

# Amphiphilic Zwitterionic Poly(dimethylsiloxane) (PDMS)-Contained Poly(Ether amine) (Z-SiPEA) as the Responsive Polymeric Dispersant

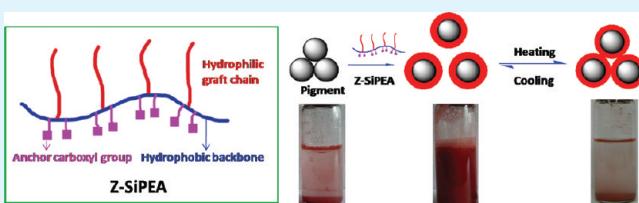
Xuesong Jiang,\* Chunfeng Di, Bing Yu, and Jie Yin

School of Chemistry and Chemical Technology, State Key Laboratory for Metal Matrix Composite Materials, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

 Supporting Information

**ABSTRACT:** We demonstrated here a novel concept of the responsive dispersant based on the amphiphilic zwitterionic poly(ether amine) (Z-SiPEAs), which can control the dispersion of dyes and pigments in water. Z-SiPEAs are composed of short poly(dimethylsiloxane) (PDMS) chain in the backbone and Jeffamine L100 as graft chain. The amino groups in the backbone and carboxyl groups grafted to the backbone make the obtained Z-SiPEAs zwitterionic. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) results revealed that the obtained Z-SiPEAs can self-assemble into nanoparticles in water, which possessed sharp response to temperature, pH, and ionic strength with the tunable clouding point (CP). In the presence of Z-SiPEAs, not only hydrophobic dyes such as Nile Red can be dispersed in water, but the hydrophilic dye Rose Bengal (RB) can be dispersed in unpolar solvents. Further more, Z-SiPEAs can enhance the dispersion of inorganic pigments Titanium White, Iron Red and Chrome Yellow very efficiently in most solvents. It should be noted that the dispersion of organic dyes and inorganic pigments in water can be controlled by temperature in the presence of Z-SiPEAs. <sup>1</sup>H NMR and FT-IR revealed the strong coordination between carboxyl groups in Z-SiPEAs and metal atoms of inorganic pigments. These characteristics will give Z-SiPEAs potential as the novel responsive polymeric dispersant.

**KEYWORDS:** poly(ether amine), amphiphilic, responsive, dispersant



## INTRODUCTION

Due to their unique and excellent properties and potential applications in many fields, the amphiphilic polymers with multiresponses have attracted much attention.<sup>1–6</sup> These polymers can self-assemble into various structures in response to external stimulus such as pH, temperature, light and chemical additives, which can find application in the fields such as the controlled drug delivery, dispersion and smart separation.<sup>7–24</sup> Generally, these amphiphilic polymers should compete with surfactants in some applications such as separation, water-treatment, and dispersion.<sup>25</sup> In this case, the cost for synthesis of amphiphilic responsive polymers will indeed play a key role. Usually, responsive polymer nanoparticles are fabricated by the self-assembly of block copolymers, which are comprised of at least one block responsive to the external stimuli.<sup>26–28</sup> Various block polymers comprised of responsive block such as poly(*N*-isopropylacrylamide) (PNIPAM) and poly(oligo(ethylene glycol) methacrylate) (POEGMA) have been reported.<sup>29–31</sup> However, it is difficult to obtain these block polymers in large-scale in industry because of some extreme reaction conditions and time-consuming postprocessing of these living polymerizations, which consequently limits the application of responsive polymer nanoparticles to a certain extent.

Recently, we synthesized a series of amphiphilic responsive poly(ether amine)s (PEAs) through one-pot synthesis of condensation polymerization of commercial diepoxy and amine monomers. These

PEAs could be dispersed directly in water to form polymer nanoparticles, which exhibited multiresponses to temperature, pH and ionic strength.<sup>32,33</sup> Motivated by these novel characteristics of PEAs such as facile synthesis and a low-cost, robust, and simple approach to formation of multiresponsive polymer nanoparticles, we here tried to use the functional PEAs in applications such as separation and dispersion. In this text, we synthesized zwitterionic poly(ether amine)s (Z-SiPEAs) by introducing poly(dimethylsiloxane) (PDMS) short chain and carboxyl acid group into the structure of PEAs. Because of the amino groups in the backbone of PEAs, the carboxyl groups grafted to the backbone make the obtained Z-SiPEAs zwitterionic. As an inorganic polymeric chain, PDMS is of interest because of its excellent hydrophobic ability, chemical and thermal stability.<sup>34–36</sup> Multiresponsive behavior of polymer nanoparticles formed by Z-SiPEAs, as well as its application in the controlled dispersion of dyes and pigments was investigated. It is interesting that the dispersion of hydrophilic and hydrophobic dyes, as well as inorganic pigments can be controlled in the presence of Z-SiPEAs.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Poly(propylene glycol) diglycidyl ether (PPO-DE, Aldrich,  $M_n = 640$  g/mol), Jeffamine L100 (Huntsman,  $M_n = 1000$  g/mol,

**Received:** February 27, 2011

**Accepted:** April 11, 2011

**Published:** April 11, 2011

Table 1. Composition and Molecular Weight Data of Z-SiPEAs

Z-SiPEAs <sup>a</sup>	mole ratio			$M_n (\times 10^4)$ (g/mol) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	CMC (g/L) <sup>c</sup>
	L100	PDMS-DE	PPO-DE			
Z-SiPEA110	1	1	0	1.0	1.2	0.047
Z-SiPEA321	3	2	1	0.78	1.3	0.050
Z-SiPEA211	2	1	1	0.73	1.5	0.055

<sup>a</sup> Z-SiPEAxyzs, where x, y, z represent the molar ratio of L100, PDMS-DE, and PPO-DE, respectively. <sup>b</sup> Due to the large amount of carboxyl group in Z-SiPEAs, the molecular weight of Z-SiPEAs was evaluated on the results of the  $M_n$  and  $M_w/M_n$  of SiPEAs, which were determined by GPC. <sup>c</sup> CMC was measured by using Nile Red as a fluorescent probe.

EO/PO is about 19/3), Poly(dimethylsiloxane) diglycidyl ether (PDMS-DE, Aldrich,  $M_n = 980$  g/mol), cellulose dialysis membrane (Shanghai Greenbird Tech. Co. Ltd, Cutoff  $M_w = 3500$ ), Ethanol absolute (Sinopharm Chemical, >99.7%), Succinic anhydride (SA, Sinopharm Chemical, AR), Rose Bengal sodium salt (RB, Sinopharm Chemical, BR), Nile Red (Aldrich), were used as received.

