Preparation and Characterization of Polysiloxane-Acrylate Latexes with MPS-PDMS Oligomer as Macromonomer

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ABSTRACT: The latexes of polysiloxane and acrylate with methacryloxypropyl trimethoxysilane (MPS)–polydimethylsiloxane (PDMS) oligomer as macromonomer and Gemini surfactant as coemulsifier were prepared by emulsion copolymerization and characterized by ^{1}H-nmr, gel-permeation chromatography (GPC), FTIR, x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

First, the oligomer of MPS-PDMS (Si—O—Si chain length = 24) were synthesized by the hydrolysis of MPS and the ring-opening polymerization of octamethyl tetracyclosiloxane (D_4), the ^{1}H-NMR and FTIR spectra indicated that when the reaction time was prolonged to 2 h, more than 90% of —Si $(OCH_3)_3$ groups were hydrolyzed; Then, the emulsion polymerization was performed with the oligomer as macromonomer and Gemini Surfactant as coemulsifier, the result of FTIR indicated that almost all the macromonomer had been exhausted because there was no C=C characteristic peaks in the spectrum. XPS investigation of the latexes showed that with the increase of siloxane content, more and more polysiloxane occupied the outer layer of the membrane, which agreed well with the conclusion of contact angle and AFM measurements. With Gemini surfactant as coemulsifier in the system, the PDMS content in the system could reach to 50%, which was far higher than the other reported value. © 2009 Wiley Periodicals, Inc. Journal of Applied Polymer Science 114: 760–768, 2009

Key words: MPS-PDMS oligomer; acrylate; macromonomer; Gemini surfactant

INTRODUCTION

Polysiloxane and their composite materials have attracted much attention due to the excellent properties, such as water repellency, high flexibility, low glass transition temperature, low surface energy, and biocompatibility, etc.[1–4] However, polysiloxane have their own insuperable disadvantages, for instance, the high cost, poor cohesiveness, and film-forming property limit their further application in many fields. In contrast, acrylate and polyacrylate were widely applied for its low cost, good cohesiveness, and excellent film-forming property. It is a common knowledge that the greater the difference between the combining polymers, the more likely synergistic properties will result from the combination.[5] Hence, the coalescence of polysiloxane and polyacryalte would bring unimaginable effect in their composite materials. Many significant works, recently, based on organic siloxane have been shown in the published articles by Park et al.,[6] Medda et al.,[7] and Bauer[8] et al., contributing to the technical synthesis of some performance-specified coatings.

The latexes of siloxane-acrylate copolymer have been widely applied in many areas because of their nontoxic and noncontaminating characteristics.[9,10] It is well known that within a proper range, the more siloxane in the copolymer, the more excellent properties of siloxane would be embodied, so the question of how to enhance the siloxane content in latexes is becoming more and more important. The most widely used method of introducing polysiloxane into the latexes is the group of Si—OH (caused by the hydrolysis of $Si(OCH_3)_3$ groups in the main chain) initiating the ring opening polymerization of D_4, that is to say the hydrolysis and the ring opening polymerization happened at the same time. Commonly, the polymerization temperature of the acrylate is higher than 80°C, under such conditions, the $Si(OCH_3)_3$ groups are easy to hydrolyze, forming a network structure even to coagulum. This is the main reason why the siloxane content in the copolymer could not be enhanced in the copolymer. Kan et al.,[11] He et al.,[12] and Yu et al.[13] have devoted themselves to introducing D_4 and vinyl septamethyl cyclotetrasiloxane (VD_4) into the reaction system to enhance the siloxane content in the copolymer. But, the long Si—O—Si chains formed by D_4 ring-opening polymerisation were hard to be emulsified, which could engender floating oil and the reaction of the multivinyl
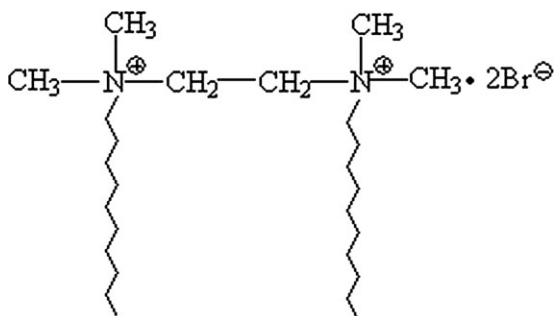
Figure 1 Molecular scheme of Gemini surfactants (average value, n = 24).

group could produce tangles in the chains causing a rapid augmentation of molecular weight so as to generate coagulum. So, the content of polysiloxane in the copolymer was no more than 30% all the time.

