

Synthesis of Dimethyldodecyl Quaternary Ammonium Polyether Polysiloxane and Its Film Morphology and Performance on Fabrics

Qiufeng An,¹ Jie Zhao,¹ Xianqi Li,² Yuanbo Wei,¹ Wen Qin¹

¹Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an 710021, China

²Tangshan Sanyou Silicon Industry, Tangshan 063305, China

Correspondence to: Q. An (E-mail: anqf@sust.edu.cn)

ABSTRACT: A novel comb-like polysiloxane (QPEPS) bearing dimethyldodecyl quaternary ammonium polyether groups (QPEs) was synthesized by reaction of epoxy polyether polysiloxane, which was prepared from polymethylhydrosiloxane (PHMS) and allyl polyether epoxy (APEE500) via hydrosilylation, with N,N-dimethyldodecylamine (DMDA) in the presence of acetic acid (HAc). Chemical structure, film morphology, and performance of the synthesized polysiloxane on cotton and its mimic substrates were investigated by Fourier transform infrared spectrum, nuclear magnetic resonance spectrum, field emission scanning electron microscopy, atomic force microscopy, and so on. As expected, the QPEPS was easily emulsified into a clear, uniform micro-emulsion with a mean size of about 20 nm. Since the presence of a large number of cationic QPEs pendant in the side chains, the QPEPS exhibited microscopic inhomogeneous morphology with many pinnacles projected on the film surface. As a result, the root mean square roughness (Rq) of the QPEPS film reached 0.615 nm in 2 $\mu\text{m} \times 2 \mu\text{m}$ scanning field and the largest height of the pinnacles achieved 7.618 nm. And under the influence of the QPEs, the QPEPS provided the treated fabrics with not only very soft handle, but also excellent hygroscopicity. And the wettability of the treated fabrics reached 1–3 s. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40612.

KEYWORDS: hydrophilic polymers; morphology; polysiloxane; properties and characterization; textiles

Received 13 December 2013; accepted 18 February 2014

DOI: 10.1002/app.40612

INTRODUCTION

Amino-functional polysiloxane is a class of siloxane polymers bearing amino alkyl groups pendant or blocked in the molecular chain or attached at the end of the siloxane backbone. As one of the most popular siloxane softeners in textile industry, amino-functional polysiloxane can impart unique softness, smoothness, silk-like or cotton-like handles to fabrics.^{1–3} However, yellowing tendency and strong hydrophobicity significantly limit the polysiloxane application.^{1,3–6} Moreover, the characteristic orientation of the polysiloxane on fiber substrates also makes the polysiloxane treated fabrics easily loss their hygroscopicity especially after high temperature cure treatment.^{1–6} Therefore, how to improve these performances of amino polysiloxane has attracted the world attentions.

Functional polysiloxanes^{1,3–5,7–11} could usually provide fabrics with distinctive performance and tactile because of the different functional groups in the molecules and the particular film-forming mechanisms of the polysiloxanes on fabrics. For example, introduction of long chain alkyl groups into the polysiloxane could render the treated fabrics with thickening and fluffy

tactile,^{9,11,12} and meanwhile the polyether groups could make the polysiloxane easily be emulsified and be able to confer the textiles with good wettability.^{3–5,7}

Conversion of amino groups into quaternary ammoniums not only limits the yellowing capacity of the amino polysiloxane, but also can improve the polysiloxane oxidation-resistance to heat and light and provide an improved wettability and whiteness as well as antibacterial properties to fabrics.^{6,8,9,13–16} Thus, more and more researches have focused on how to synthesize the quaternary ammonium containing siloxane oligomers and polymers recently.^{13–16} For example, Simionescu¹⁷ and Majumdar^{13,18} synthesized a family of quaternary ammonium containing oligomeric siloxanes or polyhedral oligomeric silsesquioxanes (Q-POSS) by hydrolysis and condensation of quaternary ammonium trimethoxysilane derived from *N*-allyldimethylamine and 3-chloropropyltrimethoxy silane or by hydrosilylation of allyl dimethylamine with a topological octasilane POSS in the presence of Pt-catalyst. Micro-morphology and antimicrobial properties of the Q-POSS oligomers in coating as well as effects of alkyl chain lengths and counter ions on the