**2.2. Synthesis of SiPEAs.** SiPEAs was synthesized through one-step according to our previous report.<sup>32a,36</sup> The reaction was conducted in a 50 mL two-neck flask equipped with a nitrogen inlet tube and a reflux condenser. The mixture of L100, PDMS-DE and PPO-DE in proportion (shown in Table 1) was refluxed in ethanol for 24 h under protection of nitrogen. After cooling to room temperature, the mixture was poured into the 10-fold hexane. After removing the supernatant, SiPEAs were collected and dried in a vacuum oven with yield of 90%.

**2.2. Synthesis of Z-SiPEAs.** SiPEAs and succinic anhydride (the molar ratio of hydroxyl group in SiPEA and anhydride of SA is about 1:3) were dissolved in chloroform at room temperature, and then the mixture was refluxed for 24 h. All the products were moved into dialysis bag to dialyze in ethanol for 3 days to remove succinic anhydride. Then ethanol was removed through rotary evaporation to get Z-SiPEAs.

**2.3. Characterization.** Fourier Transform Infrared (FTIR). Fourier transform infrared spectra were recorded with a Paragon 1000 (Perkin-Elmer Co.).

**Nuclear Magnetic Resonance Spectroscopy (NMR).** <sup>1</sup>H NMR measurements were carried out on a Varian Mercury Plus spectrometer operating at 400 MHz for protons equipped with a temperature control unit. Solvent for NMR were CDCl<sub>3</sub> (TMS internal standard).

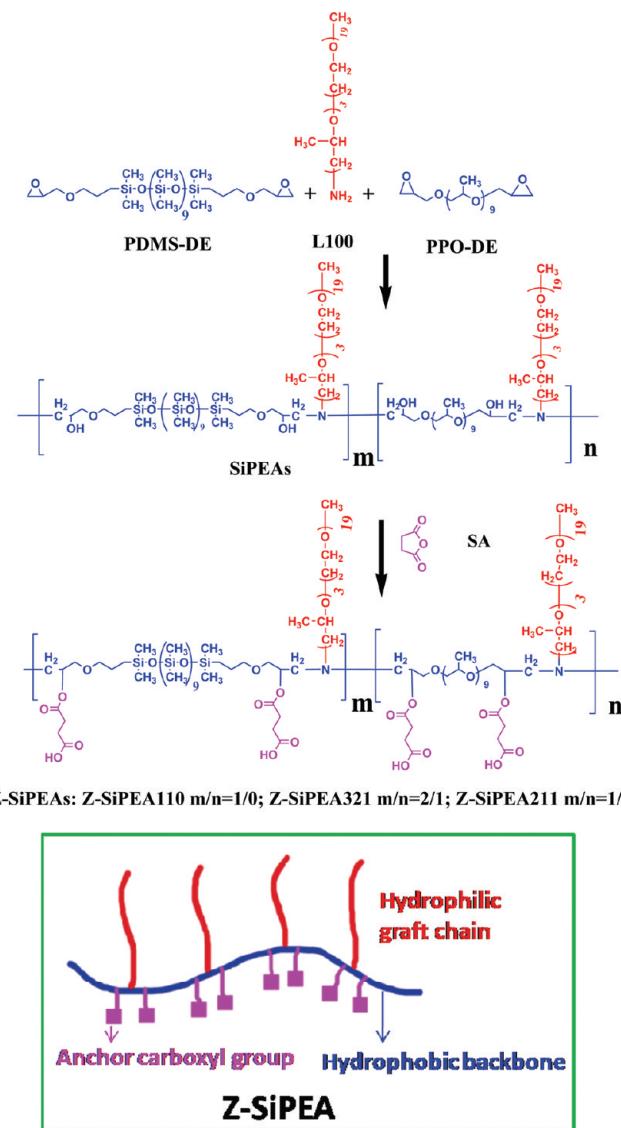
**Thermogravimetric Analysis (TGA).** TGA was performed in nitrogen at a heating rate of 20 °C/min from 100 to 800 °C using a TA Q5000IR TGA. For each measurement, the sample cell was maintained at 100 °C for 30 min to evaporate solvent in the sample before measurement.

**Cloud Point (CP) Measurement.** The CP of the polymer solutions were measured on a GBC Cintra 10e UV-visible spectrophotometer by monitoring the turbidity of the polymer solutions as a function of temperature at 550 nm under the heating rate of 1 °C/min. The temperature at 90% light transmittance of the polymer solution was defined as the CP. The concentration of polymer for CP determination was 3 g/L.

**Dynamic Light Scattering (DLS).** Dynamic light scattering studies of the copolymers at concentrations of 3 g/L were conducted using a Malvern Instruments Zetasizer Nano ZS instrument equipped with a 4mW He-Ne laser ( $\lambda = 633$  nm) at an angle of 90°, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple  $\tau$  digital correlator electronics system. The CONTIN analysis method was used.

**Transmission Electron Microscopy (TEM).** A drop of the 1 g/L copolymer solution was placed onto a copper grid and the excess solution was removed by a filter paper. The sample was examined in a JEOL 2100F microscope, operating at 200 kV.

Scheme 1. Process for Synthesis of Z-SiPEAs



**Critical Micellization Concentration Measurements (CMC).** The CMC of Z-SiPEA was determined by using Nile red as a fluorescent probe. Solutions of Z-SiPEAs with concentrations ranging from  $1 \times 10^{-4}$  to 1 g/L were prepared. The emission spectra were recorded under LS-50B luminescence spectrometer (Perkin-Elmer Co.). The excitation wavelength was set at 559 nm. The Fluorescence emission spectra were recorded from 580 to 750 nm. All fluorescence spectra were recorded at room temperature.

### 3. RESULTS AND DISCUSSION

**3.1. Synthesis of Z-SiPEAs and Formation of Z-SiPEAs Nanoparticles in Aqueous Solution.** Z-SiPEAs were synthesized through nucleophilic substitution/ring-opening reaction of commercial PDMS and PPO short chain contained diglycidyl ether and Jeffamine L100, followed by functionalizing the hydroxyl groups in the backbone by succinic anhydride (SA). The whole process for synthesis of Z-SiPEAs was illustrated in Scheme 1. PDMS short chain in the backbone of Z-SiPEAs is designed as hydrophobic part, which can lead to formation of the stable nanoparticles through self-assembly of Z-SiPEAs in aqueous solutions. The amino groups and carboxyl groups make Z-SiPEAs zwitterionic in aqueous solution responsive to pH in aqueous solution. Furthermore, carboxyl groups can act as anchor attached on the surface of metals and their oxides, which provide the potential of Z-SiPEAs as dispersant of metal pigments.

