

Synthesis and Morphology of Carboxylated Polyether-*block*-polydimethylsiloxane and the Supermolecule Self-Assembled from It

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ABSTRACT: In this research, hydroxyl-terminated polyether-*block*-polydimethylsiloxane (PESO) was synthesized as an intermediate through the hydrosilylation of Si-H-terminated polydimethylsiloxane with allyl polyoxyethylene polyoxypropylene ether. Then, carboxylated polyether-*block*-polydimethylsiloxane (CPES) was prepared through the reaction of maleic anhydride with PESO. First, the chemical structures of the synthesized polysiloxanes were characterized with IR and $^1\text{H-NMR}$ spectroscopy, and then the film morphology of CPES and the supermolecule self-assembled from CPES and *N*- β -aminoethyl- γ -aminopropyl polydimethylsiloxane (ASO-1) was investigated by atomic force microscopy in detail. Experi-

mental results indicated that the superpolysiloxane that self-assembled from CPES and ASO-1 showed a film morphology very different from those of CPES and ASO-1. There were not only many small, bright dots but also some big and marvelous dots circled by dots on the film surface. The morphology of dots circled by dots was estimated to result from aggregates of CPES micelles adsorbed onto the curled ASO-1 molecule interface. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2595–2600, 2008

Key words: morphology; polysiloxane; self-assembly; structure; supramolecular structures

INTRODUCTION

Supermolecules self-assembled from different functional siloxanes or polysiloxanes have attracted worldwide attention recently for their innovative properties and potential applications in fields including superhydrophobic nanoparticle films, molecular devices and systems, mesostructures, nanocluster catalysts, bioactive capsules for medical transfer and diagnosis, and nanotubes.^{1–5} However, little data have been reported about polyether-functional polysiloxanes and their modification products used as architectural units to build up novel superpolysiloxane molecules and their film morphology and performance.

Amino-functional polysiloxane,^{6–8} one of the most popular siloxane softeners in the textile industry,

can impart unique soft, smooth, silk-like handling and improved mechanical properties to treated fabrics. However, compounded cationic amino-substituted polysiloxane with anionic functional polysiloxane in (emulsion) applications has been considered taboo for a long time because the compounded system is unstable and easily causes precipitation. However, we recently discovered that precipitation could be avoided through the mixing of amino-functional polysiloxane with hydrophilic carboxyl-modified polyether polysiloxane. The new mixture system not only is stable but also can provide improved performance properties and a novel finishing style to treated fabrics. Why does this occur? Are the new performance and finishing style associated with the particular film morphology of the prepared polysiloxane system?

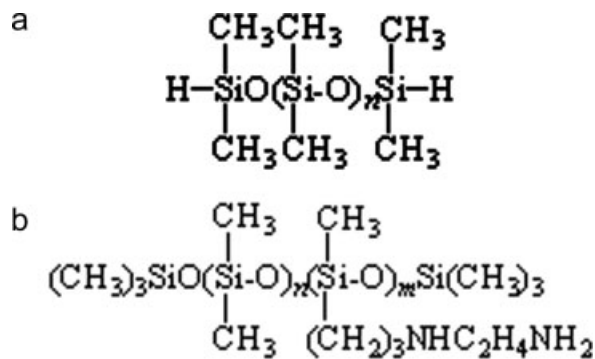
In this article, the preparation of carboxyl acryl polyoxypropylene polyoxyethylene oxypropyl-*block*-polydimethylsiloxane [also known as carboxylated polyether-*block*-polydimethylsiloxane (CPES)] and a superpolysiloxane (CPES/ASO-1) molecule self-assembled from it and *N*- β -aminoethyl- γ -aminopropyl polysiloxane (ASO-1) is reported for the first time. Moreover, the film morphology and microstructures of CPES and CPES/ASO-1 were investigated by atomic force microscopy (AFM) in detail. As a result, a series of marvelous micromorphology images were obtained in this research.

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Scheme 1 Chemical structures of (a) PHMS and (b) ASO-1.

EXPERIMENTAL

Materials and reagents

Si-H-terminated polydimethylsiloxane [PHMS; Scheme 1(a)] was telomerized⁹ and characterized with IR and ¹H-NMR. The Si-H content was 0.08 mmol/g; it was determined by quantitative IR spectroscopy¹⁰ and expressed as the moles of Si-H groups per gram of PHMS. The average molecular weight of PHMS was about 2410, which was calculated from the integration area of Si-H at δ 4.7 to Si-CH₃ at δ 0.05 in the ¹H-NMR spectrum of PHMS.

ASO-1 [Scheme 1(b)] had an amino content of 0.5905 mmol of NH/g of ASO-1, a number-average relative molecular weight of 14,100, and a mass-average relative molecular weight of 37,500 (measured with a Waters gel permeation chromatography instrument (Waters Co., Milford, MA) using tetrahydrofuran as an eluent and polystyrene of a narrow average molecular weight as a reference sample).