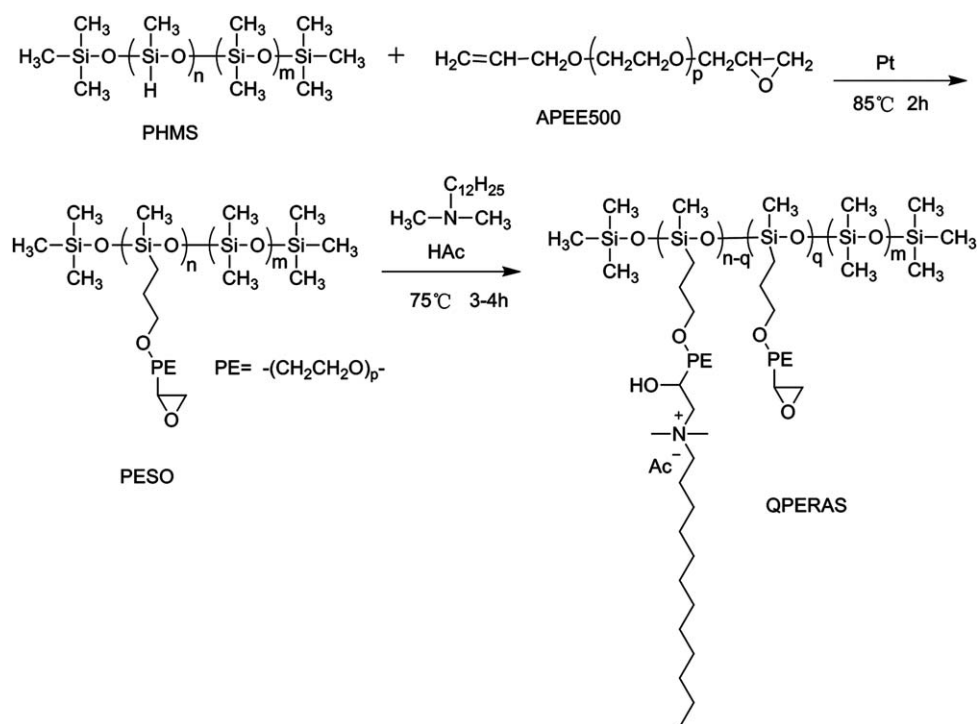


Figure 1. Synthesis route of QPEPS.

performance of the Q-POSS were also investigated in the researches. In addition, Chen⁹ synthesized a QAS silicone by hydrosilylation of polymethylhydrosiloxane with 2-dimethylaminoethyl acrylate first and then quaternization of the resultant polymer with 1-bromohexane in the second step reaction. It was discovered the QAS silicone could provide the celluloses with potent biocidal activities and great washing and UV irradiation stability. However in the reported references,^{9,13,18} all the highlights of the researches were laid on the antibacterial properties, only a little was paid on the softening fabric performance of these materials.

Combination of quaternary ammonium with highly hygroscopic polyether groups could greatly reduce the yellowing tendency of the polysiloxanes and improve the softening, anti-bacterial properties and wettability of the treated fabrics. Accordingly, a novel, comb-like polysiloxane QPEPS with pendant dimethyldodecyl quaternary ammonium polyether groups (QPEs) in the side chains was designed and synthesized in the research. Chemical structure, morphology and performance of the QPEPS on cotton and its mimic substrate, the silicon wafer were investigated by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and the other instruments.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PHMS), with a Si-H content of 0.06 % (the moles of Si-H groups contained in per 100 g of PHMS) and a viscosity of 170 mPa s at 20°C, was obtained from Tangshan Sanyou Silicon Co., Ltd. Allyl polyoxyethylene epoxy ether (APEE500) was kindly obtained from Changzhou Xianran Auxiliaries Co. with an average molecular weight of about 500.

N,N-dimethyldodecylamine (DMDA) was purchased from J&K Scientific Ltd. Glacial acetic acid (HAc), an analytical reagent, was purchased from Xi'an Chemical Reagent Co.. Resins and auxiliaries such as DMDHEU (dimethylol dihydroxy ethylene urea resin), VBL (anionic fluorescent brightener) and Lanasyne Red F-5B 150 (anionic dye) and so on, were kindly supplied by Clariant or Zhejiang Transfer.

The cotton fabric, with yarn counts of 474×235 [the number of warp (w) and filling (f) yarns, 10×10 cm], obtained from Shaanxi Huarun Dyeing & Finishing Co., was washed with acetone by ultrasound at room temperature for 15 min and then rinsed with distilled water, and dried at 100°C and kept in a desiccator until used.

Synthesis of QPEPS

Shown as in Figure 1, QPEPS was synthesized in two-step reaction. First in a three-necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer, 20.00 g 0.06 % PHMS (containing 0.012 mol of Si-H groups) reacted with 6.20 g (0.0124 mol) APEE500 in the catalytic amount of H_2PtCl_6 at 80–85°C for 2 h to give an oily intermediate, an epoxy polyether polysiloxane (PESO). Then the reaction temperature was cooled to 70°C, the tertiary amine, N,N-dimethyldodecylamine (DMDA) and acetic acid (HAc) dissolved in iso-propanol were added to react with the PESO in mole ratios of about 0.5 : 1, 0.8 : 1, 0.9 : 1, 1 : 1, 1.1 : 1 (the ratio of DMDA to epoxy in the intermediate). After the 3–4 h reaction at 70°C, the polymeric resultant was distilled to recovery the iso-propanol and then stripped off the residual solvent by vacuum. Finally, a transparent, viscous polysiloxane with pendant dimethyldodecyl quaternary ammonium polyoxyethylene groups was obtained.

Table I. Dosages of Staples in Synthesis of QPEPS

	PHMS (g)	APEE500 (g)	DMDA (g)	Mole ratios of the epoxy to DMDA
QPEPS-1	20.00	6.20	1.32	1 : 0.5
QPEPS-2			2.12	1 : 0.8
QPEPS-3			2.38	1 : 0.9
QPEPS-4			2.65	1 : 1.0
QPEPS-5			2.91	1 : 1.1

The dosages of the staples in QPEPS synthesis were shown in Table I.