The successful functionalization of hydroxyl groups of Z-SiPEAs by SA was confirmed by FT-IR and  $^1\text{H}$  NMR. As shown in the FT-IR spectra in Figure 1, the peak at  $1733\text{ cm}^{-1}$  is attributed to the carbonyl stretch. The appearance of peak at  $1733\text{ cm}^{-1}$  reveals that carboxyl chain was successfully grafted to SiPEAs backbone. The  $^1\text{H}$  NMR spectra (Figure 2) of Z-SiPEAs in  $\text{CDCl}_3$  exhibit signals at  $\delta = 2.62\text{ ppm}$ , which can be assigned to protons of  $-\text{CH}_2-$  of the carboxyl chain. The peaks (a–h) in  $^1\text{H}$  NMR spectrum of Z-SiPEA110 can be assigned to the related proton. The amount of SA grafted to the backbone can be determined by  $^1\text{H}$  NMR. Because of the high reactivity between hydroxyl groups and anhydride groups, almost all hydroxyl groups were esterified by SA according to the integral of  $^1\text{H}$  NMR spectra. The molecular weight and component of the obtained Z-SiPEAs are summarized in Table 1.

Z-SiPEAs are comprised of hydrophobic PDMS and PPO chains in the backbone, and hydrophilic L100 graft chain. Due to their amphiphilicity, Z-SiPEAs are expected to self-assemble into particles in aqueous solution, which are comprised of hydrophobic PDMS and PPO chains as core and hydrophilic L100 chains as shell (Scheme 2). As a strong evidence for self-assembly of amphiphilic polymers into micelle, CMC value for Z-SiPEAs was determined by a fluorescence spectroscopy using Nile Red as a fluorescence probe. The dependence of the emission intensity of Nile Red on the logarithm of Z-SiPEA110 concentration is plotted. A sudden increase in emission intensity was observed at a concentration of about  $5.5 \times 10^{-2}\text{ g/L}$  of Z-SiPEA110, indicating the onset of the nanoparticle's formation (Figure 3a). The formation of nanoparticles in aqueous solution was further confirmed by DLS experiments which were carried out in aqueous solutions at  $25^\circ\text{C}$ . As shown in Figure 3b, Z-SiPEA211 and Z-SiPEA321 can form nanoparticles with size of about  $16\text{ nm}$  in diameter, and their polydispersity index (PDI) is less than 0.2. Besides the peak at  $16\text{ nm}$  in DLS size-distribution of Z-SiPEA110, the peak around  $180\text{ nm}$  was observed, which might be ascribed to the microaggregation of Z-SiPEA110 nanoparticles. Compared with Z-SiPEA211 and Z-SiPEA321, Z-SiPEA110 contained more PDMS chains and is more hydrophobic, which might lead to the tendency of aggregation of Z-SiPEA110 nanoparticles. The morphology of the formed Z-SiPEAs particles was further revealed by TEM. As shown in Figure S1a in the Supporting Information, large particles with diameter more than  $100\text{ nm}$  were observed, which might be ascribed to the microaggregation of Z-SiPEA110 particles, whereas only uniform-sized nanoparticles of Z-SiPEA211 and Z-SiPEA321 were revealed in Figure S1b,c in the Supporting Information. This is comparable to the DLS results.

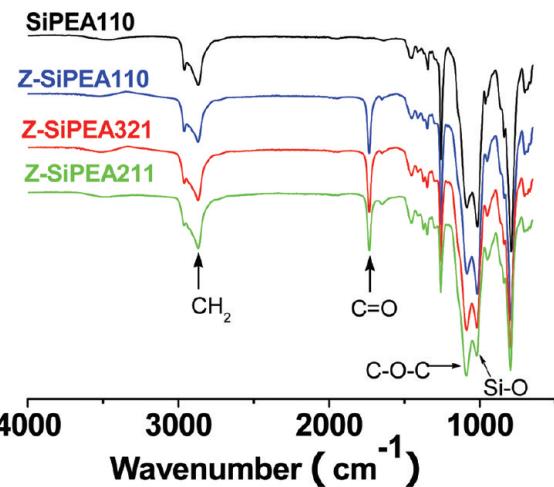


Figure 1. FT-IR of SiPEA110 and Z-SiPEAs.

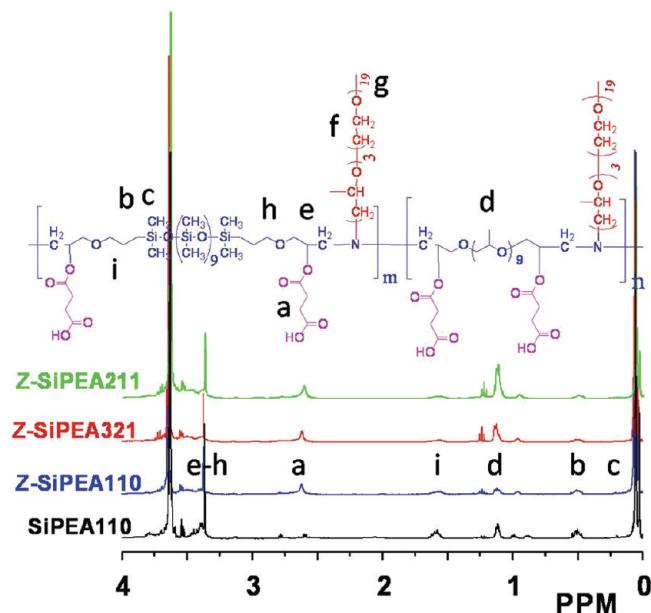
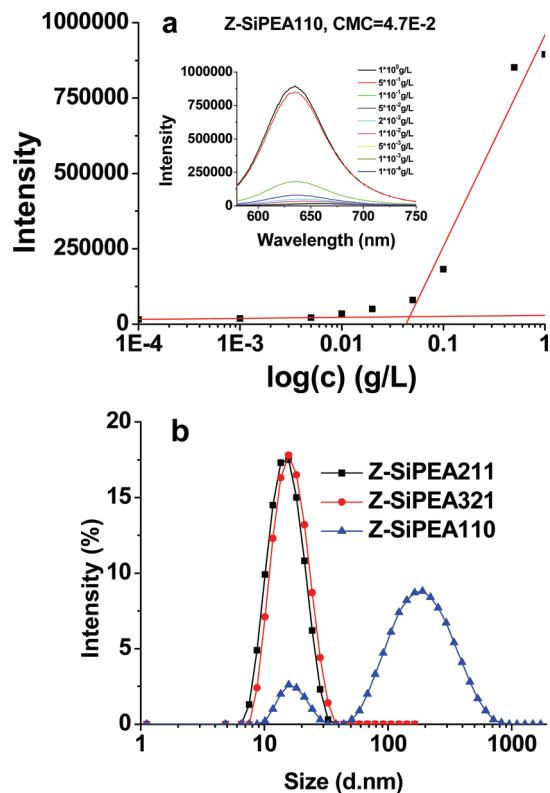
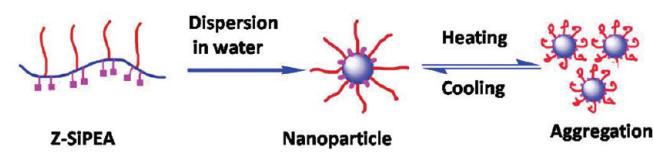


Figure 2.  $^1\text{H}$  NMR of SiPEA110 and Z-SiPEAs in  $\text{CDCl}_3$ .

