rate of 100 rpm, and the temperature was maintained at 65 °C. After 5 min, 10 w% of total amount of the monomer mixture was added to the flask in a period of 20 min. Then, the temperature was kept at 80 °C until the end of polymerization (4 hrs). The polymerization was performed with feeding rate of 1.0 mL/min under N<sub>2</sub> atmosphere to investigate the effect of TESPMA, MPTES or TEVS concentrations and also PU/P (VAc–Veova) ratios on monomer conversion. A typical recipe for the preparation of a product is given in Table 2. In order to determine the conversion percent during the

**Table 2. Recipe for Semi-continuous Emulsion Polymerization of PU/P(VAc-Veova)/Si**

Ingredients	Charge (g)
PUDs (20 wt% solid)	30.00
D.D.W	100.00
HEC	0.60
NaCl	0.20
NaHCO <sub>3</sub>	0.20
Initiator: K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.20
VAc	48.00
Veova	21.00
TESPMA, TEVS or MPTES	0.00~4.00

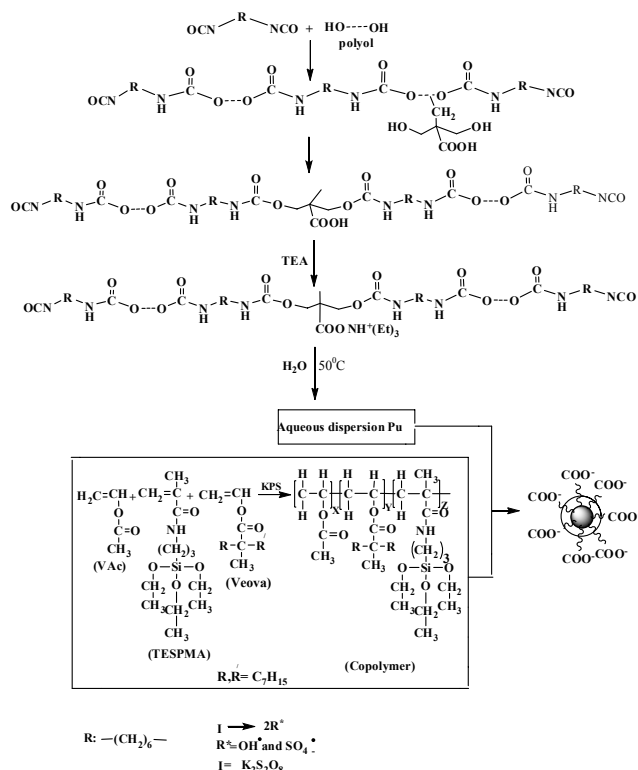
polymerization process, it was necessary to withdraw samples at various intervals from the reaction vessel. These samples are relatively small so that the overall composition in the reactor is not seriously affected; once a sample is removed and put in a watch glass, polymerization is terminated by the addition of 7 ppm hydroquinone. Then, two drops of ethanol was added to the sample as a coagulant and the contents of the watch glass were evaporated at room temperature and then dried to a constant weight in a vacuum oven. The conversion percent was determined gravimetrically. The purification and precipitation of the polymer were done using a reported method.<sup>15</sup> The number of polymer particles per unit volume of water ( $N_T$ ) was calculated from the monomer conversion  $X_M$  and the volume average diameter of the polymer particles,  $d_v$  was determined by a scanning electron microscope, using the following equations:

$$d_v^3 = \frac{\sum n_i d_i^3}{\sum n_i} \quad (1)$$

$$N_T = \frac{6M_0 X_M}{\pi d_v^3 \rho_p} \quad (2)$$

where  $M_0$  is the initial monomer concentration per mL, and  $\rho_p$  is the density of the polymer ( $\text{g/cm}^3$ ).<sup>16-18</sup> The volume average diameter ( $d_v^3$ ) of the latexes was found to be  $3.8 \times 10^{-12}$ ,  $4.9 \times 10^{-12}$ , and  $1.7 \times 10^{-12}$  mL for P(VAc-Veova), PU/P(VAc-Veova) and PU/P(VAc-Veova)/TESPMA, respectively. The preparation Scheme of the PU/P(VAc-Veova)/TESPMA hybrid emulsions has done according to S. Chen *et al.*<sup>19</sup> and is illustrated in Scheme 1.

**Particle Size and Distribution of PU/P (VAc-Veova)/TESPMA.** The morphology and particle sizes of emulsions were measured by using SEM (JEOL-JXA 840 A) and TEM (Hitachi H-600). The samples of emulsions were diluted with deionized water to adjust the solid content to around 1 w% and directly placed in the cell. The temperature of the cell was kept at


**Scheme 1.** Reaction scheme of PU/P(VAc-Veova)/TESPMA hybrid emulsion.

around 25 °C and the measuring time was 300 s.

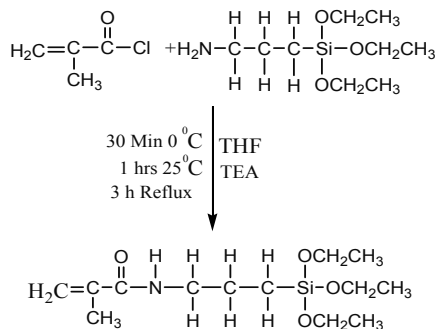
**Film Formation.** Films were prepared with a dry thickness of about 0.5 mm. After casting the emulsion onto glass plates (20 cm × 20 cm), the films were allowed to dry for 1 week at ambient temperature (25 °C).