Characterization and Physical Properties of QPEPS

The chemical structures of the intermediate and the resultant polysiloxanes were characterized by Fourier transform infrared spectrum (FTIR) and nuclear magnetic resonance spectrum (¹H-NMR). The FTIR was acquired on a Bruker VECTOR-22 spectrometer, a KBr liquid film. ¹H-NMR analysis was recorded by a Bruker 400 spectrometer, CDCl₃ as a solvent, and tetrathylsilane (TMS) as an internal standard.

The surface tensions of the synthesized polysiloxanes were measured with DCAT surface tensiometer (German Dataphysics Instrument). The viscosity was determined by NDJ-7 rotational viscometer (Shanghai Balance Instrument) at 20 ± 2°C.

Observation of Film Morphology of QPEPS

Sample Preparation. Natural cotton fiber is irregular and rugged on surface and easily distorted in AFM observation.¹⁹ So, an oxidized, rigid silicon wafer with many Si–OH groups on the wafer surface (the treatment procedure shown in the Ref. 12) was used as a mimic substrate to investigate the film morphology and microstructure of the QPEPS. And the samples were prepared as follows:

0.0300 g of the QPEPS was dissolved in ethyl acetate to form a 0.03% QPEPS solution. The silicon wafer and cotton fabric samples were vertically dipped in the 0.03% QPEPS solution for several seconds, then dried at 105°C for 5 min, cured at 160°C for 1 min, and finally conditioned in a desiccator for 24 h at room temperature.

Observation of Film Morphology. Micro-morphology of the QPEPS coated on an oxidized wafer or cotton substrates was investigated by AFM and FESEM. The FESEM photographs were acquired on a Sirion 200 FESEM (FEI) after the fabrics coated with gold in a vacuum. The amplifications of photographs were respectively 100, 5000, and 20,000 times based on the originals. High resolution AFM images of the QPEPS on wafer substrates were acquired by Nanoscope IIIA atomic force scanning microscope (Digital Instrument) at 22°C in air with relative humidity of 48%. And all the scanning was performed in tapping mode.

Evaluation of Performance of QPEPS on Fabrics

Emulsification of the QPEPS. To make sure all of the QPEPSs easily dispersed into water to be miscible, the QPEPSs were emulsified as follows. 20.0 g QPEPS was mixed with 4.0 g

iso-propanol vigorously to form a diluted solution, then 0.5 mL glacial acetic acid and 108.8 g distilled water were added respectively. After a period of well-mixing and by help of homogenizer, a clear, transparent micro-emulsion was obtained with a pH of about 6–7 and a solid content of 15%. Then, the mean sizes and the distribution of the micro-emulsion particles were measured by H-600 transmission electron microscope (Hitachi Company, Japan).

Fabric Treatment and Measurement of Performance. In this procedure, 2.0 g 15% QPEPS micro-emulsion was diluted with 100.0 g H₂O to form a finishing bath. A piece of 16 cm × 13 cm (w × f) fabric was impregnated in the bath for several seconds, then padded to wet pick-up of about 70%, then dried at 100–105°C for 10 min and cured at 160°C for 30 s, finally air-conditioned at 20 ± 2°C and at 65% relative humidity for 24 h. The performance of the treated fabrics was measured as follows.

The bending rigidity (BR) was measured with a DC-RRY1000 computer controlled rigidity tester (Jinan Deruik Instrument). The smaller the BR is, the softer the fabric. The whiteness was determined with YQ-Z-48B digital fluorescent whiteness meter (Shanghai Xinrui Instruments). Wettability, expressed by the time of the fabric absorbing one drop of water (25 drops = 1 g), was evaluated according to the reference.¹⁹ The shorter the time, the better the wettability is. The water contact angle (CA) was measured by a JC 2000C static contact angle test instrument (Shanghai Zhongchen Digital Technology Equipment) at 20 ± 2°C. The water droplet volume is 5 μL, and the contact time of the water with the treated substrates was 2–6 s.

In addition, the compatibility of the QPEPS with different resins or auxiliaries used in textile industry was evaluated in the follow method: 15% the QPEPS micro-emulsion was diluted with water to form a finishing bath containing 2% of the polysiloxane, and then mixed with the tested resin or auxiliary solution in the same amount. After well stirring, the mixture was kept at the room temperature to observe whether there was any change in the mixing system.

RESULTS AND DISCUSSION

Chemical Structure of QPEPS

In this procedure, the QPEPS-4 was used as an example.