**Multiresponsive Aggregation Behaviors of Z-SiPEA Nanoparticles.** Because the outer shell comprises hydrophilic L100 chains and carboxyl groups, Z-SiPEAs nanoparticles are expected to respond to temperature, pH, and ionic strength. The hydrophilic outer shell leads to the stable dispersion of Z-SiPEAs nanoparticles and prevents their aggregation further. The thermal responsive aggregation behaviors of Z-SiPEAs nanoparticles under different conditions were investigated by measuring its cloud point (CP). The concentration of Z-SiPEAs solution was  $3\text{ g/L}$  in all cases, which was much higher than its CMC to ensure the formation of polymer nanoparticles. The typical transmittance vs temperature curves for Z-SiPEAs solution with photograph at pH 4.0 was shown in Figure 4a. The transparent Z-SiPEAs solution at room temperature suddenly became turbid when the temperature is above CP, which can be reflected visibly by photograph. The CP increased from Z-SiPEA110 to Z-SiPEA211, which should be ascribed to the less content of hydrophobic PDMS in the backbone of Z-SiPEAs. The turbid

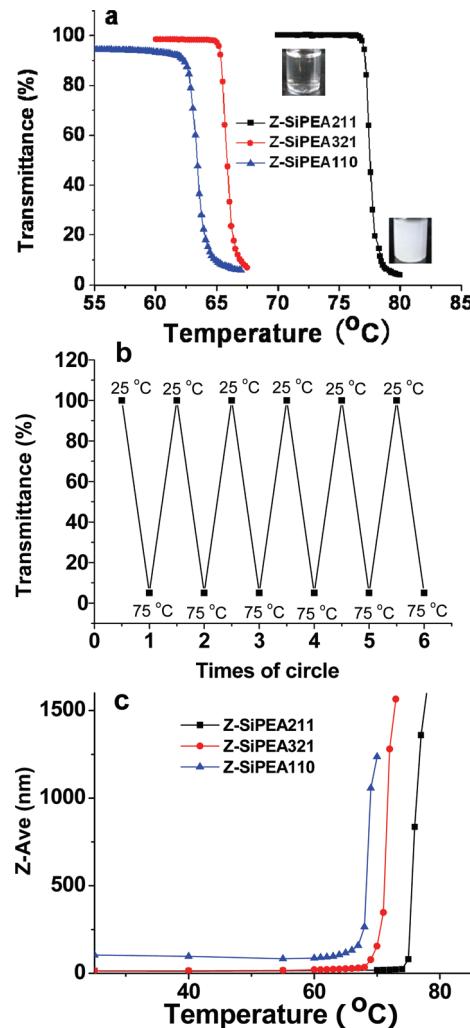
**Scheme 2. Proposed Process for Formation and Responsive Aggregation of Z-SiPEA Nanoparticle**



**Figure 3.** (a) Plot of the maximum fluorescence emission intensity of the Nile Red vs concentration of Z-SiPEA110. Inset: fluorescence emission spectra of Nile Red solution with different Z-SiPEA110 concentration; (b) size distribution of nanoparticles formed by Z-SiPEA110, Z-SiPEA321, and Z-SiPEA211 determined by DLS at 25 °C in aqueous solution. Polymer concentration is 3 mg/mL.

solution should be resulted from the aggregation of Z-SiPEAs nanoparticles. Z-SiPEAs solution exhibited sharp response to temperature and the range of transition temperature is less than 1.5 °C. It should be noted that the thermal responsive aggregation of Z-SiPEAs nanoparticles is completely reversible (Figure 4b).

To further understand the responsive aggregation of Z-SiPEAs nanoparticles, we did DLS experiments to investigate the temperature dependence of the average hydrodynamic radius (Z-ave) of Z-SiPEAs in aqueous solutions (Figure 4c). All Z-SiPEAs solution exhibited sharp increase in Z-ave around CP, which indicates the fast phase transition and formation of large particles. Z-SiPEAs dispersed as nanoparticles in water, which keep stable when the temperature is below CP. The Z-SiPEAs nanoparticles started to aggregate into the microparticles very fast when the temperature is higher than CP. The morphology of the aggregation of Z-SiPEAs nanoparticles at high temperature (80 °C) was revealed by TEM. As shown in Figure S2 in the Supporting

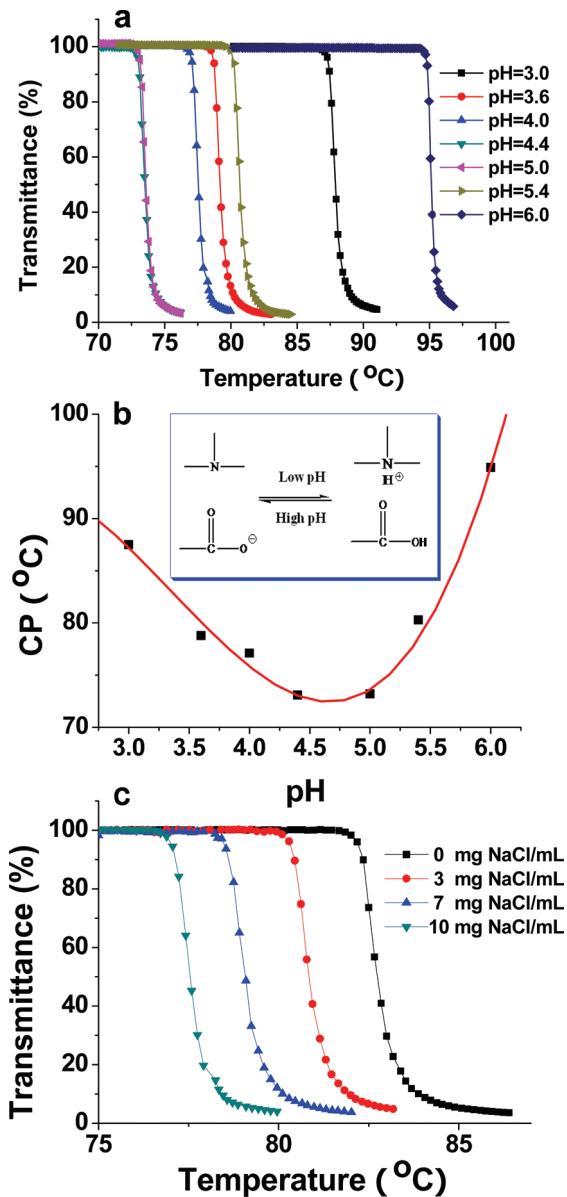


**Figure 4.** (a) Temperature dependence of optical transmittance at 550 nm for Z-SiPEAs aqueous solution (3 g/L) at pH 4.0. Inset: photograph of Z-SiPEA211 aqueous solutions at low (25 °C) and high temperature (80 °C); (b) Reversible change of transmittance at 550 nm for Z-SiPEA211 aqueous solution at pH 7.4 between 25 and 80 °C; (c) Temperature dependence of the average hydrodynamic radius (Z-Ave) of Z-SiPEAs in aqueous solutions determined by DLS.