**Water Absorption.** Dried films (30 mm × 30 mm; original weight designated as  $W_0$ ) were immersed in water for 24 hrs at 25 °C. After the residual water was wiped from the films using filter paper, the weight ( $W_1$ ) was measured immediately.<sup>20</sup> It was calculated as follows:

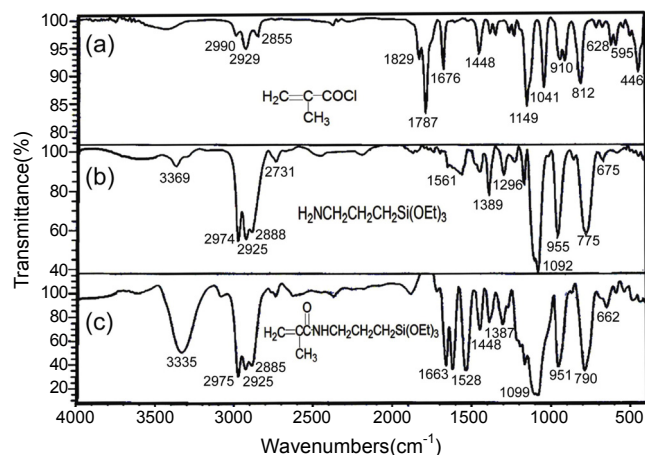
$$\text{Water Absorption, } R(\%) = ((W_1 - W_0) / W_0) \times 100$$

## Results and Discussion

**Synthesis of Si Containing Vinylic Monomer(TESPMA).** In a 50 mL three-necked round bottom flask which was dried, purged with nitrogen, equipped with a reflux condenser, a dropping funnel and nitrogen inlet, 2.6 g (25 mmol) MCl, 20 mL, THF and 2 g (20 mmol) TEA were taken. To this, 5.5 g (25 mmol) APTES was added drop-wise maintaining temperature at 0 °C under nitrogen atmosphere. After complete addition, the reaction mixture was maintained at room temperature for 1 hr and then 2 hrs under stirring at reflux temperature (65 °C). Use of TEA promotes the desirable con-



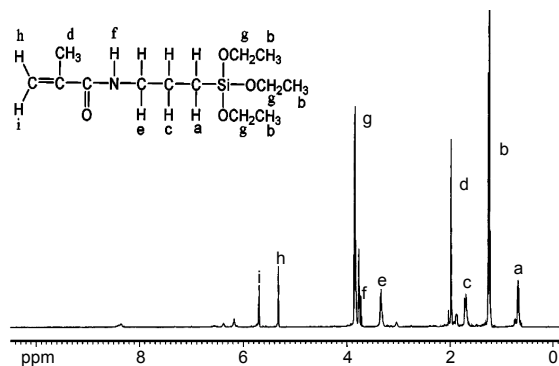
**Scheme 2.** Preparation of TESPMA.



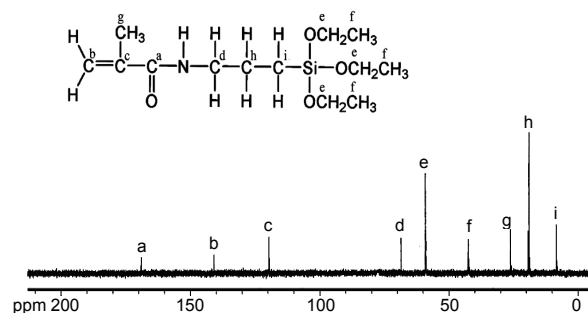
**Figure 1.** FTIR spectra of (a) MCl; (b) APTES; (c) TESPMA.

densation between methacryloyl chloride-Cl and 3-aminopropyltriethoxysilane -H. Then, the pale yellow by product salt was filtered off quickly to minimize contamination of the product by hydrolysis when the salt is exposed to moisture. The viscous crude product was recovered after removing the solvent using an evaporator and the residue was finally dried in a vacuum at 25 °C. The final product was viscous yellow oil. Yield=7.225 g, 83%. The reaction path is presented in Scheme 2.

**FTIR Spectrum of TESPMA.** Figure 1 shows the typical FTIR spectra of (a) MCl, (b) APTES and (c) TESPMA. It can be seen from Figure 1(a) that there are absorption peaks at 2990, 2929, 2855 and 1787  $\text{cm}^{-1}$  which are ascribed to the vibration of  $-\text{CH}_2$  and  $\text{C}=\text{O}$  respectively. Figure 1(b) indicates strong absorption peaks at 3369, 2974, 2925, 2888 and 1092  $\text{cm}^{-1}$ , which are ascribed to the vibration of  $-\text{NH}_2$ ,  $-\text{CH}_2$ , and  $\text{Si}-\text{O}-\text{R}$ , respectively. As shown in Figure 1(c) a new sharp peak appeared at 3335  $\text{cm}^{-1}$ , which was attributed to  $\text{N}-\text{H}$  absorption. Also, the absorption peak at 1528  $\text{cm}^{-1}$  was attributed to  $\text{N}-\text{H}$  bond vibration and  $\text{C}-\text{N}$  symmetry stretch vibration, and the sharp and strong peak at 790  $\text{cm}^{-1}$  was absorption due to  $\text{C}-\text{N}$  bond vibration. The peak at 1099  $\text{cm}^{-1}$  was protected



**Figure 2.**  $^1\text{H}$  NMR spectrum of TESPMA.

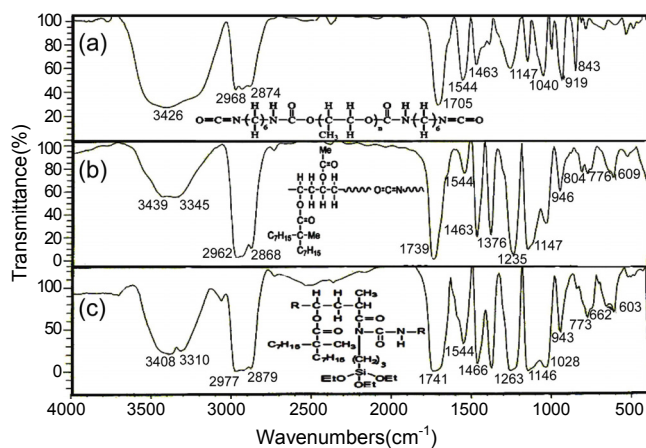


**Figure 3.**  $^{13}\text{C}$  NMR spectrum of TESPMA.

which is attributed to the  $\text{Si}-\text{O}-\text{R}$ , stretch vibration and a peak appeared at 1448  $\text{cm}^{-1}$  which was attributed to vinyl group in the Si containing vinylic monomer.