IR and ¹H-NMR can give us information about the structures or functional groups of the polysiloxanes.^{1,7,8,12–15} Obviously from Figure 2, the IR spectra of QPEPS-4 and its precursors, it can be discovered that the characteristic absorption band attributed to Si–H groups had disappeared from the intermediate, the epoxy polyether polysiloxane (PESO) and the target, the quaternary ammonium polyether polysiloxane (QPEPS-4). In accord with this, the signals at about 2870 cm⁻¹ due to the C–H vibration of –CH₂– and at 1110 cm⁻¹ due to the polyether C–O vibration enhanced at the peak intensity, which should result from a large number of polyether groups bonded in the side chains of PESO or from the pendant dimethyldodecyl quaternary ammonium polyoxyethylene groups in QPEPS-4.

Figure 3 shows ¹H-NMR spectrum of QPEPS-4 and the partial spectrum of PESO. The peaks at δ_H 0.45 indicated that Si–CH₂

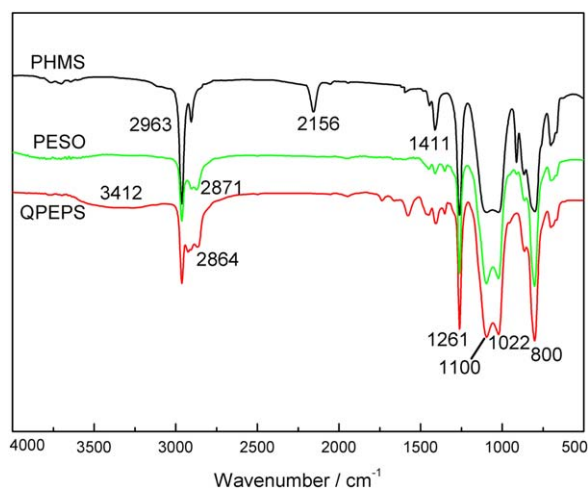


Figure 2. IR spectra of QPEPS-4 and the precursors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

had presented in the QPEPS-4 and PESO. In the PESO molecule, the absorptions attributed to epoxy $-CH-$ and $-CH_2-$ groups respectively appeared at δ_H 2.52, 2.71, and 3.06, while the strong signals belonged to $-(CH_2CH_2O)_n-$ occurred at δ_H 3.6, indicating the epoxy polyether group had been bonded into the intermediate polysiloxane. But after the reaction of PESO with DMDA, the signals at the range of δ_H 2.52–3.06 (attributed to epoxy) faded away, illustrating that the epoxy groups had reacted with DMDA and been converted into the expected quaternary ammonium groups. As a result, a series of new signals belonged to QPEs were respectively observed at δ_H 3.22 [$N^+(CH_3)_2-$, hH], 3.33 [N^+CH_2CHOH- , gH], 3.58 [$N^+CH_2CH_2-$, iH, and dH). All these are very consistent with the reported 1H -NMR results about the quaternary ammonium groups,^{8,9,13} indicating dimethyldodecyl QPEs have been really bonded into the resultant polysiloxane, the QPEPS.

Physical Properties of QPEPS

Linking the dimethyldodecyl QPEPS into the polysiloxane skeleton will perhaps lead the surface tension, solubility and emulsifying ability of the polysiloxane to be changed. Thus, the physical properties of the synthesized polysiloxanes, PESO and the QPEPSs, were investigated, and the results were shown in Table II.

Like the other polysiloxanes in nature,²⁰ PESO and the QPEPSs are still low surface tension materials and of surface tensions about 18–22 mN/m, although the long hydrophilic polyether and the quaternary ammonium groups linked in the molecule could partially cause the polysiloxane surface tension to somewhat increase. From Table II, it could be discovered that under the influence of the quaternary ammonium polyether groups, the miscibility of the intermediate and the resultant polysiloxanes had been significantly improved. As a result, the PESO and the QPEPSs were miscible in water and easily converted into transparent micro-emulsions with mean sizes of about 20 nm in diameter (shown as Figure 4) by the aid of iso-propanol. However, the mole ratio of the epoxy in PESO to DMDA had an effect on viscosity and stability of the resultant polysiloxane. As the mole ratio of epoxy to DMDA increased from 1:0.5 to 1 : 1,

the viscosities of the QPEPSs decreased greatly and meanwhile the stability of the polysiloxanes was improved. Obviously, the residual large number of epoxy groups in the target polysiloxanes (such as in QPEPS-1/-2) caused the polysiloxanes to be unstable and easily to gel in reaction or in storage. In the experiments, we also discovered when the mole ratio of epoxy to DMDA achieved to or exceeded 1 : 1, the synthesized polysiloxanes, such as QPEPS-4/-5, not only had suitable viscosities in the range of 5600 to 5700 mPa s, but also possessed good stability and miscibility in water since the epoxy groups were fully consumed in reaction and the cross-linking side reaction from the epoxy groups and hydroxyls had been prohibited. In such a case, the QPEPSs were easily emulsified into stable and transparent micro-emulsions and of particle sizes of about 20 nm. Obviously, these behaviors are very similar to those of amino silicones and polyether polysiloxanes.^{1,3–7}

Allowing some of the epoxy groups to residue in the QPEPS side chains was favorable for the polysiloxane to form a cross-linked film, which would contribute to softness and elasticity but easily cause the polysiloxane to gel in vacuum treatment (Table II) and to obtain a less stability and a high viscosity in product storage. Thus, the QPEPS-4 with a mole ratio of epoxy to DMDA about 1 : 1 in synthesis was chosen as the tested sample in the following evaluation.