A Gemini surfactant is a molecule composed of two identical hydrophilic head groups and two hydrophobic tail groups (Fig. 1). It is very similar to two single-chain surfactants linked covalently by a spacer group. The spacer group can vary in length and chemical structure, be flexible or rigid, and be hydrophilic or hydrophobic.[14] Gemini surfactants have some excellent solution and interfacial properties. First, the critical micelle concentration (CMC) values of Gemini surfactants lower one to two orders of magnitude than that of corresponding single-chain surfactants.[15] Second, they are much more efficient than their corresponding monomeric surfactants in decreasing the surface tension of water.[16] For example, the C20 (surfactant concentration required for lowering the surface tension of water by 20 mN/m) for 12-2-12 Gemini is 0.0083 wt %, whereas that for C12TAB is 0.25 wt %[14]. Finally, Gemini surfactants with short spacers form large, threadlike aggregates, while the single-chain equivalent forms only small spherical micelles. For example, 12-2-12 Gemini has been shown to form long wormlike micelles at a concentration as low as 1.5 wt %.

So, in this article, the MPS-PDMS oligomer (Si—O—Si chain length = 24) was prepared aforehand as the macromonomer to react with acrylate. Because of the oligomer do not contain $Si(OCH_3)_3$ groups, it will not hydrolyze in the course of reaction, so the siloxane content would be enhanced. Consequently, $C_{12}H_{25}N^+(CH_3)_2$—CH_2—CH_2—$N^+(CH_3)_2C_{12}H_{25}\cdot2Br^-$ was introduced into the system as one of coemulsifiers, the latexes with 50% congtent of siloxane was prepared, and the siloxane content ws far higher thant the other reported values. The latexes prepared in the current study was characterized by ^{1}H-NMR, x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and gel-permeation chromatography (GPC). Besides, the surface property was also measured by static contact

angle. All the measurements were consistent with the conclusion that the copolymer of siloxane and acrylate with high siloxane content had been prepared successfully.

EXPERIMENTAL SECTION

Materials

Butyl acrylate (BA), methyl methacrylate(MMA), acrylic acid, and acrylamide were supplied by the Xilong Chemical Co. (China); octamethyl tetracyclosiloxane (D_4), 3-(methacryloxypropyl)-trimethoxysilane (MPS), and hexamethyldisiloxane (HMDS) came from Yudeheng Couple Agent Factory (China), respectively, and all the monomer were purified by vacuum distillation before use. Dodecyl benzenesulfonic acid (DBSA) and span-20 were purchased from Xilong Chemical Co. (China), $C_{12}H_{25}N^+(CH_3)_2$—CH_2—CH_2—$N^+(CH_3)_2C_{12}H_{25}\cdot2Br^-$ was supplied by Daochun Chemical Co. (China) and potassium persulphate was supported by Jinshan Chemical Factory (China), all the surfactants and initiator were used as received.

Synthesis of the MPS-PDMS oligomer

Fisrt, D_4 (10 g), H_2SO_4 (1 ml), MPS (1.25 g) and a quantity of water was added into a 100 mL four-necked flask fitted with a mechanical stirrer, nitrogen inlet, and reflex condenser, the temperature was maintained at 80°C, then the mixture of D_4 (12.7 g) and HMDS (1.30 g) were introduced into the system within 15 min, the reaction was maintained for 2 h. After this, the oligomer was taken out from the flask and dissolved in 50 mL toluene solution, then 15 mL H_2SO_4 (30%) was added into the system to readjust the long Si—O—Si chain for getting a more even preformed polymer, after stirring for 30 min, H_2SO_4 was washed by deionized water from the system, the oligomer was separated from toluene solution through vacuum distillation. The schematic formation of oligomer was listed in Figure 2.