**NMR Analysis of TESPMA.**  $^1\text{H}$  NMR is the most useful instrument for the measurement of hydrogen chemical environment because of its high sensitivity to hydrogen bond strength, while the area of apex also evidently reflects the abundance of hydrogen in different chemical shift.<sup>21</sup> The  $^1\text{H}$  NMR of TESPMA is shown in Figure 2. It could be seen that all the relevant peaks of monomer could be found in this figure. The peak at 0.68, 1.8 and 3.4 ppm results from the group of  $-\text{CH}_2$  in the chain of  $\text{Si}-\text{CH}_2$  in the molecule of TESPMA. A small signal has been shown at 3.8 ppm belonging to  $-\text{NH}$  bond. Also two small peaks were observed at 5.3 and 5.7 ppm which belong to vinyl group ( $\text{CH}_2=\text{CH}-$ ) in the molecule of TESPMA. Figure 3 indicates the  $^{13}\text{C}$  NMR spectrum of TESPMA. The number of carbons in the TESPMA is compatible with the number of peaks in the  $^{13}\text{C}$  NMR spectrum.

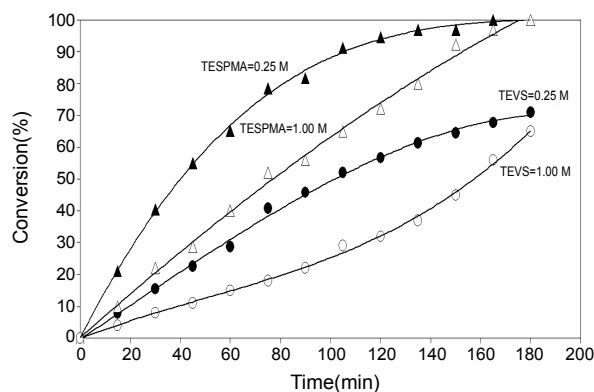
**FTIR Spectra of PU, PU/P(VAc-Veova) and PU/P(VAc-Veova)/TESPMA.** Figure 4 illustrates the FTIR spectra of (a) PU, (b) PU/P(VAc-Veova) and (c) PU/P(VAc-Veova)/TESPMA, respectively. It can be seen from Figure 4(a) that there are strong absorption peaks at 3426, 2968, 2874 and 1705  $\text{cm}^{-1}$ , which are ascribed to the vibration of  $-\text{OH}$ ,  $-\text{CH}_3$ ,  $-\text{CH}_2$  and  $\text{C}=\text{O}$ , respectively. After cross-linking



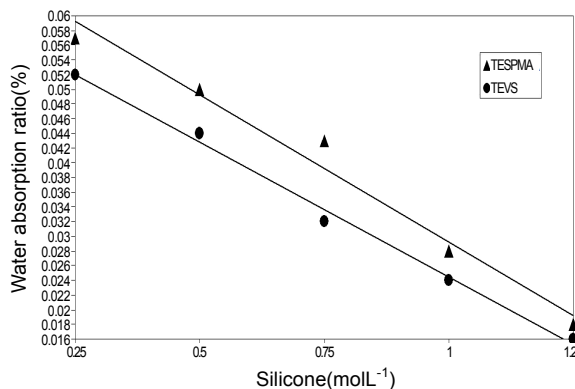
**Figure 4.** FTIR spectra of (a) PU; (b) PU/P(VAc-Veova); (c) PU/P(VAc-Veova)/TESPMA.

(see Figure 4(b)), the wide and strong  $-OH$  absorption  $3426\text{ cm}^{-1}$  disappeared and two new peaks appeared between  $3439$  and  $3345\text{ cm}^{-1}$ , which were attributed to  $N-H$  absorption. The  $NCO$  absorption peak at  $2273\text{ cm}^{-1}$  did not appear, perhaps indicating that the  $-NCO$  group had reacted completely. The absorption peak at  $1544\text{ cm}^{-1}$  was attributed to  $N-H$  bond vibration and  $C-N$  symmetry stretch vibration, and the sharp and strong peak at  $776\text{ cm}^{-1}$  was absorption due to  $C-N$  bond vibration. These indicated the presence of urethane bond and urea bond formation. A new peak appeared at  $1028\text{ cm}^{-1}$  Figure 4(c) that was attributed to the  $Si-O-R$ .

**Effect of TESPMA Concentration on Reaction Rate.** Modification with organosilicone is one of the ideal methods available for improving the hydrophobicity of the surfaces of thermoplastic PU coats. The most widely used organosilicone is polydimethylsiloxane (PDMS).<sup>22-27</sup> For example, Wynne *et al.*<sup>28</sup> synthesized PDMS-urea-urethane copolymers by two-step polymerization method. Rochery *et al.*<sup>29</sup> also incorporated PDMS into polytetramethyleneoxide (PTMO) based PUs by using both hydroxyl-terminated PDMS and isophorone diisocyanate (IPDI). All of the above prepared Si-containing PUs showed a reduction in surface-free energy. In addition, for a long product life, strong adhesion between Si and the target matrix is required. The inherently hydrophobic nature of Si compounds coupled with their ability to segregate to the surface facilitates their use as a surface modifier for other materials. This property has been exploited in the preparation of Si-modified U/A emulsion copolymers. Although copolymerization of Si/U/A has been well established,<sup>30-33</sup> their copolymerization in the presence of TESPMA has not been reported. The TESPMA is compatible with acrylic chains due to carry on functional group double bond of vinyllic linkage. During copolymerization process,



**Figure 5.** Effect of initial Si concentration on monomer conversion versus time at ( $\blacktriangle$ )  $0.25$  and ( $\triangle$ )  $1.00\text{ molL}^{-1}$  for TESPMA; ( $\bullet$ )  $0.25$  and ( $\circ$ )  $1.00\text{ molL}^{-1}$  for TEVS.  $T=80\text{ }^\circ\text{C}$ ,  $100\text{ rpm}$ ,  $[I]_0=2.2 \times 10^{-3}\text{ molL}^{-1}$ .