Allyl polyoxyethylene polyoxypropylene ether (F6), with an average molecular weight of approximately 1250, was purchased from Nanjing Well Chemical Corp. (Nanjing, China). Maleic anhydride (MAN), an analytical reagent, was bought from Aldrich (Sigma-Aldrich, Shanghai, China). Ethyl acetate, an analytical reagent, was purified before use by distillation. Silicon wafers, kindly supplied by Jinghua Electronic Material Co. (Shanghai, China), were washed and dried according to the literature.¹¹

Synthesis of CPES (Scheme 2)

In a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer, a mixture of PHMS and F6 in a molar ratio of 1 : 2 was added and gently stirred and then bubbled by N₂ for 5–10 min. When the mixture was heated to 75–80°C under N₂ protection, a catalytic amount of H₂PtCl₆ in an isopropyl alcohol solution was added. The mixture was maintained at 80–100°C for 4–6 h and then evaporated at a reduced pressure to strip off the low-boiling-point impurities. Finally, a clear, viscous fluid, hydroxyl-terminated polyether-*block*-polydimethylsiloxane (PESO), was obtained and used as an intermediate in the following procedure.

In another clean three-necked flask charged with a mechanical stirrer, a reflux condenser, and a thermometer, some PESO was added and heated to about 70°C, and then some MAN was added in a PESO/MAN molar ratio of 1 : 1.2. In the presence of a small amount of sulfonic acid as a catalyst, the mixture was maintained at 70–75°C for another 3 h. Then, the mixture was cooled to room temperature and thoroughly washed with xylene and chloroform as solvents, respectively. After the residual solvents were removed by a vacuum, a light yellow to brown fluid (CPES) was obtained.

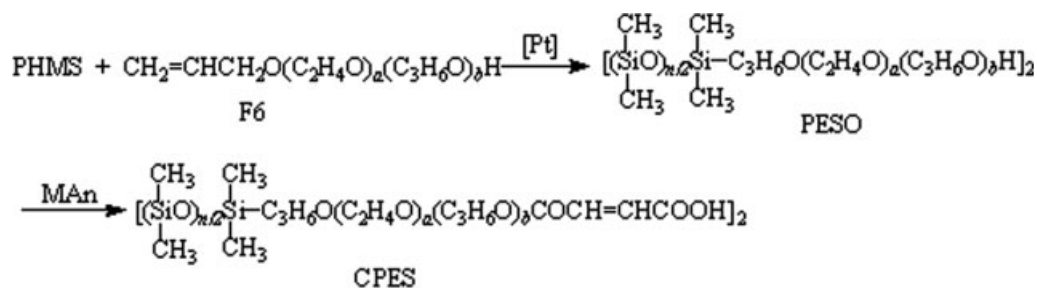
Characterization

IR spectroscopy was performed on a Bruker Vector-22 spectrometer (Bruker GmbH Co., Osnabrückerland, Germany) with a KBr liquid film. ¹H-NMR spectra were recorded with an Inova 400 spectrometer (Varian Co., Palo Alto, CA); CDCl₃ was used as a solvent, and tetramethylsilane was used as an internal standard.

Film morphology of CPES and the superpolysiloxane molecule self-assembled from CPES and ASO-1

Film preparation

CPES (0.0164 g) and 0.0131 g of ASO-1 (accurate to 0.0001 g) were placed in a beaker and dissolved with 98.43 g of redistilled ethyl acetate as a solvent



Scheme 2 Synthesis of CPES.

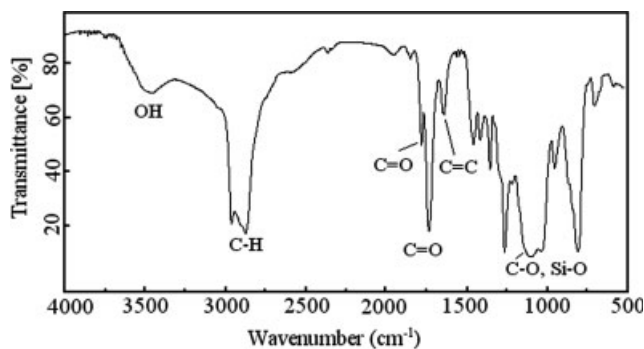


Figure 1 IR spectrum of CPES.

to form a diluted, well-mixed polysiloxane solution with a mass concentration of about 0.03%. The clean silicon wafer was immersed in the freshly prepared polysiloxane solution for a couple of seconds, pulled out, and immediately dried at 100°C for 10 min, and then it was cured at 160°C for 2 min. After it was balanced in a desiccator at room temperature for 24 h, a superpolysiloxane film (CPES/ASO-1) self-assembled from CPES and ASO-1 anchored on the silicon wafer surface was obtained.