Information, the microsphere aggregation was observed for all Z-SiPEAs solution.

Because of the amino and carboxyl groups in Z-SiPEAs that can be protonated or deprotonated at the different pH, Z-SiPEAs nanoparticles are responsive to pH. Taking Z-SiPEA211 as examples, Figure 5a shows the temperature dependence of transmittance for Z-SiPEA211 aqueous solutions at different pH. The CP of Z-SiPEA211 decreased with the increase of pH from 3.0 to 4.4, and then increased at the higher pH. As shown in Figure 5b, the lowest CP of Z-SiPEA211 aqueous solution was found around pH 4.7. Unlike the previous reports, in which the CP of PEAs always decreased with the increase of pH, the special behavior responsive to pH can be explained by the zwitterionic structure of Z-SiPEA211. As shown in the inset of Figure 5b, the carboxyl groups can be deprotonated at high pH, whereas amino groups become less hydrophilic at this stage.

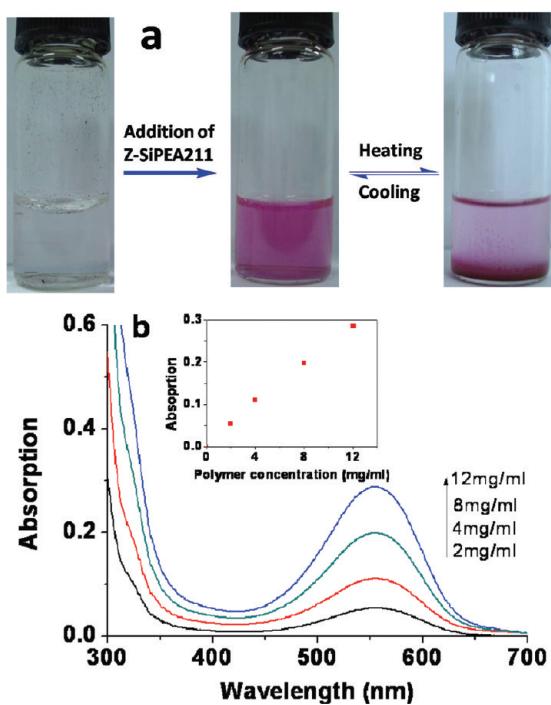
As one of the dominating parameters in various aqueous systems, ionic strength has significant effect on formation of



**Figure 5.** (a) pH dependence of optical transmittance at 550 nm for Z-SiPEA211 aqueous solution (3 g/L); (b) the effect of pH on the CP of Z-SiPEA211 aqueous solution (3 g/L). Inset: mechanism of carboxyl and amino groups deprotonated at different pH; (c) NaCl concentration dependence of optical transmittance at 550 nm for Z-SiPEA211 aqueous solution (3 g/L) at pH 4.0.

hydrogen bond between ether group and water molecules. To investigate the effect of ionic strength on aggregation behavior of Z-SiPEAs nanoparticles, a series of aqueous solutions of Z-SiPEA211 with different concentration of NaCl were prepared. Figure 5c shows transmittance versus temperature for Z-SiPEA211 at different NaCl concentration. Z-SiPEA211 exhibited very sharp phase transition in wide range of NaCl concentration. CPs decreased obviously with the increasing NaCl concentration because of the typical salting-out effect.<sup>37,38</sup>

**Controlled Dispersion of Dyes.** Motivated by the novel characteristics of Z-SiPEAs such as facile synthesis, zwitterionic, low cost and ability to directly form polymer nanoparticle with

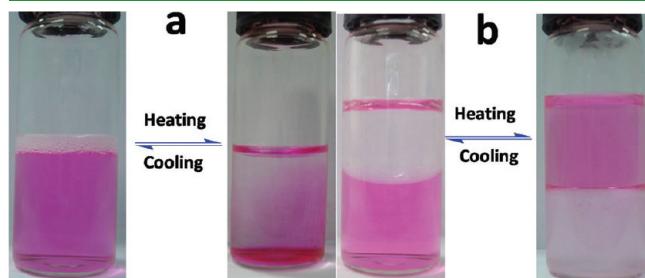


**Figure 6.** Encapsulation of hydrophobic guest molecules in water: (a) Photographs of Nile Red in water before (left), after (middle) the addition of Z-SiPEA211 (12 g/L) at room temperature, and (right) heating to high temperature (80 °C); (b) UV-vis spectra of Nile Red dispersed in water by various concentrations of Z-SiPEA211, inset: plots of maximum absorbance of Nile Red vs Z-SiPEA211.

multiresponses in aqueous solution, we tried to develop a new concept of the responsive dispersant and used Z-SiPEAs in the controlled dispersion of dyes and pigments. Just like the polymer nanoparticles formed by self-assembly of amphiphilic copolymer in water, Z-SiPEAs nanoparticles could encapsulate hydrophobic guest molecules because of its structure of hydrophobic core/hydrophilic shell and large surface area. As shown in Figure 6a, hydrophobic dye Nile Red, which is insoluble in water, was dispersed immediately in aqueous solution after addition of Z-SiPEA211, which can be reflected by change of the solution color visible to eye. This could be further proved by the UV-vis spectra (Figure 6b). Upon addition of Z-SiPEA211, the absorption band at ~553 nm increases linearly with the increasing Z-SiPEA211 concentration. The encapsulation efficiency is about 0.5% based on the UV-vis spectra. The dispersion behavior of Nile Red in water in presence of Z-SiPEA211 can be explained by the encapsulation properties of nanoparticles. Hydrophobic dye Nile Red can be encapsulated in hydrophobic core of Z-SiPEA211 in water, resulting in good dispersion of Nile Red in water. Because of multiresponses of Z-SiPEA211 nanoparticles, the dispersion of Nile Red in the presence of Z-SiPEA211 in water could be controlled by temperature, pH and ionic strength. For example, Nile Red participated with Z-SiPEA211 in the bottom after heating to high temperature (80 °C, Figure 6a). This process is reversible and Nile Red could be dispersed well in water again after cooling to room temperature.