**Figure 6.** Effects of TESPMA ( $\blacktriangle$ ) and TEVS ( $\bullet$ ) content seed latex to water absorption ratio of the latex films.

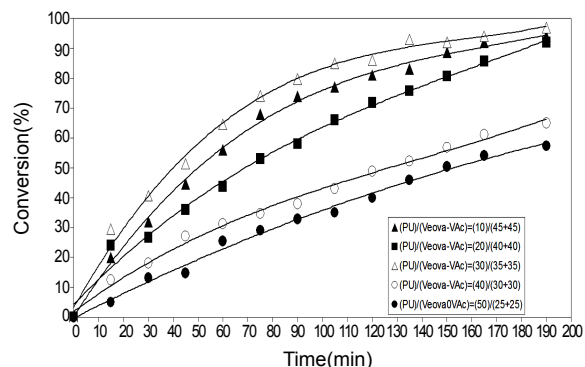
this monomer makes part of the copolymer chain. However, the extent of its incorporation in the polymer chain has not measured. Figure 5 shows the effect of TESPMA on the monomer conversion versus time, where the initial initiator and total monomer concentrations were fixed. This figure shows that the rate of reaction changes with the Si concentration. As shown in Figure 5, the reaction rate decreases by increasing TESPMA and the same results were obtained for the other silane compounds.<sup>34-38</sup> It is known that the rates of propagation and consequently copolymerization in a radical copolymerization reaction are inversely related to the termination rate constant. As the amount of Si increased, it acted as a chain transfer agent and the rate of polymerization decreased. Although chain transfer generally does not decrease the polymerization rate, this matter has been observed by the authors for many times and it can be justified as follows, the radicals obtained from vinyl silanes are more stable in comparison with other radicals which exist in the Si containing emulsion copolymers. This stability could be due to the  $\pi$ -bonds and resonance effects of double bonds,

and consequently a reduction in the reaction rate was observed.

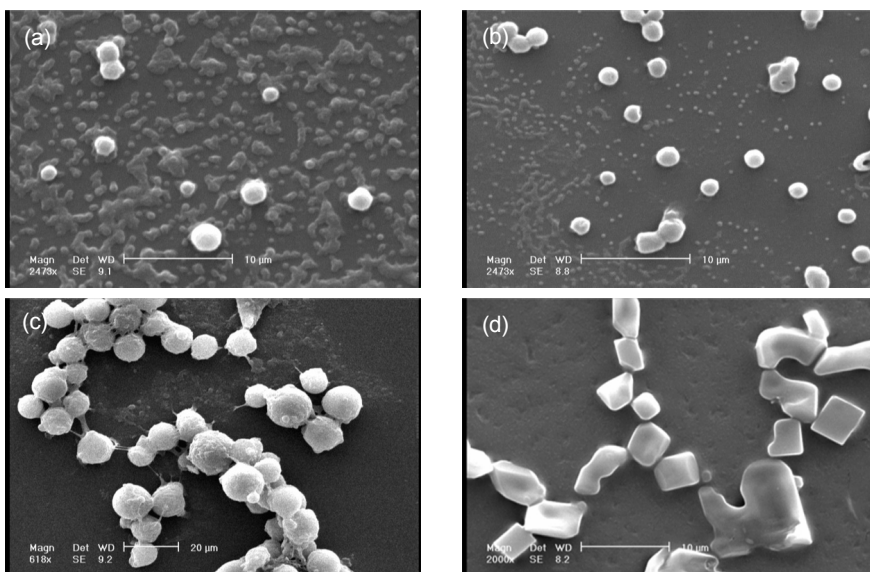
**Water Absorption Ratio of the PU/P(VAc-Veova)/Si.** The water absorption ratio of the PU/P(VAc-Veova)/TESPMA or PU/P(VAc-Veova)/TEVS films is an important evidence of hydrophobicity. As shown in Figure 6, the absorption ratio was greatly influenced by TESPMA or TEVS concentrations. With the increase of the Si content, the water absorption ratio of the PU/P(VAc-Veova)/TESPMA or PU/P(VAc-Veova)/TEVS films decreased, which can be contributed to the excellent hydrophobicity of the TESPMA and TEVS monomers. When the Si content increased from 0.25 to 1.25 molL<sup>-1</sup>, the water absorption of the films decreased sharply from 0.06 to 0.018%. According to this figure, we conclude that an increase in TESPMA concentration would give better water resistance than TEVS.

**Effects of PU Content on the Reaction Rate of PU/P(VAc-Veova)/TESPMA Hybrid Emulsion.** PU/P(VAc-Veova)/

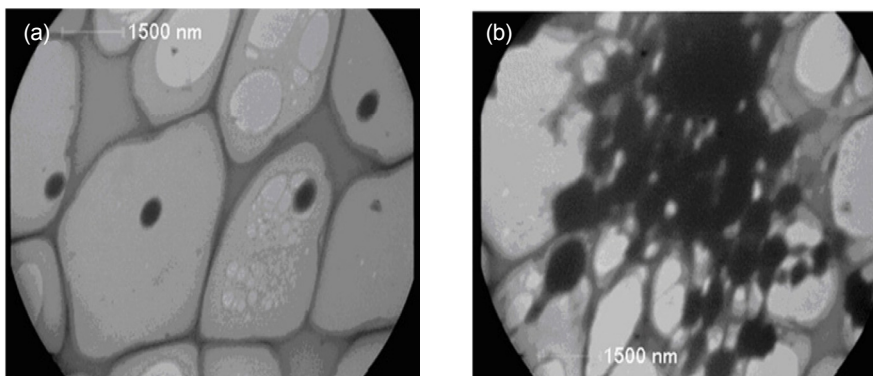
TESPMA hybrid emulsions were prepared by polymerizing a mixture of (VAc-Veova) monomers and TESPMA in the presence of PU dispersion. The weight ratio between PU component and P(VAc-Veova) component was varied by changing the amount of both PU and P(VAc-Veova) while