Film Morphology of QPEPS

Chemical structure has a great influence on micro-morphology of film-forming materials and could subsequently exert a significant effect on performance of functional polysiloxanes in utilization. In previous study, we found bonding long alkyl groups such as dodecyls into the polysiloxane molecule could cause the target polysiloxane to generate an inhomogeneous film with many pinnacles on the treated substrates,^{11,12} and it was those paraffin alkyl pinnacles that conferred an unique thickening and fluffy tactile to fabrics.^{8,9,11,12} Similar to the dodecyl polysiloxane in film-forming mechanism, the dimethyldodecyl quaternary ammonium polyether polysiloxane, the QPEPS-4, also exhibited an uneven, rugged morphology in AFM observation (Figure 5). And there were many pinnacles-likes scattered on the treated wafer surface, evidently which derived from a large

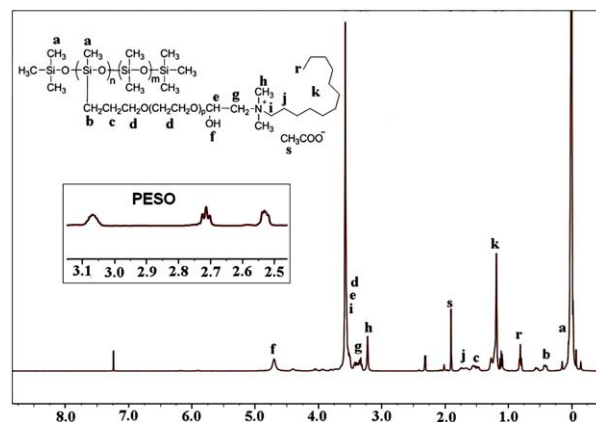


Figure 3. 1H -NMR spectra of QPEPS-4 and PESO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Surface Tension, Viscosity, and Stability of the Synthesized Polysiloxanes

	Mole ratio of epoxy to DMDA	Surface tension (mN/m)	Viscosity (mPa s)	Stability	Miscibility of QPEPS in H ₂ O
PHMS		20.84	170	☼	⊗
PESO		20.85	3200	☼	○
QPEPS-1	1 : 0.5	18.66	9800	Gel after a week	○
QPEPS-2	1 : 0.8	20.25	6300	Gel after 1–2 months	○
QPEPS-3	1 : 0.9	20.80	5700	☼	○
QPEPS-4	1 : 1.0	21.09	5620	☼	○
QPEPS-5	1 : 1.1	21.19	5600	☼	○

☼, stable; ○, miscible in water; and ⊗, insoluble.

number of dimethyldodecyl quaternary ammonium polyether group pendant in the polysiloxane side chains.

Because the epoxy polyether groups were introduced in blocked way in synthesis of the intermediate, PESO, the paraffin pinnacle bundles resulted from the aggregates of dodecyl QPEPS were more or less strong. Accordingly, the root mean square roughness (R_q) of the QPEPS-4 reached 0.615 nm in $2\ \mu\text{m} \times 2\ \mu\text{m}$ scanning field. And the largest height of the pinnacles achieved 7.618 nm. By mean of theoretical calculation, we found the whole length of dimethyldodecyl quaternary ammonium polyoxyethylene groups, $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OCH}_2\text{CH}_2)_9\text{OC}_3\text{H}_6^-$, was about 6.972 nm in length, which was very approximate to the largest pinnacles in height. This gives us a proof that the pinnacles in the QPEPS AFM image maybe really resulted from the upstanding aggregates of long alkyl quaternary ammonium polyether groups.

Rough morphology was beneficial for water to spread on rugged hydrophilic substrates.²¹ In accord with this, the water contact angle on the QPEPS-4 treated silicon wafer was near 0 and the wettability of the treated cotton fabrics reached 1.73 s.

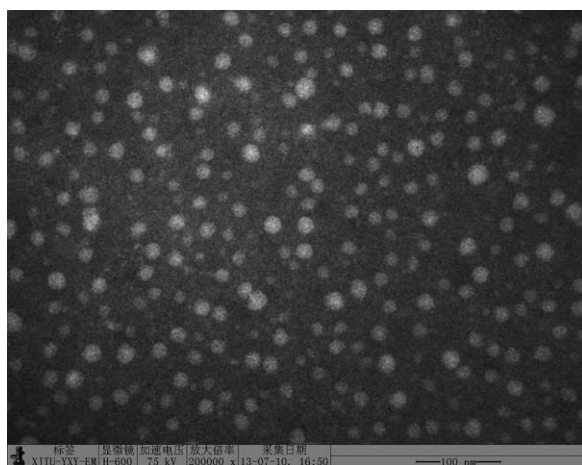


Figure 4. TEM image of QPEPS-4 micro-emulsion particles.

Obviously, very easily wetted fabrics were created by hygroscopic QPEPS-4 and the homologous.