Preparation of the PDMS-acrylate latexes

The latexes were prepared in aqueous media by successive monomer addition under kinetically controlled conditions.[17] Potassium persulphate (0.2 g, dissolved with 10 mL water) was used as initiator, a series of polymerizations was performed under the same conditions. The monomer, including BA (17.0 g), MMA (9.0 g), and the oligomer (0–26.5 g) were mixed together in a container and stirred with a magnetic stirrer for half an hour. Acrylic acid (0.5 g) and acrylamide (1.0 g) were dissolved with 10 mL water. Then all the surfactants (DBSA 1.5 g, Span-20
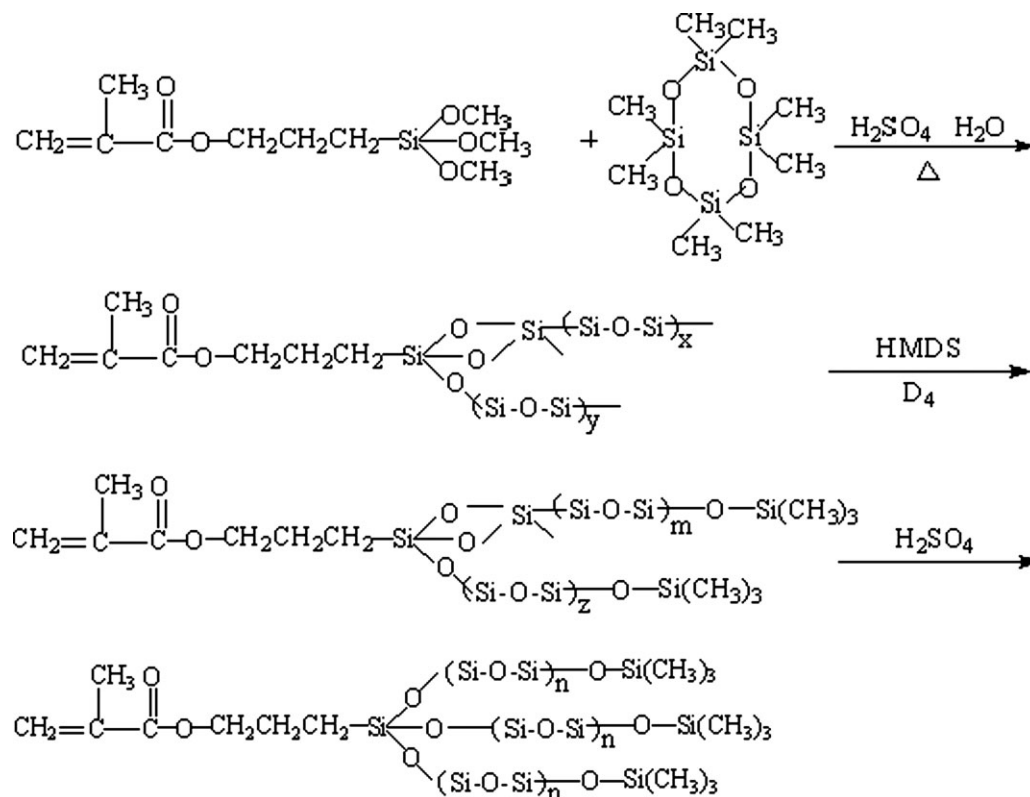
Figure 2 Schematic formation of MPS-PDMS oligomer.

1.0 g, Gemini Surfactant 0.1 g), about 30% of the mixed monomer, a third of initiator and 80 g deionized water were put into a 250 mL four-necked flask fitted with a mechanical stirrer, nitrogen inlet and reflex condenser. After removing air with nitrogen gas for 30 min, the polymerization was performed at 85°C. After 30 min, the other monomer and the initiator (which were put into the dropping funnel at first) were added into the system within 120 min and the temperature was maintained for another 6 h.

The latexes with corresponding percentages of siloxane (w/w %) were labeled as PDMS-15, PDMS-30, PDMS-40, and PDMS-50, when no siloxane was used, we named the particles as PDMS -0.

Analysis of ^{1}H-NMR, AFM, and GPC

^{1}H-NMR spectra of the oligomer were measured by a BRUKER AM 500 spectrometer using DUAL-5 mm probe for ^{1}H-NMR. The samples were dissolved in $CDCl_3$ (10–15 wt/vol %) at 25°C. The AFM analysis was performed by MMAFMLN2068EX (vecco instruments, USA). GPC analysis of the molecular weight distribution of these oligomers was performed on a Waters system comprised of a U6K injector, a 510 HPLC pump, and a R401 refractive index detector. The eluting solvent was THF at a flow rate of 0.8 mL/min. The retention time were calibrated against

known monodipersed polystyrene whose M_w/M_n ratio are less than 1.10.

Measurement of XPS and FTIR

XPS measurement was made on a KRATOS Analytical AXISHISi spectrometer with a monchoromatized AL Ka X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms. A concentric hemispherical analyzer (CHA) was performed in the constant analyzer transmission mode to measure the binding energies of emitted photoelectrons. The binding energy scale was calibrated by the Au $4f_{7/2}$ peak at 83.9 eV as well as Cu $2p_{3/2}$ peak at 76.5 and 932.5 eV. In addition, FTIR spectra were recorded using a NICOLET MX-1E FTIR spectrometer and KBr plates were used in preparing the samples.