**Figure 7.** Effects of PU content on reaction rate of PU/P(VAc-Veova)/TESPMA hybrid emulsion.



**Figure 8.** SEM pictures of (a) P(VAc-Veova); (b) PU/P(VAc-Veova); (c) PU/P(VAc-Veova)/TESPMA; (d) PU/P(VAc-Veova)/TEVS at 80 °C, 100 rpm,  $[I]_0=2.2 \times 10^{-3}$  molL<sup>-1</sup>.



**Figure 9.** TEM pictures of (a) PU/P(VAc-Veova); (b) PU/P(VAc-Veova)/TESPMA at 80 °C, 100 rpm,  $[I]_0=2.2 \times 10^{-3}$  molL<sup>-1</sup>.

keeping the amount of Si constant ( $0.50 \text{ molL}^{-1}$ ). Figure 7 shows the effect of weight ratio between PU component and P(VAc-Veova) component versus time. According to this figure, 30% PU and 70% (20+50) VAc-Veova shows the maximum conversion percent. This result suggests that the best ratio of PU/P(VAc-Veova) is 30/70, a phenomenon observed by many researchers.<sup>39,40</sup>

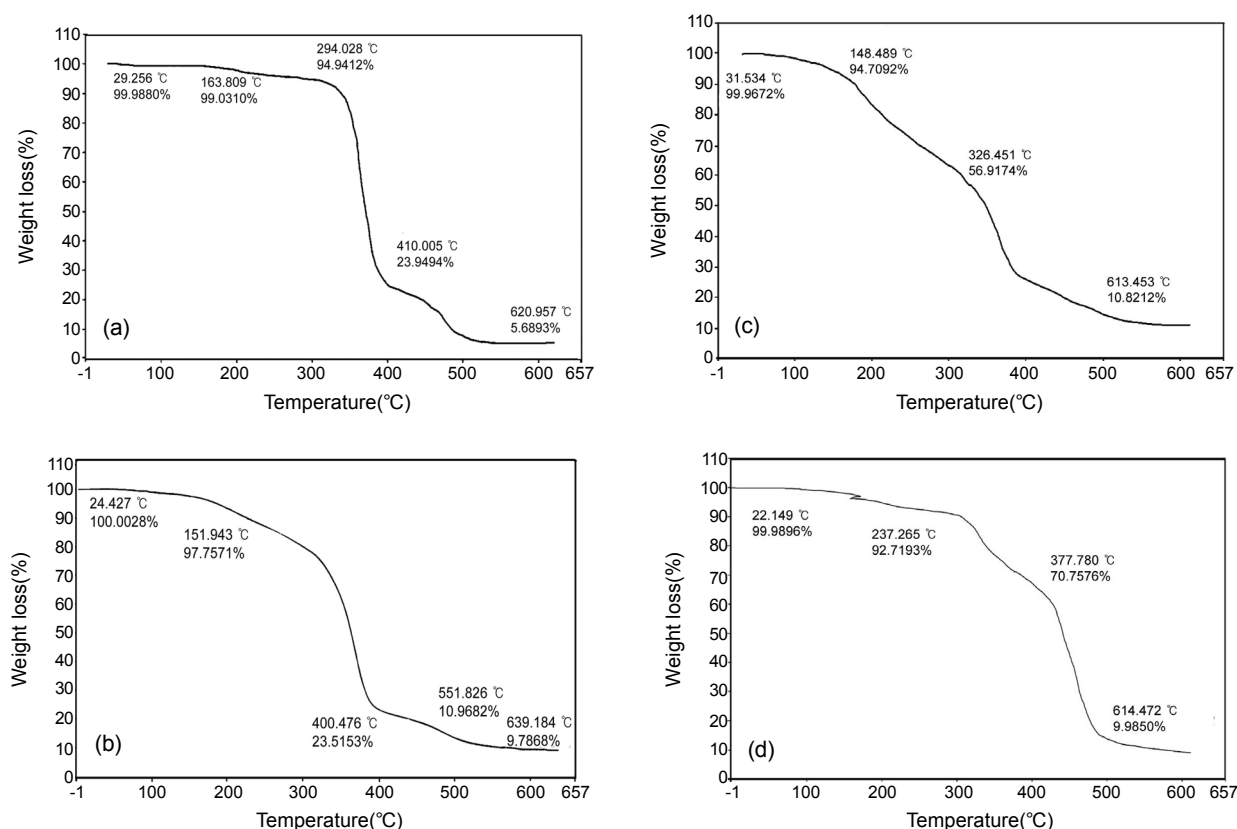
**Morphologies of Latex Particles of P(VAc-Veova), PU/P(VAc-Veova), and PU/P(VAc-Veova)/Si.** The particle morphologies of the P(VAc-Veova), PU/P(VAc-Veova), PU/P(VAc-Veova)/TESPMA and PU/P(VAc-Veova)/TEVS were examined by SEM and TEM, respectively. The micrographs are shown in Figure 8(a-d), and Figure 9(a-d) and data for TESPMA are given in Table 3. According to Figure 8(a-d) the P(VAc-