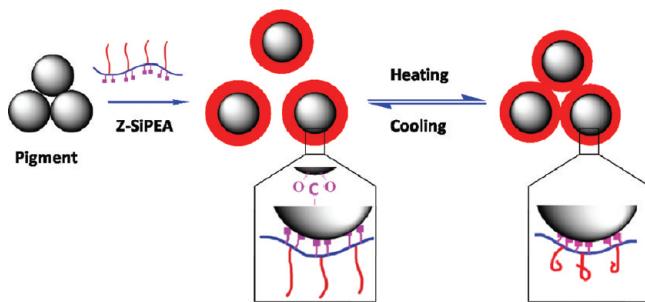
On the other hand, water-soluble dye Rose Bengal (RB) which is insoluble in toluene, can be dispersed in toluene in the presence of Z-SiPEA211 (see Figure S3 in the Supporting

Information). The absorption of RB in toluene increased linearly with the Z-SiPEA211 concentration, and the encapsulation efficiency is about 0.8%. The dispersion of RB in toluene could



**Figure 7.** (a) Photograph of RB dispersion in water at room temperature and high temperature (80 °C); (b) photograph of RB transfer between water (down layer) and toluene phase (uplayer) at room temperature and high temperature (80 °C), the concentration of Z-SiPEA211 is 12 g/L.

**Scheme 3. proposed Mechanism of the Controlled Dispersion of Metal-Based Pigments Particles in the Presence of Z-SiPEAs**

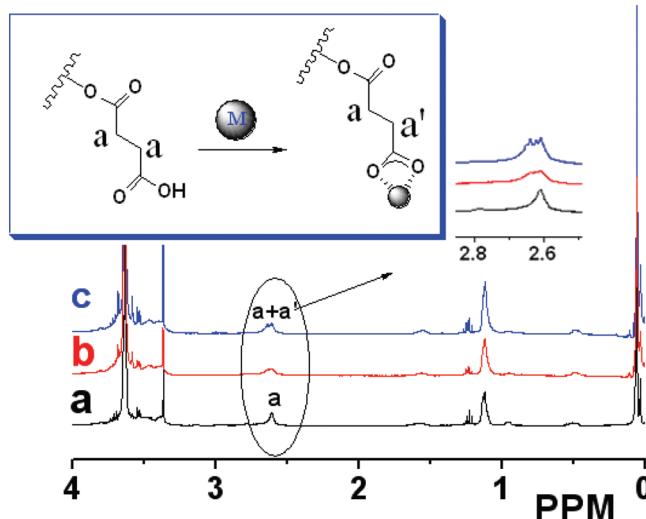


be ascribed to the encapsulation properties, and is easily understood in the presence of amphiphilic Z-SiPEAs. Even if in water, Z-SiPEA211 nanoparticles can also encapsulate or adsorb water-soluble RB, and then control RB dispersion. As shown in Figure 7a, RB can participate with Z-SiPEA211 nanoparticles into the bottom in water after heating to high temperature, indicating that RB should be encapsulated in Z-SiPEA211 nanoparticles. In the presence of toluene layer (Figure 7b), RB preferred to be transferred into toluene phase after heating. It should be noted that both processes shown in Figure 7 are reversible, and can be triggered by the change of pH and ionic strength besides temperature. These results indicated that the dispersion of hydrophobic dye RB in water could be also controlled in the presence of Z-SiPEA211. Thayumanavan<sup>39</sup> and Wan<sup>40</sup> also reported that in aqueous solution the hydrophobic dyes can be transferred selectively to organic solvent in the presence of amphiphilic polymers. Because of unresponsive polymer used; however, the process of the dye's transfer is not responsive to external stimulus in their reports.

**Controlled Dispersion of Pigments.** Pigments are widely used in the fields such as coating, ink and paint, and play an important role in our daily life. The properties of pigment dispersion really depend on the interaction between pigment particles and dispersant, and are expected to be tuned for the different application. Most widely used pigments are based on the metals or metal oxides, which could form the strong coordination with carboxyl and amino groups (Scheme 3). Because of the carboxyl and amino groups in the polymeric chain, and the excellent amphiphilicity and response to external stimulus, it is interesting to know whether our Z-SiPEAs can work as dispersant of pigments and control their dispersion for different applications. To verify this idea, we chose three types of pigments with different size: Titanium White ( $TiO_2$ ,  $d = 40-50$  nm), Iron Red ( $Fe_2O_3$ ,  $d = 400-500$  nm), and Chrome Yellow ( $d = 2$   $\mu m$ ),



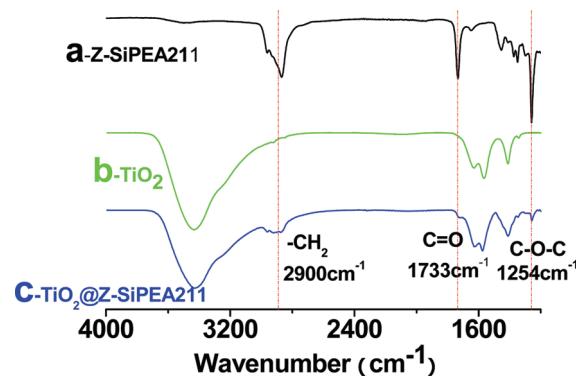
**Figure 8.** Photograph of dispersion of pigments in different solvents with (left) and without Z-SiPEA211 (right): (a) Titanium White; (b) Iron Red; (c) Chrome Yellow, the concentration of pigments and Z-SiPEA211 is 10 and 5 g/L, respectively. The pictures were taken after the samples were stirred for 30 min and then stood for 30 min.



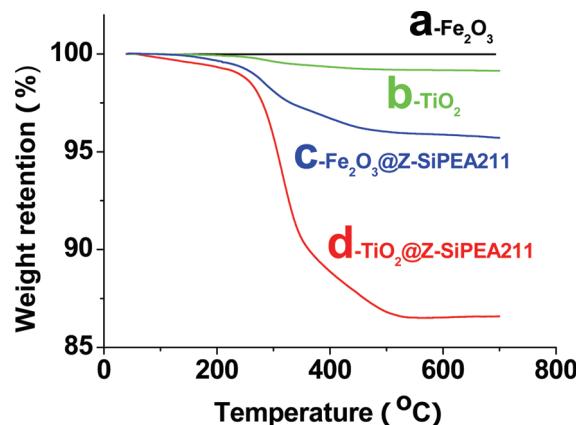
**Figure 9.**  $^1\text{H}$  NMR of Z-SiPEA211 with different amount of  $\text{TiO}_2$  in  $\text{CDCl}_3$ : (a) 10 mg Z-SiPEA211 in 0.5 mL  $\text{CDCl}_3$ ; (b) 10 mg Z-SiPEA211 and 10 mg  $\text{TiO}_2$  in 0.5 mL  $\text{CDCl}_3$ ; (C) 10 mg Z-SiPEA211 and 20 mg  $\text{TiO}_2$  in 0.5 mL  $\text{CDCl}_3$ .