Static contact angle

For measuring the contact angle, some membranes were formed from the latexes.The latexes were spread on a cleaned glass plate and allowed to dry and form membranes at room temperature, and then the membranes were placed into a vacuum oven (DZF-6050, Shanghai, China) for 24 h at 60°C to remove any remaining water. Static contact angle was measured with an optical contact angle
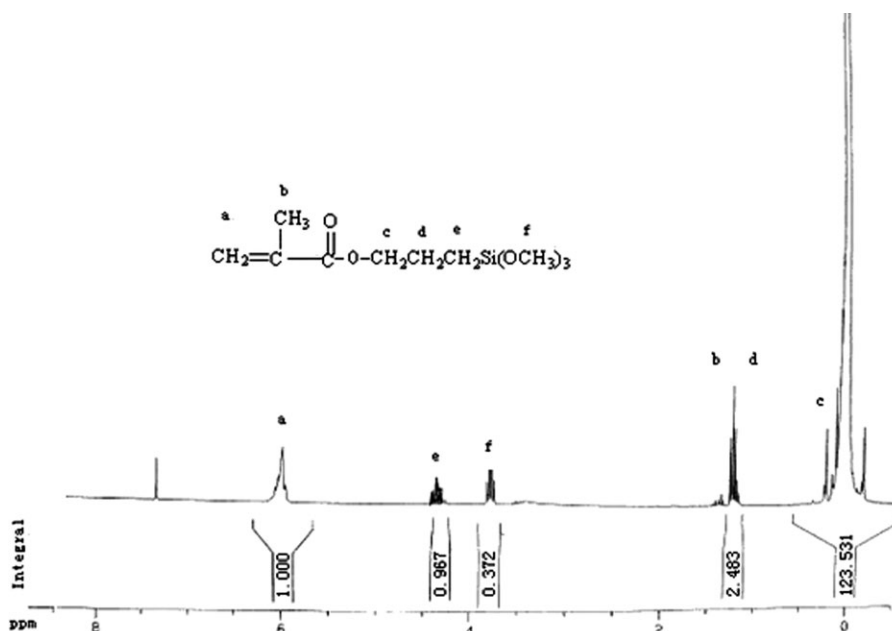
Figure 3 ^{1}H-NMR of MPS-PDMS oligomer.

goniometer (ERMAG-1, Japan)[18]. The reported values were the average values of three measurements performed on different parts of the sample surface.

RESULTS AND DISCUSSION

Analysis of MPS-PDMS oligomer

^{1}H-NMR of MPS-PDMS oligomer

It is well known that H_2SO_4 could break the Si—O—Si long chain in toluene solution, so, in this article, H_2SO_4 was used to destroy and rearrange the Si—O—Si structure (including the Si—O—Si short chain formed in the intramolecule of MPS), the catalyst and balance were conducted under the condition of concentrated sulphuric acid in order that the silane could be combined in an amount equal to the reactive mole ratio. ^{1}H-NMR is the most useful for the measurement of hydrogen chemical environment because of its high sensitivity to hydrogen bond strength, whereas the area of apex also evidently reflects the abundance of hydrogen in different chemical shift.[18-20] The ^{1}H-NMR of oligomer was shown in Figure 3, it could be seen that all the relevant peaks of MPS could be found in the figure, the peaks at 0 and 6 ppm result from the group of CH_3 in the long chain of Si—O—Si and the vinyl group (CH_2=C) in the molecule of MPS. According to the H atom numbers of MPS, before hydrolysis, there should be a strong peak at 3.7 ppm caused by the group of Si $(OCH_3)_3$ (peak are ~4.5), with the process of hydrolysis, the area of peak would lessen, after 2 h, there was only a weak peak at 3.7 ppm (peak are ~0.442), that is to say more than 90% of

$Si(OCH_3)_3$ groups have been hydrolyzed in the reaction (calculated from the peak area in the figure).

In additon, the molecular weight distribution of oligomers was determined by GPC, it could be found that all the measured values were less than the theoretical values, but not exceeding 8%, the deviation might be aroused by operate miss. So, it could be said that the oligomers were synthesized successfully.