Figure 6 shows FESEM photographs of the fabrics treated or untreated by QPEPS-4. At magnification of 5000 and 20,000 times, a more or less relatively smooth resin film (from the macroscopic point of the view) generated from the QPEPS-4

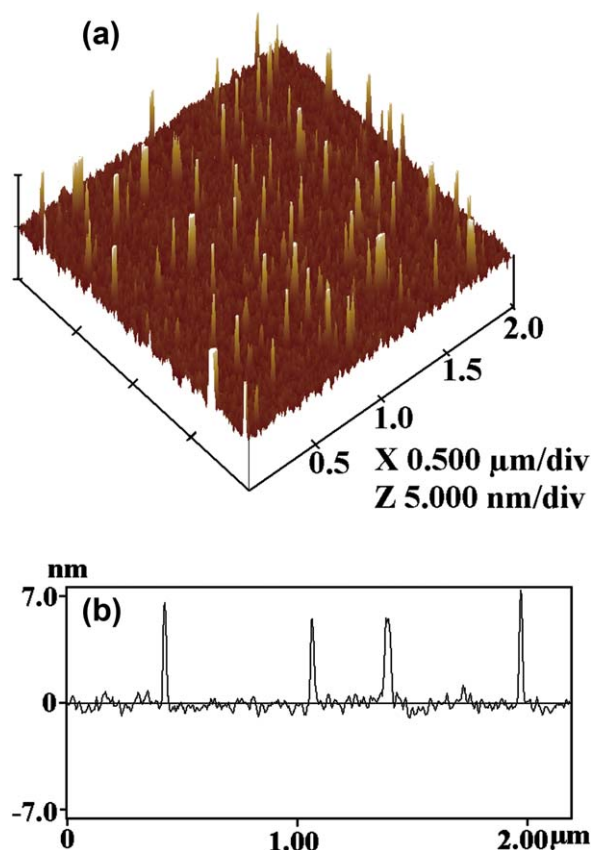


Figure 5. AFM images of QPEPS-4 on an oxidized silicon wafer. (a) Three dimensional image. (b) The surface profile along a line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