for dispersion experiments. The dispersion of these pigment particles in different solvents was tested in the presence of Z-SiPEA211, and the results are shown in Figure 8. The properties of three pigment's dispersion were obviously enhanced with the help of Z-SiPEA211. This should be ascribed to the well-known coordination between metal atom of pigment and carboxyl groups of Z-SiPEA211. Because of the attachment of Z-SiPEA211 on the surface of pigment particles, we proposed that Z-SiPEA211 form the brushlike outer-layer on the pigment particles, resulting in their good dispersion in solvents. The dispersion of these pigments in water could be also controlled by temperature in the presence of Z-SiPEA211 (Scheme 3). Taking Titanium White as example, in the presence of Z-SiPEA211, the pigment particles can be dispersed well in water at room temperature, but aggregated together and participated in the bottom after heating to high temperature (see Figure S4 in the Supporting Information). After being cooled to room temperature and lightly shaken, pigment particles can be dispersed again in water.

To understand the interaction of pigment/Z-SiPEA211, we checked the  $^1\text{H}$  NMR of Z-SiPEA211 with the different concentration of Titanium White. As a powerful method to analyze the interaction between ligand and colloidal surface,  $^1\text{H}$  NMR is expected here to provide potential to investigate the interaction of pigment/Z-SiPEA211, which could have possible effect on the chemical shift of Z-SiPEA211. As shown in Figure 9, the peak at 2.6 ppm ascribed to  $-\text{CH}_2-$  of SA shifted to the high field, and became wider and split with the increase of Titanium White, indicating the coordination interaction between carboxyl groups and metal atom of pigment.<sup>41,42</sup> Because of the strong interaction between carboxyl groups and metal atom of pigments, Z-SiPEA211 can be grafted on the surface of pigment particles to form polymer brush-like layer. We separated the pigment particles from Z-SiPEA211 solution through centrifugation, and proved the existence of Z-SiPEA211 layer on the surface of pigment particles by the following FT-IR (Figure 10) and TGA (Figure 11). To remove the physical adsorption of Z-SiPEA211, pigment particles were purified by centrifugation/redisposition in tetrahydrofuran



**Figure 10.** FT-IR spectra of (a) Z-SiPEA211; (b) Titanium White (raw  $\text{TiO}_2$ ); (c)  $\text{TiO}_2@$ Z-SiPEA211.



**Figure 11.** TGA curves of (a) Iron Red (raw  $\text{Fe}_2\text{O}_3$ ); (b) Titanium White (raw  $\text{TiO}_2$ ); (c)  $\text{Fe}_2\text{O}_3@$ Z-SiPEA211; (d)  $\text{TiO}_2@$ Z-SiPEA211.

(THF) three times. As a comparison to the FT-IR spectrum of raw  $\text{TiO}_2$  particles (Figure 10b), the appearance of the absorption band at 2900, 1733, and 1254  $\text{cm}^{-1}$  in Figure 10c, which ascribed to C—H, C=O, and C—O—C vibrations of Z-SiPEA211, respectively, indicated the existence of Z-SiPEA211 graft layer. The amount of grafted Z-SiPEA211 on the surface of pigment particles can be determined by TGA. If the density of Z-SiPEA211 graft layer is about 1.0  $\text{g}/\text{cm}^3$ , the Z-SiPEA211 layer's thickness of  $\text{TiO}_2@$ Z-SiPEA211 and  $\text{Fe}_2\text{O}_3@$ Z-SiPEA211 is about 5 and 12 nm, respectively, based on TGA data. Both FT-IR and TGA results provided that Z-SiPEA211 can be grafted on the surface of pigment through the strong coordination between carboxyl groups and metal atom.

## CONCLUSIONS

In summary, we developed a novel zwitterionic PDMS-contained poly(ether amine) (Z-SiPEAs). The obtained amphiphilic Z-SiPEAs could directly self-assemble into the stable uniform-sized nanoparticles in aqueous solution, whose aggregation can be controlled by temperature, pH and ionic strength. Based on these amphiphilic and multi-responsive Z-SiPEAs, we demonstrated a new concept of the responsive dispersant, which can control the dispersion of dyes and pigments in water through external stimulus. In the presence of Z-SiPEAs, hydrophobic dye Nile Red can be dispersed in water, and hydrophilic dye RB can be

dispersed in toluene. Moreover, the dispersion of Nile Red and RB in water can be controlled by temperature. Z-SiPEAs can also enhance the dispersion of metal pigments very obviously in different solvents. This could be explained that Z-SiPEAs were grafted on the surface of pigment particles to form the brushlike layer due to the strong coordination between carboxyl groups of Z-SiPEAs and metal atom of pigments. <sup>1</sup>H NMR revealed the coordination interaction between carboxyl groups and metal atom of the pigment's surface, which was further confirmed by FT-IR and TGA. Because of these novel characteristics such as facile synthesis, amphiphilicity, multiresponses, and ability to self-assemble directly into polymer nanoparticle in aqueous solution, Z-SiPEA is believed to find wide application in the controlled dispersion of dyes and pigments.

## ■ ASSOCIATED CONTENT

**Supporting Information.** TEM images of Z-SiPEAs in water, photograph of dispersion of RB in toluene, and photograph of pigment's dispersion in water in the presence of Z-SiPEA211. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Tel.: +86-21-54743268. Fax: +86-21-54747445. E-mail: ponygle@sjtu.edu.cn.

## ■ ACKNOWLEDGMENT

We thank the National Nature Science Foundation of China (50803036) and the Shanghai Leading Academic Discipline Project (B202) for their financial support. X.S.J. is supported by the SMC Project of Shanghai Jiao Tong University.