FTIR characterization

FTIR analysis result of MPS-PDMS oligomer was shown in Figure 4. The peaks corresponding to CH_2=C stretching at 1640.5 and 3100.2 cm^{-1} suggested the existence of C=C in the polymer. At the positions of 796.5 and 1258.3 cm^{-1}, there were two strong peaks, which could be ascribed to the group of Me_2SiO (D) in the structure of PDMS, the characteristic peaks of Si—O—Si also were showed at 1026.7 and 1090.9 cm^{-1} in the spectrum. Besides, at the area of 1090–1075 cm^{-1}, there were no clear peaks, that is to say, almost all of D_4 had participated into the polymerization and no monomer was left. In addition, there were only weak peaks at the point of 2846.9 and 1190.8 cm^{-1}, which could account for that nearly all group of Si—O—CH_3 had been hydrolyzed, tally with the conclusion of ^{1}H-NMR, there were no peaks concerning about $(CH_3)_3Si$-O—Si $(CH_3)_3$ at the region of 1080–1040 cm^{-1}. All the data could prove that nearly all organic siloxane had participated into the reaction and no monomer left.
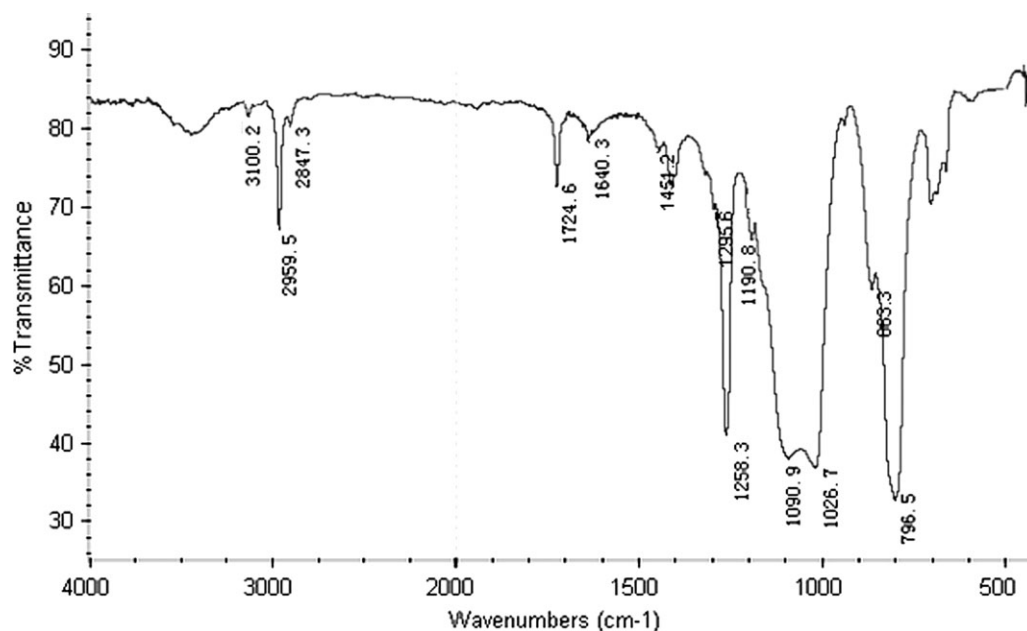
Figure 4   FTIR spectra of MPS-PDMS oligomer.

Analysis of PDMS-acrylate latexes

FTIR spectrum

In addition, the latexes without adding Gemini surfactant were also studied tentatively, the outcome displayed that the content of PDMS could only reach 30% at the most. Once the content of PDMS was higher than 30%, there would appear floating oil phenomenon. With the introduction of Gemini Surfactant in the system, the polysiloxane content in the latexes could reach 50%. Because of the special structure of Gemini Surfactant, the tails could not tightly arranged like conventional surfactant, besides the polarity of the ionic polar was stronger than that of conventional surfactant, so, there would form micelles with worm shape, which could greatly tone the emulsifying efficiency, so the dosage was far lower than that of the conventional surfactant. The mixture of conventional/Gemini Surfactants would exhibit the synergism in the decline of surface tension and the formation of mixed micelles.[15]At the end of the reaction, the conversion of the monomer reached to 95% (determined gravimetrically in an independent experiment), which was consistent with
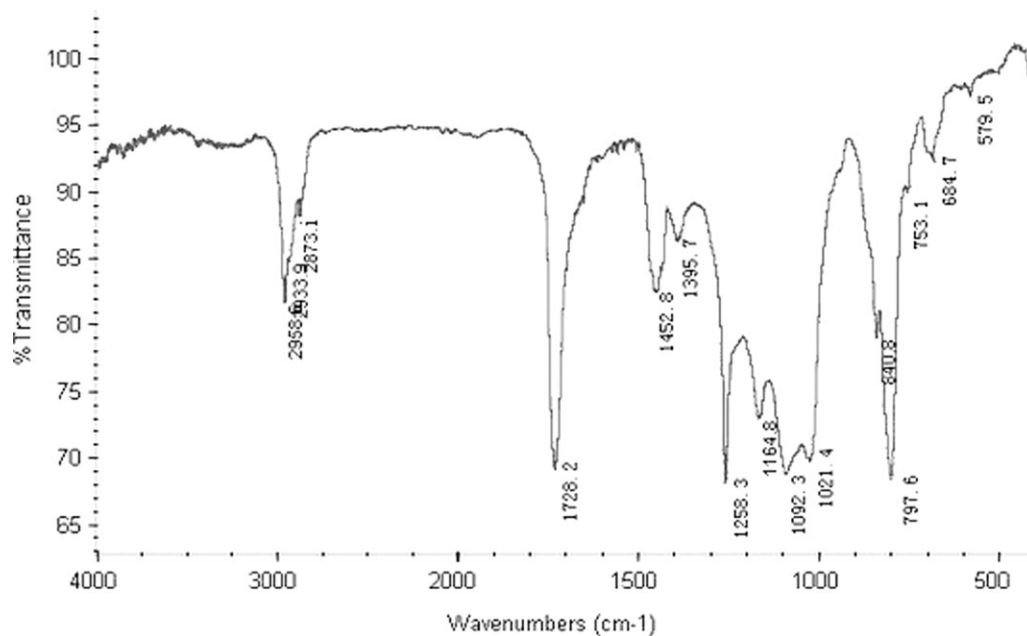