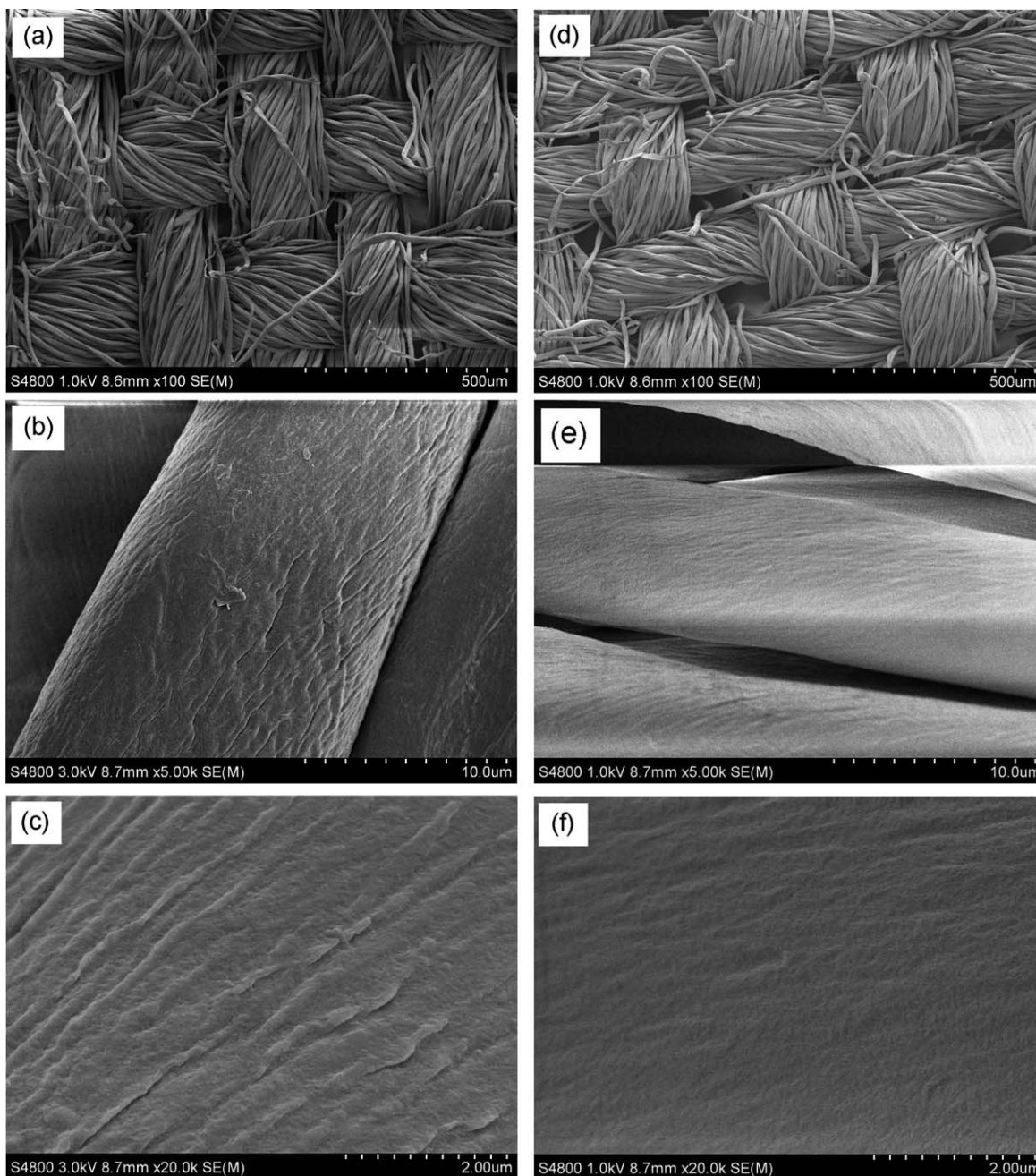


Figure 6. The SEM images of the treated and untreated cotton fabric. (a, b, c) The control, untreated cotton fabric. (d, e, f) The cotton treated by QPEPS-4.

was clearly observed from the treated fiber surface. The macroscopic smooth film was benefit for the treated fibers to show good friction-reduce property and fabric-softening performance.^{1–5} But from the microscopic point of view, the QPEPS film was actually rough and uneven in morphology and very hydrophilic. Thus, as such a film sheathed the fibers, it could not only increase the distance among the fiber bundles, but also be helpful to produce a thick or fluffy and soft tactile on fabrics.^{8,9,11,12} Therefore, combination of macro- and micro-morphology of the QPEPS and delicate balance of the structure and functional groups finally allowed the QPEPS to create the

treated fabrics with good softness, fluffy tactile and good wettability.

Performance and Compatibility of QPEPS

By combination of long alkyl quaternary ammonium groups with the polyether groups can improve the hygroscopicity and inhibit the yellowing tendency of amino polysiloxane greatly. Moreover, the cationic quaternary ammonium group is beneficial for the polysiloxane electrostatically bonded and oriented onto the negatively charged fiber surface and to exhibit good softness and tactile.

Table III. Performance of Cotton Fabrics Treated by the QPEPSs

	BR (mN)		Whiteness (°)	CA (°)	Wettability (s)
	W	f			
PESO	738	328	82.63	81	9.51
QPEPS-1	724	306	82.57	56	2.84
QPEPS-2	890	309	82.21	37	2.51
QPEPS-3	597	296	82.34	-	1.94
QPEPS-4	618	290	82.36	-	1.73
QPEPS-5	665	289	82.22	-	2.12
The control	1049	424	82.82	-	0.53

The control, untreated cotton fabric; BR, bending rigidity; CA, the water contact angle on the treated fabric; -, cannot be measured by static contact angle test instrument.

Table III illustrates the performance of cotton fabrics treated by the QPEPSs. Clearly, the new synthesized polysiloxanes had the expected performance properties. The QPEPSs could decrease the bending rigidity of the treated fabrics from 1049 mN (w) and 424 mN (f) before treatment (the control) to 597 mN (w, QPEPS-3) and 289 mN (f, QPEPS-4) after treatment, and conferred the fabrics with wettability of about 1–3 s. It is good wettability that let the water contact angles not be determined

Table IV. Compatibility of QPEPS with Resins and Auxiliaries

	QPEPS-4
Appearance	Transparent microemulsion
Stability to a weak acid or base	
5% NH ₃ ·H ₂ O	No change
5% HAc	No change
Compatibility ^a with anionic resin or auxiliary	
2.0% aqueous sodium dodecyl benzene sulfonate solution	No significant change
1.0% aqueous sodium alkyl polyether sulfate solution	No change
1.0% VBL aqueous solution	Flocculent precipitate
1.0% BTCA solution	Flocculent precipitate
0.5% anionic Lanasy Red F-5B 150 aqueous solution	Turbidity, creaming
Compatibility ^a with non-ionic, cationic resin or auxiliary	
5% DMDHEU resin	No change
1% 1831 aqueous solution	No change
1% amphoteric carboxyl methyl imidazoline aqueous solution	No change

^aMixing 2% diluted QPEPS micro-emulsion with the tested solution in the same amount.

HAc, acetic acid; VBL, anionic fluorescent brightener; BTCA, 1,2,3,4-butanetetracarboxylic acid; Lanasy Red F-5B 150, an anionic dye; DMDHEU, dimethylol dihydroxy ethylene urea; 1831, octadecyltrimethylammonium chloride.

on the fabrics treated from QPEPS-3 to QPEPS-5. Besides, the whiteness for all the QPEPS treated fabrics changed little and the values, from 82.57 for QPEPS-1 to 82.21 for QPEPS-5, were very near to that of the untreated fabric, 82.82. All indicate that the QPEPSs had softening fabric properties and low yellowing tendency, and could provide the treated fabrics with softness, good wettability and whiteness.