Veova) and PU/P(VAc-Veova) copolymers have very low particle size compared to PU/P(VAc-Veova)/Si samples. By increasing the Si concentration the particle size increases in a linear manner and their size distributions get narrower. On the other hand, by comparison of the SEM micrographs of Figure 8(c) and 8(d), it can be seen that the particles of Figure 8(d) are not spherical. This may result from the procedure used for the sample preparation. It seems that there are two different types of particles in Figure 8(a-c). They actually are one type and the other is air bubbles. From the data in Table 3, it could be inferred that the number of polymer particles increase by increasing the TESPMA concentration. In addition, it is obvious that the number of polymer particles for the emulsions obtained increase by

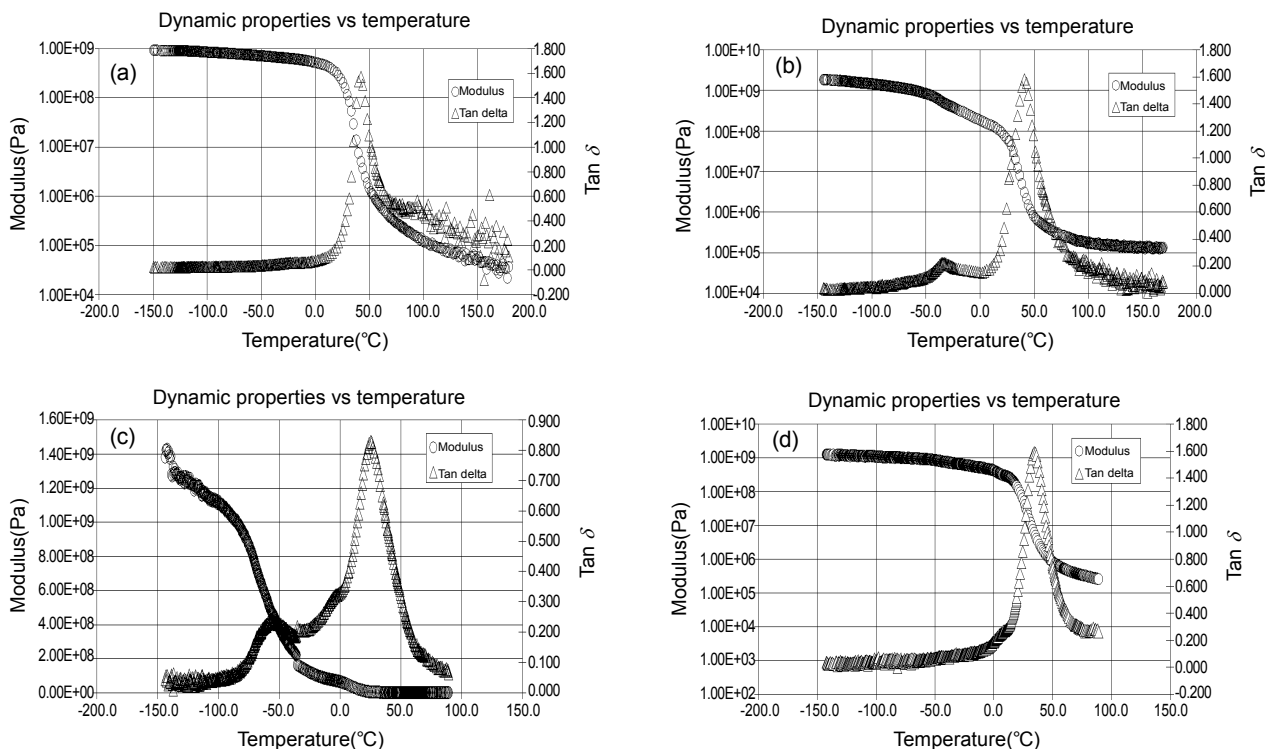
**Table 3. Morphologies of Latex Particles of P(VAc-Veova), PU/P(VAc-Veova) and PU/P(VAc-Veova)/TESPMA**

P(VAc/Veova)	$\bar{X}_M$	33.00	38.00	52.00	61.00	70.00	72.00	100.00
$d_p^3 = 3.8 \times 10^{-12}$	$N_T \times 10^{12}$	7.50	8.60	10.18	13.80	15.80	16.30	22.70
PU/P(VAc/Veova)	$\bar{X}_M$	21.00	25.00	30.00	33.00	40.00	59.00	78.00
$d_p^3 = 4.9 \times 10^{-12}$	$N_T \times 10^{12}$	3.40	4.00	4.80	5.30	6.40	9.50	12.50
PU/P(VAc/Veova)/TESPMA	$\bar{X}_M$	25.00	35.00	40.00	51.00	58.00	66.00	73.00
$d_p^3 = 1.7 \times 10^{-12}$	$N_T \times 10^{12}$	11.70	16.40	18.70	23.80	27.10	30.80	34.10

$M_0 = 0.50 \text{ g/mL}$ , P(VAc-Veova) ( $\rho_p = 1.24 \text{ g/mL}$ ), PU/P(VAc-Veova) ( $\rho_p = 1.21 \text{ g/mL}$ ) and PU/P(VAc-Veova)/TESPMA ( $\rho_p = 1.19 \text{ g/mL}$ ),  $T = 80 \text{ }^\circ\text{C}$ ,  $[I]_0 = 2.2 \times 10^{-3} \text{ molL}^{-1}$ .



**Figure 10.** TGA/DTG thermograms of (a) P(VAc-Veova); (b) PU/P(VAc-Veova); (c) PU/P(VAc-Veova)/TESPMA; (d) PU/P(VAc-Veova)/TEVS in  $\text{N}_2$  atmosphere,  $T = 80 \text{ }^\circ\text{C}$ , 100 rpm,  $[I]_0 = 2.2 \times 10^{-3} \text{ molL}^{-1}$ .