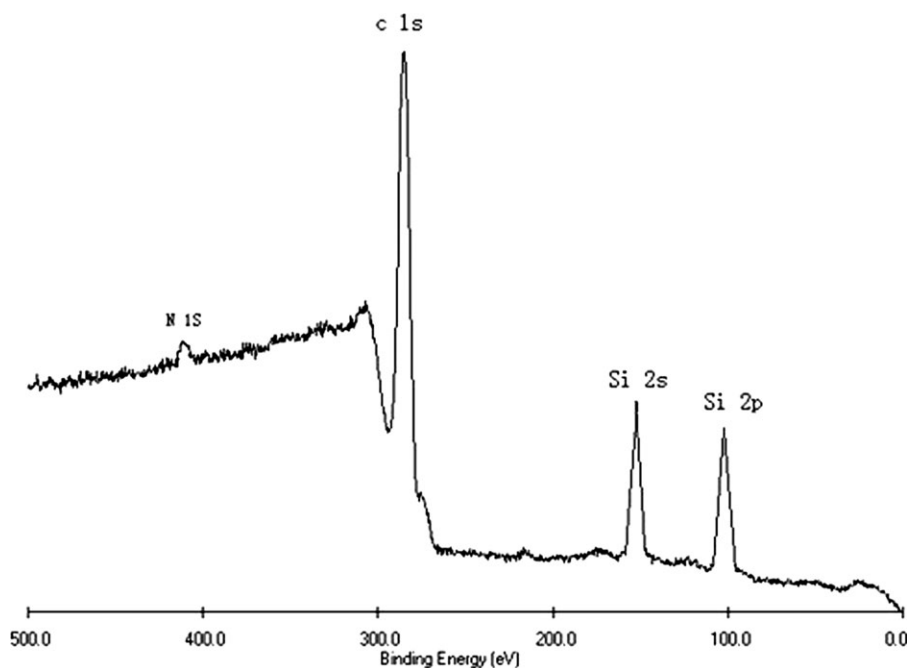**Figure 5**   FTIR spectra of PDMS-acrylate latexes.

Figure 6 XPS characterization of PDMS-acrylate latexes.

the view that nearly all monomer had participated in the reaction.

The FTIR outcome of PDMS-50 was shown in Figure 5. The strong bands at 1732.3 cm^{-1} attributed to the C=O stretching of acrylate. There were no peaks corresponding to C=C and C—H stretching at 1640 and 3102 cm^{-1}, which suggested that almost all the monomer had participated in the reaction and there was no C=C bonds left in the system. The characteristic peaks of PDMS were similar with that of MPS-PDMS oligomer. The group of Si—O—CH$_3$ could not be observed in the spectrum because of the hydrolysis in the course of reaction.

X-ray photoelectron spectroscopy (XPS)

The surface properties of polymer are very important for understanding their physical, chemical, and optical properties. Although the investigation can be performed by the normal analytic techniques, such as NMR and FTIR, it cannot deeply probe the structure and bonding state of polymer in subsurface level even the extreme layer.[21,22] The technology of XPS had been widely used to study the elements composition of surface containing Si element and the atomic ratio of C/Si.[23-25] Clearly, if PDMS had been successfully reacted with acrylate, there would present the characteristic peaks of Si element and the atomic ratio of C/Si in the given sample would be agreed well with the C/Si ratio calculated from the monomer. To confirm this idea, the elements on the surface of the membrane were measured by XPS.

The characteristic peaks of Si 2s and Si 2p in Figure 6 manifested that the presence of Si element on
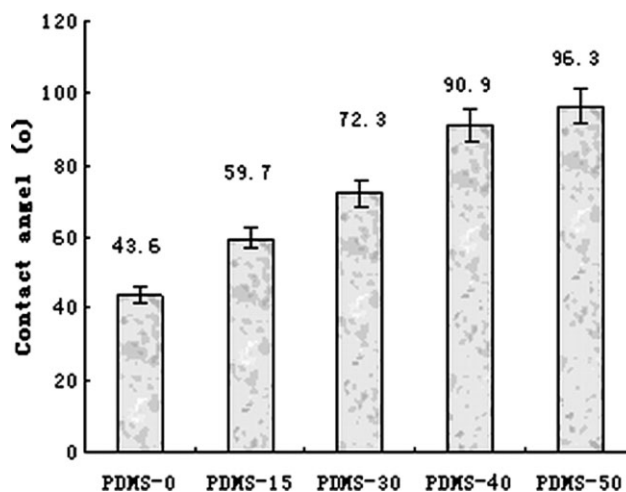
TABLE I
The Atomic Ratio of C/Si in Different Samples