## ■ REFERENCES

- Owens, D. E.; Jian, Y. C.; Fang, J. E.; Slaughter, B. V.; Chen, Y. H.; Peppas, N. A. *Macromolecules* **2007**, *40*, 7306–7310.
- Zhang, Y. F.; Luo, S. Z.; Liu, S. Y. *Macromolecules* **2005**, *38*, 9813–9820.
- Hantuschel, N.; Zhang, F. B.; Eckert, F.; Pich, A.; Winnik, M. A. *Langmuir* **2007**, *23*, 10793–10800.
- O'Reilly, R. K.; Hawker, C. J.; Wooley, K. L. *Chem Soc Rev* **2006**, *35*, 1068–1083.
- Vancaeyzeele, C.; Ornatsky, O.; Baranov, V.; Shen, L.; Abdelrahman, A.; Winnik, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 13653–13660.
- Klaikherd, A.; Nagamani, C.; Thayumanavan, S. *J. Am. Chem. Soc.* **2009**, *131*, 4830–4838.
- Bromberg, L. E.; Ron, E. S. *Adv Drug Deliver Rev* **1998**, *31*, 197–221.
- Willet, N.; Gohy, J. F.; Auvray, L.; Varshney, S.; Jerome, R.; Leyh, B. *Langmuir* **2008**, *24*, 3009–3015.
- Kikuchi, A.; Okano, T. *Prog. Polym. Sci.* **2002**, *27*, 1165–1193.
- VandenMooter, G.; Maris, B.; Samyn, C.; Augustijns, P.; Kinget, R. *J. Pharm. Sci.* **1997**, *86*, 1321–1327.
- Mahkam, M.; Assam, M. G.; Zahedifar, R.; Ramesh, M.; Davaran, S. *J. Bioact Compat Pol* **2004**, *19*, 45–53.
- Loudwig, S.; Bayley, H. *J. Am. Chem. Soc.* **2006**, *128*, 12404–12405.
- Inoue, Y.; Kuad, P.; Okumura, Y.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 6396–6397.
- Ferri, V.; Elbing, M.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samori, P.; Mayor, M.; Rampi, M. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3407–3409.
- Rapoport, N. *Prog. Polym. Sci.* **2007**, *32*, 962–990.
- Stayton, P. S.; Shimoboji, T.; Long, C.; Chilkoti, A.; Chen, G. H.; Harris, J. M.; Hoffman, A. S. *Nature* **1995**, *378*, 472–474.
- Tang, T.; Castelletto, V.; Parras, P.; Hamley, I. W.; King, S. M.; Roy, D.; Perrier, S.; Hoogenboom, R.; Schubert, U. S. *Macromol. Chem. Phys.* **2006**, *207*, 1718–1726.
- Hoogenboom, R.; Rogers, S.; Can, A.; Becer, C. R.; Guerrero-Sanchez, C.; Wouters, D.; Hoeppenera, S.; Schubert, U. S. *Chem. Commun.* **2009**, 5582–5584.
- Lin, S. L.; He, X. H.; Li, Y. L.; Lin, J. P.; Nose, T. *J. Phys. Chem. B* **2009**, *113*, 13926–13934.
- Lutz, J. F.; Hoth, A. *Macromolecules* **2006**, *39*, 893–896.
- Wang, Y. C.; Tang, L. Y.; Li, Y.; Wang, J. *Biomacromolecules* **2009**, *10*, 66–73.
- Cohn, D.; Lando, G.; Sosnik, A.; Garty, S.; Levi, A. *Biomaterials* **2006**, *27*, 1718–1727.
- Lutz, J. F. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3459–3470.
- Lin, S. L.; Numasawa, N.; Nose, T.; Lin, J. P. *Macromolecules* **2007**, *40*, 1684–1692.
- Motornov, M.; Roiter, Y.; Tokarev, I.; Minko, S. *Prog. Polym. Sci.* **2010**, *35*, 174–211.
- Yang, Y. Q.; Zheng, L. S.; Guo, X. D.; Qian, Y.; Zhang, L. J. *Biomacromolecules* **2011**, *12*, 116–122.
- Ding, L.; Huang, Y. Y.; Zhang, Y. Y.; Deng, J. P.; Yang, W. T. *Macromolecules* **2011**, *44*, 736–743.
- Smith, A. E.; Xu, X. W.; Abell, T. U.; Kirkland, S. E.; Hensarling, R. M.; McCormick, C. L. *Macromolecules* **2009**, *42*, 2958–2964.
- Adelsberger, J.; Kulkarni, A.; Jain, A.; Wang, W. N.; Bivigou-Koumba, A. M.; Busch, P.; Pipich, V.; Holderer, O.; Hellweg, T.; Laschewsky, A.; Muller-Buschbaum, P.; Papadakis, C. M. *Macromolecules* **2010**, *43*, 2490–2501.
- Mei, A. X.; Guo, X. L.; Ding, Y. W.; Zhang, X. H.; Xu, J. T.; Fan, Z. Q.; Du, B. Y. *Macromolecules* **2010**, *43*, 7312–7320.
- (a) Schramm, O. G.; Pavlov, G. M.; Erp, H. P.; Meier, M. A. R.; Hoogenboom, R.; Schubert, U. S. *Macromolecules* **2009**, *42*, 1808–1816. (b) Schramm, O. G.; Meier, M. A. R.; Hoogenboom, R.; Erp, H. P.; Gohy, J. F.; Schubert, U. S. *Soft Matter* **2009**, *5*, 1662–1667.
- (a) Ren, Y. R.; Jiang, X. S.; Yin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1292–1297. (b) Ren, Y. R.; Jiang, X. S.; Yin, G. L.; Yin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 327–335.
- (a) Wang, R.; Jiang, X. S.; Di, C. F.; Yin, J. *Macromolecules* **2010**, *43*, 10628–10635. (b) Yu, B.; Jiang, X. S.; Wang, R.; Di, C. F.; Yin, J. *Macromolecules* **2010**, *43*, 10457–10465.
- Cheng, C.; Powell, K. T.; Khoshdel, E.; Wooley, K. L. *Macromolecules* **2007**, *40*, 7195–7207.
- Neugebauer, D.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8687–8693.
- Di, C. F.; Jiang, X. S.; Wang, R.; Yin, J. *J. Mater. Chem.* **2011**, *21*, 4416–4423.
- Durme, K. V.; Rahier, H.; Mele, B. V. *Macromolecules* **2005**, *38*, 10155–10163.
- Alexandridis, P.; Holzwarth, J. F. *Langmuir* **1997**, *13*, 6074–6082.
- (a) Kale, T. S.; Klaikherd, A.; Popere, B.; Thayumanavan, S. *Langmuir* **2009**, *25*, 9660–9670. (b) Basu, S.; Vutukuri, D. R.; Thayumanavan, S. *J. Am. Chem. Soc.* **2005**, *127*, 16794–16795.
- (a) Wan, D. C.; Pu, H. T.; Cai, X. Y. *Macromolecules* **2008**, *41*, 7787–7789. (b) Wan, D. C.; Wang, G. C.; Pu, H. T.; Jin, M. *Macromolecules* **2009**, *42*, 6448–6456.
- Chen, X. B.; Mao, S. S. *Chem. Rev.* **2007**, *107*, 2891–2959.
- Dass, A.; Guo, R.; Tracy, J. B.; Balasubramanian, R.; Douglas, A. D.; Murray, R. W. *Langmuir* **2008**, *24*, 310–315.