In addition, compatibility of the QPEPSs with resins or auxiliaries used in textile industry was also investigated. Shown as the results in Table IV, the QPEPS-4 had good compatibility with non-ionic and cationic resins or auxiliaries, but was incompatible with the anionics or anionic dyes in aqueous solution. When mixed with non-ionic or cationic resins and auxiliaries such as DMDHEU or octadecyl trimethyl ammonium chloride solution in finishing bath, the diluted QPEPS-4 micro-emulsion showed no change in the state and appearance. However, when mixed with anionic resins or dyes, such as VBL (a fluorescent brightener), or BTCA (1,2,3,4-butanetetracarboxylic acid), or Red F-5B 150 (an anionic dye) in finishing bath, the QPEPS-4 reacted with these anionic resins or dyes, and generated flocculent precipitates or creaming in mixing, which obviously resulted from strong interaction among positively charged polysiloxanes and negatively charged resins or dyes. But unlike the situation occurred in anionic resins and dyes, the QPEPS-4 was compatible with anionic surfactants such as sodium dodecyl benzene sulfonate solution and exhibited little changes when mixed. Clearly, strong hydration effect derived from polyether segments in the polysiloxane molecule played an important role in the process.

CONCLUSIONS

A comb-like polysiloxane (QPEPS) with pendant dimethyldodecyl QPEPS was designed and synthesized in the research. As expected, the QPEPS possessed low surface tension of 18–22 mN/m and was easily emulsified into a transparent micro-emulsion with a mean size of about 20 nm. Under the influence of the hydrophilic dimethyldodecyl quaternary ammonium polyether groups, the QPEPS formed a macroscopic smooth but actually microscopic rugged film on the treated substrate surface. There were many pinnacles, which might be resulted from dimethyldodecyl quaternary ammonium polyether groups, scattered on the film surface. Consequently the R_q of the QPEPS film reached 0.615 nm in 2 μm × 2 μm scanning field and the largest height of the pinnacles achieved 7.618 nm. Characteristic structure and rugged film morphology made the QPEPS easily exhibit a soft, fluffy, and comfortable tactile on the treated fabrics and provide the fabrics with wettability of about 1–3 s.

REFERENCES

- Xu, Y. J.; Yin, H.; Yuan, S. F.; Chen, Z. R. *Appl. Surf. Sci.* **2009**, *255*, 8435.
- Burrell, M. C.; Butts, M. D.; Derr, D.; Genovese, S.; Perry, R. *Appl. Surf. Sci.* **2004**, *227*, 1.
- An, Q. F.; Li, L. S.; Huang, L. X.; Chen, K. C. *AATCC Rev.* **2006**, *6*, 39.
- Song, X. Y.; Zhai, J.; Wang, Y. L. *Col. Interf. Sci.* **2006**, *298*, 267.

5. Joyner, M. M. *Text Chem Colorist* **1986**, 18, 34.
6. Czech, A. M.; Sabia, A. *J. Am Dyestuff Rep* **1993**, 9, 58.
7. An, Q. F.; Wang, Q. J.; Wang, Y.; Huang, L. X. *Fiber Polym* **2009**, 10, 40.
8. Hou, A. Q.; Shi, Y. Q. *Mater. Sci. Eng. B* **2009**, 163, 99.
9. Chen, Y.; Niu, M. Q.; Yuan, S.; Teng, H. *Appl. Surf. Sci.* **2013**, 264, 171.
10. Hao, L. F.; An, Q. F.; Xu, W. *Fiber Polym* **2012**, 13, 1145.
11. An, Q. F.; Wang, K. F.; Jia, Y. *Appl. Surf. Sci.* **2011**, 257, 4569.
12. An, Q. F.; Cheng, G. W.; Li, L. S. *J. Appl. Polym. Sci.* **2006**, 101, 4480.
13. Majumdar, P.; Lee, E.; Gubbins, N. *Polymer* **2009**, 50, 1124.
14. Gong, S. Q.; Niu, L. N.; Kemp, L. K.; Yiu, C. K. Y. *Acta Biomater.* **2012**, 8, 3270.
15. Fouda, M. M. G.; Abdel-Halim, E. S.; Al-Deyab, S. S. *Carb. Polym.* **2013**, 92, 943.
16. Munoz-Bonilla, A.; Fernandez-Garcia, Marta. *Prog. Polym. Sci.* **2012**, 37, 281.
17. Simionescu, B.; Bordianu, I. E.; Aflori, M.; Doroftei, E.; Mares, M.; Patras, X.; Nicolescu, A.; Olaru, M. *Mater. Chem. Phys.* **2012**, 134, 190.
18. Majumdar, P.; Lee, E.; Gubbins, N.; Christianson, D. A.; Stafslie, S. J.; Daniels, J.; Vander Wal, L.; Bahr, J.; Chisholm, B. J. *J. Com. Chem.* **2009**, 11, 1115.
19. Gunnars, S.; Wagberg, L.; Stuart, M. A. C. *Cellulose* **2002**, 9, 239.
20. Noll, W. In *Chemistry and Technology of Silicones*; Academic Press: New York, **1968**; pp 467.
21. An, Q. F.; Yang, F.; Cao Z.; Li, X. Q.; Hao L. F.; Huang, L. X. *Polym. Mater. Eng. (Chinese)* **2011**, 27, 69.