Sample	Element	CPS	Sensitivity	C/Si
PDMS-15	C	2073.8	0.25	4.8
	Si	501.2	0.29	
PDMS-30	C	2354.3	0.25	3.6
	Si	758.6	0.29	
PDMS-40	C	2466.1	0.25	3.0
	Si	953.6	0.29	
PDMS-50	C	2697.8	0.25	2.6
	Si	1203.6	0.29	

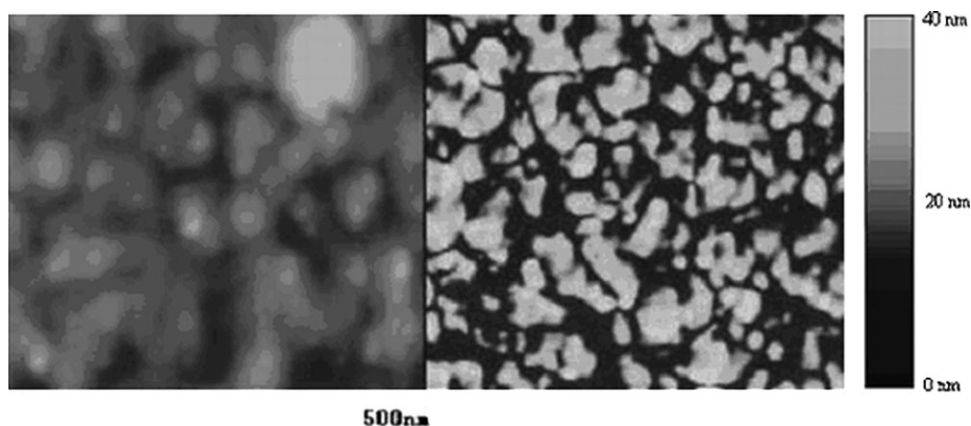**Figure 7** The surface contact angle (water).

Figure 8 AFM image of PDMS-15.

the surface of the membrane was evident, that is to say that the oligomer of MPS-PDMS had been successfully grafted with acrylate in the micelles, and the obvious peak about 402 eV might be ascribed to the present of N element in Gemini surfactant.

From Table I, it could be surveyed that the atomic ratio of C/Si in different samples were lower than the C/Si ratio calculated from the monomer. It is well known that polysiloxane have the phenomenon of surface segregation, the surface segregation of copolymers or their blends is derived by the components with low surface tension.[26] Just because of the surface enrichment property, the atomic ratios of C/Si in all samples were lower than that calculated from the monomer (PDMS-50, 6.9). In addition, the atomic ratio of C/Si decreased with the increase of PDMS content in the system, that is to say, the more PDMS was used, the more obvious of surface segregation could be observed. In the sample of PDMS-50, the atomic ratio of C/Si is 2.6, which very closed to the C/Si ratio of PDMS (2.0), it could be said that

almost the surface of PDMS-50 was covered by PDMS.

Surface hydrophobicity

Polysiloxane have been widely used in textile finishing for imparting desirable properties, such as softness, crease resistance, and particularly water repellency.[27,28] Because of the hydrophobicity and low surface energy of polysiloxane, if the Polysiloxane had been grafted with acrylic particles, the membranes should have higher water contact angle and create hydrophobic surface. While the water contact angle commonly be used as a criterion for the evaluation of hydrophobicity of a solid surface.[29-31]

From Figure 7, it could be observed that the contact angle of water evidently increased with the increase of the content of PDMS, which revealed that the effect of water repellency became more obvious. The results might be ascribed to the
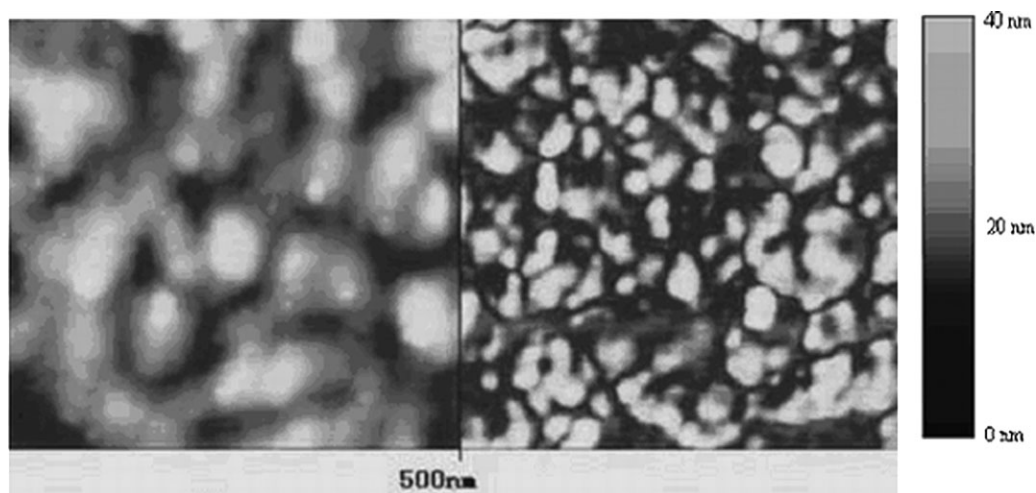