**Figure 11.** DMTA thermograms of (a) P(VAc-Veova); (b) PU/P VAc-Veova; (c) PU/P(VAc-Veova)/TESPMA; (d) PU/P VAc-Veova/TEVS in  $\text{N}_2$  atmosphere,  $T=80$   $^{\circ}\text{C}$ , 100 rpm,  $[I]_0=2.2 \times 10^{-3}$   $\text{mol L}^{-1}$ .

increasing the time and conversion monomers to copolymer. Also Figure 8(a) and 8(b) show very smaller particle sizes compared to 8(c). It could be clearly observed in Figures 8(c) that some Si containing PU/P(VAc-Veova) particles agglomerate together. The results obtained from the TEM micrographs are displayed in Figure 9(a) and 9(b), the white section and the dark points were PU/P(VAc-Veova) and PU/(VAc-Veova)/TESPMA respectively, are in accordance with the expected result. The PU prepolymer could act as a macromolecular emulsifier for its hydrophilic carboxy group. The hydrophobic (VAc-Veova)/Si monomers could migrate into the PU particle adequately before the radical polymerization to achieve the homogeneous particle size. It may be concluded that the outer component is mostly PU while the inner component is mostly hydrophobic P(VAc-Veova)/Si. It could further be inferred from Figure 9(a) and (b) that there is little influence to particle configuration when Si is introduced into PU/(VAc-Veova).

These results suggest that VAc, and Veova monomers were completely polymerized in the presence TESPMA.

**Thermal Properties.** The thermal properties of P(VAc-Veova), PU/P(VAc-Veova), PU/P(VAc-Veova)/TESPMA and PU/P(VAc-Veova)/TEVS were evaluated by means of TGA/DTG and dynamic mechanical thermal analysis (DMTA)

under nitrogen atmosphere. The TGA/DTG curve of the copolymers is shown in Figure 10(a) for P(VAc-Veova), 10(b) for PU/P(VAc-Veova), 10(c) for PU/P(VAc-Veova)/TESPMA and 10(d) for PU/P(VAc-Veova)/TEVS, respectively. The P(VAc-Veova) emulsion (Figure 10(a)) shows a stable situation up to 340  $^{\circ}\text{C}$ . The chemical decomposition will start after this temperature and the maximum decomposition is around 400  $^{\circ}\text{C}$ . The PU/P(VAc-Veova) emulsion (Figure 10(b)) shows a stable situation up to 350  $^{\circ}\text{C}$  and the chemical decomposition starts after this temperature and the maximum decomposition is around 400  $^{\circ}\text{C}$ . In addition, the PU/P(VAc-Veova)/TESPMA (Figure 10(c)) and PU/P(VAc-Veova)/TEVS, (Figure 10(d)) show stable situations up to 200  $^{\circ}\text{C}$  and the maximum decompositions are around 400  $^{\circ}\text{C}$ . From a comparison of the TGA thermograms of Figure 10(c) and (d), it could be concluded that the synthesized monomer (TESPMA) is more effective than TEVS as the char yield weight of polymer with TESPMA at 614  $^{\circ}\text{C}$  was about 10.82% while in the case of polymer with TEVS it was about 9.98%. Based on these results, it could be concluded that the existence of TESPMA or TEVS moieties in the copolymers causes some thermal stability.

The DMTA curve of the temperature dependence of the storage modulus and loss factor ( $\tan \delta$ ) of the P(VAc-Veova), PU/P(VAc-Veova), PU/P(VAc-Veova)/TESPMA



and PU/P(VAc-Veova)/TEVS copolymers is shown in Figure 11(a-d), respectively. From the DMTA curves, the plateau of the elastic modulus in the rubbery state can be used to make qualitative comparisons of the level of cross-linking and  $T_g$  among the various polymers. This figure also shows that the storage modulus change with temperature. The storage modulus of the Si adducts based urethane prepolymer above room temperature showed lower values than any other copolymers. The peak position related to the  $T_g$  was higher in the order P(VAc-Veova) > PU/P(VAc-Veova) > PU/P(VAc-Veova)/TESPMA > PU/P(VAc-Veova)/TEVS. The higher  $T_g$  for P(VAc-Veova) or PU/P(VAc-Veova) was interpreted as being due to the effect of the more difficult micro Brownian motion of the stiffer chains rather than Si containing polymer chains. The  $T_g$  values estimated from the maximum peak of  $\tan \delta$  are given as 42.3, 41.0, 35.5 and 26.2 °C, for the P(VAc-Veova), PU/P(VAc-Veova), PU/P(VAc-Veova)/TESPMA and PU/P(VAc-Veova)/TEVS, respectively. One might then conclude that the presence of TESPMA or TEVS moiety causes the change in thermal behavior and it particularly affects  $T_g$ .

### Conclusions

A new Si containing vinyllic monomer, TESPMA based on APTES and MCl, has been synthesized for formulation of WPU. MPTES and TEVS were used for comparison of the effects of Si kinds on the WPU. A series of new siliconized WPU, (VAc-Veova), TESPMA, MPTES, and TEVS hybrid latexes have been successfully prepared by the emulsion polymerization in the presence of a WPU dispersion by using KPS as an initiator. The WPU dispersion has been prepared by a polyaddition reaction of HMDI, on PPG-1000 and DMPA as chain extender.

From this study, the following conclusions can be made: TESPMA has been prepared successfully as a new Si containing monomer with one functional group, double bond of vinyl.  $^{13}\text{C}$  NMR,  $^1\text{H}$  NMR and FTIR analysis showed that TESPMA segments are present in the structures of monomer and copolymer. PU/P(VAc-Veova)/TESPMA improves the water resistance of PU latex. The presence of TESPMA in the PU/P(VAc-Veova) copolymer caused an increase in the heat stability while the  $T_g$  decreased. The reaction rate decreases by increasing TESPMA. The obtained results show that 30% PU and 70% (20+50) VAc-Veova is the best ratio of PU/P(VAc-Veova) in the TESPMA containing copolymer. In addition, MPTES containing copolymers did not show good results due to its incompatibility with this polymer system but TEVS was a compatible monomer. The above

results suggest that TESPMA containing copolymer is better than TEVS.