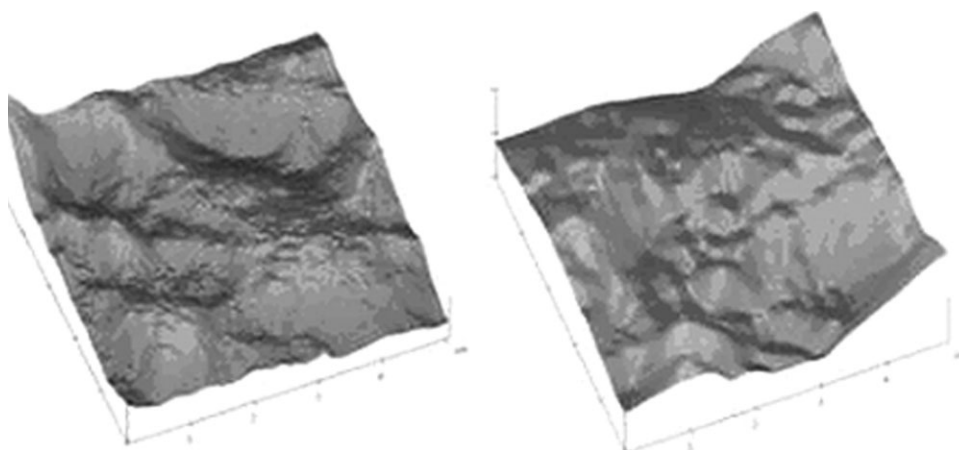**Figure 9** AFM image of PDMS-50 (a,b).

Figure 10 AFM topography mapping images of PDMS-15 (a) and PDMS-50 (b).

enrichment of PDMS on the surface of the particles, which agreed well with the other measurements.

AFM analysis

AFM has become an advanced microscopic method for examining polymer materials for such applications as engineering plastics, paint and coating, rubber, packing, fiber and a wide range of consumer goods. More recently, the spectrum of AFM applications to polymers has been broadened substantially from relatively simple visualizations of morphology to more advanced examinations of polymer structure and properties on a nanometer scale due to the discovery of new AFM capabilities.[32-34]

Figures 8 and 9 showed the AFM images of PDMS-Poylacrylate polymer membrane (PDMS-15 and PDMS-50). The left area of these figures exhibited the roughness of the membranes, the brighter phase was the phase with higher position and the darker phase was the phase with lower position; the right area exhibited the difference of modulus of the membranes, the brighter phase was the phase with higher modulus and the darker phase was the phase with lower modulus.

Because of the property of surface enrichment, the more dosage of polysiloxane used in the experiment, the more surface enrichment would be occurred. It could be seen that the brighter area of roughness phase in Figure 9 was larger than that of Figure 8, agreed well with the above conclusion. Besides, polysiloxane with lower modulus compared with polyacrylate, from these figures, it could be seen that the dark area of modulus phase in Figure 9 was larger than that of Figure 8, accorded with the phenomenon of surface enrichment.

Roughness profiles of PDMS-15 and PDMS-50 were shown in Figure 10(a,b), respectively, the average roughness was described as the distance between the deepest and highest point on the given surface (5×5 μm^2). The analysis showed that the average roughness of PDMS-50 ($R_a = 38.56$ nm) was higher than that of PDMS-15 ($R_a = 29.03$ nm), but the variation in roughness was not distinct (no more than 40 nm). This indicated that the film surfaces were comparatively smooth but with the increase of siloxane contnet, the roughness of the surface became more obvious, the outcome agreed well with the conclusion of contact angle.

CONCLUSION

It has been shown that the copolymer of acrylate and organic siloxane with different content of polysiloxane have been prepared by emulsion polymerisation. Because the oligomer was pre-prepared, almost all the groups of $Si(OCH_3)_3$ have been hydrolyzed, which benefit to the synthesis of latexes, besides, by the introduction of Gemini surfactant, the siloxane content could reach 50%, which is greater than the values reported in other literature.

^{1}H-NMR spectra indicated that when the reaction time was prolonged to 2 h, more than 90% of the —Si $(OCH_3)_3$ were hydrolyzed, FTIR also proved that the conclusion. XPS investigation of membranes with different siloxane content showed that with the increase in PDMS dosage, the C/Si ratio in these samples decreased, that is to say the excellent properties of polysiloxane would be more fully embodied which accorded with the results of contact angle and AFM measurements. All the outcomes from the characterization testified that the siloxane-acrylate copolymer with 50% siloxane was successfully prepared in the experiment.

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