### References

1. Y. S. Kwak, E. Y. Kim, H. D. Kim, and J. B. Lee, *Colloid Polym. Sci.*, **283**, 880 (2005).
2. P. J. A. Geurink, T. Scherer, R. Buter, A. Steenbergen, and H. A. Henderiks, *Prog. Org. Coat.*, **55**, 119 (2006).
3. E. Fekete and B. Lengyel, *Prog. Org. Coat.*, **54**, 211 (2005).
4. J. Davis, *Mater. Performance*, **42**, 24 (2003).
5. L. Huang and S. Nabar, *Adhes. Age*, **45**, 19 (2002).
6. K. Landfester, U. Pawelzik, and M. Antonietti, *Polymer*, **46**, 9892 (2005).
7. A. Vuillequez, J. Moreau, M. R. Garda, B. Youssef, and J. M. Saiter, *J. Polym. Res.*, **15**, 89 (2008).
8. E. H. Kim, S. W. Myoung, Y. G. Jung, and U. Paik, *Prog. Org. Coat.*, **64**, 205 (2009).
9. R. J. Pieper, A. Ekin, D. C. Webster, F. Casse, J. A. Callow, and M. E. Callow, *J. Coat. Technol. Res.*, **4**, 453 (2007).
10. F. A. Zhang and C. L. Yu, *J. Coat. Technol. Res.*, **4**, 289 (2007).
11. J. Yang, S. Zhou, B. You, and L. Wu, *J. Coat. Technol. Res.*, **3**, 4 (2006).
12. C. Zhang, X. Zhang, J. Dai, and C. Bai, *Prog. Org. Coat.*, **63**, 238 (2008).
13. M. F. Tsai, Y. D. Lee, and Y. C. Long, *J. Polym. Res.*, **7**, 73 (2000).
14. Y. Lu and R. C. Larock, *Biomacromolecules*, **8**, 3108 (2007).
15. A. Shaffie, A. B. Moustafa, E. S. Mohamed, and A. S. Badran, *J. Polym. Sci. Part A: Polym. Chem.*, **35**, 3141 (1997).
16. P. N. Kumar, G. S. P. Sanghvi, D. O. Shah, and D. Surekha, *Langmuir*, **16**, 5864 (2000).
17. A. S. Badran, A. B. Moustafa, A. A. Yehia, and S. M. M. Shendy, *J. Polym. Sci. Part A: Polym. Chem.*, **28**, 411 (1990).
18. R. Lambourne, *Paint and Surface Coatings Theory and Practice*, Ellis Horwood market Cross House, Editor, Chichester, West Sussex, England, Ch. 9, pp 59-363 (1987).
19. L. Chen and S. Chen, *Prog. Org. Coat.*, **49**, 252 (2004).
20. Y. Okamoto, Y. Hasegawa, and F. Yoshino, *Prog. Org. Coat.*, **29**, 175 (1996).
21. Y. Ba, C. I. Ratcliffe, and J. A. Ripmeester, *Adv. Mater.*, **12**, 603 (2000).
22. Y. Jun, Z. Shuxue, Y. Bo, and W. Limin, *J. Coat. Technol. Res.*, **3**, 333 (2006).
23. L. F. Wang, T. E. Q. Ji, T. C. Glass, J. E. Ward, M. McGrath, G. Muggli, and U. S. Burns, *Polymer*, **41**, 5083 (2000).
24. X. Chen, J. A. Gardella, T. Ho, and K. J. Wynne, *Macromolecules*, **28**, 635 (1995).
25. G. Cho, A. Natansohn, T. Ho, and K. J. Wynne, *Macromolecules*, **29**, 2563 (1996).
26. J. K. Pike, T. Ho, and K. J. Wynne, *Chem. Mater.*, **8**, 856 (1996).

27. J. A. Gardella, T. Ho, K. J. Wynne, and H. Z. Zhuang, *J. Colloid Interf. Sci.*, **176**, 277 (1995).
28. T. Ho, K. J. Wynne, and R. A. Nissan, *Macromolecules*, **26**, 7029 (1993).
29. M. Rochery, I. Vroman, and T. M. Lam, *J. Macromol. Sci. Pure Appl. Chem.*, **40**, 321 (2003).
30. H. Wang, Y. Shen, G. Fei, X. Li, and Y. Liang, *J. Colloid Interf. Sci.*, **324**, 36 (2008).
31. F. A. Zhang and C. L. Yu, *J. Coat. Technol. Res.*, **4**, 289 (2007).
32. C. Zhang, X. Zhang, D. Jiabing, and C. Bai, *Prog. Org. Coat.*, **63**, 238 (2008).
33. H. Jiang, Z. Zheng, W. Song, Z. Li, and X. Wang, *Polym. Bull.*, **59**, 53 (2007).
34. H. J. Naghash, A. Karimzadeh, and A. R. Massah, *J. Appl. Polym. Sci.*, **112**, 1037 (2009).
35. H. J. Naghash, S. Mallakpour, P. Y. Forushani, and N. Uyanik, *Polymer(Korea)*, **32**, 95 (2008).
36. H. J. Naghash, A. Karimzadeh, A. R. Momeni, A. R. Massah, and H. Alian, *Turk. J. Chem.*, **31**, 257 (2007).
37. H. J. Naghash, S. Mallakpour, and N. Mokhtarian, *Prog. Org. Coat.*, **55**, 375 (2006).
38. H. J. Naghash, S. Mallakpour, and N. Kayhan, *Iran. Polym. J.*, **14**, 211 (2005).
39. C. Wang, F. Chu, C. Graillat, A. Guyot, C. Gauthier, and J. P. Chapel, *Polymer*, **46**, 1113 (2005).
40. D. B. Otts, S. Dutta, P. Zhang, O. W. Smith, S. F. Thames, and M.W. Urban, *Polymer*, **45**, 6235 (2004).