With reference to the aforementioned method, CPES and ASO-1 films, immobilized on the silicon wafer surface, were prepared and used as controls for CPES/ASO-1 in the morphology study.

Morphology observations

The film morphology and precise microstructure of the self-assembled superpolysiloxane film as well as its control films were observed with a Nanoscope IIIA atomic force scanning microscope (Digital Instruments, Inc., Tonawanda, NY) at 22°C and 48% relative humidity in air. All scanning was performed in the tapping mode.

RESULTS AND DISCUSSION

Characterization results of CPES

The molecular structure can influence the film morphology. Therefore, the chemical structures of the synthesized polysiloxanes were characterized with IR and NMR spectroscopy.

If we compare the IR spectrum of CPES (Fig. 1) with the IR spectrum of PHMS (Fig. 2), we can see that the absorption band due to residual Si-H groups at 2150 cm⁻¹ is not present anymore in the IR spectrum of CPES, but new absorption bands have emerged at 3480 (ν_{O-H}), 1640 (ν_{C=C}), 1729 (ν_{C=O}, -COOH), and 1781 cm⁻¹ (ν_{C=O}, -COOR). The broad, weak absorption band at 3480 cm⁻¹ should be derived from the O-H stretching vibration of the hydroxyl of -COOH in CPES. The sharp, moderately intense absorption band at 1640 cm⁻¹ is

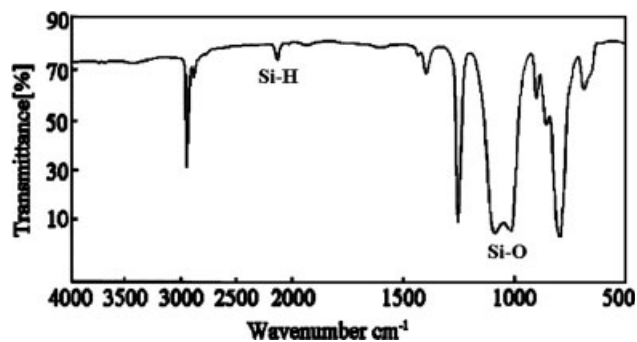


Figure 2 IR spectrum of PHMS.

due to the conjugated C=C stretching vibration. Because the characteristic carbonyl absorptions due to the precursor, MAn, occur at 1850 (strong, ν_{C=O}) and 1800 cm⁻¹ (strong, ν_{as} C=O),¹² the absorption bands at 1729 (ν_{C=O}, -CH=CHCOOH) and 1781 cm⁻¹ (ν_{C=O}, -CH=CHCOOR) have been estimated to possibly result from the C=O groups of the conjugated carboxyl and conjugated ester functionalities of CPES.

In Figure 1, the intensity of the absorption band at 2860 cm⁻¹ due to the C-H stretching vibration of the -CH₂- groups is broader than that of PHMS or the reported polysiloxane.¹² The shoulder peak occurring in the range of 1100–1020 cm⁻¹ also differs from those of functional polysiloxanes¹² and PHMS. The intensity of the absorption band at 1100 cm⁻¹ clearly increases, and this obviously results from a great number of C-O bonds and Si-O bonds in CPES molecules and their overlapping absorption positions.

Figure 3 shows the ¹H-NMR spectrum of CPES and its analysis results. The chemical shift signals associated with the terminal functional group, carboxyl acryl polyoxypropylene polyoxyethylene oxypropyl (in short, carboxylated polyether), appear in

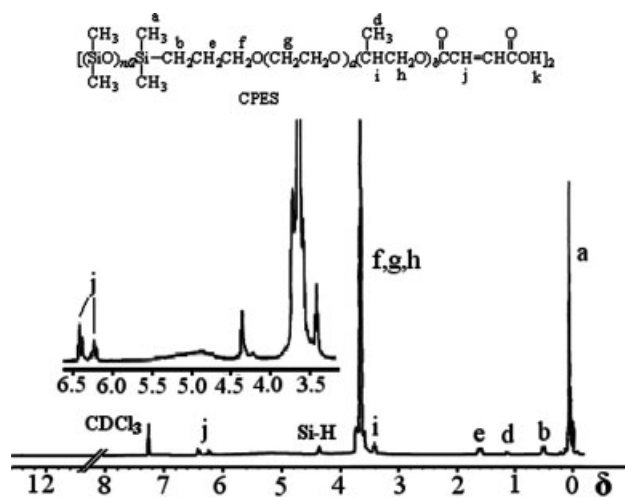


Figure 3 ¹H-NMR spectrum of CPES.

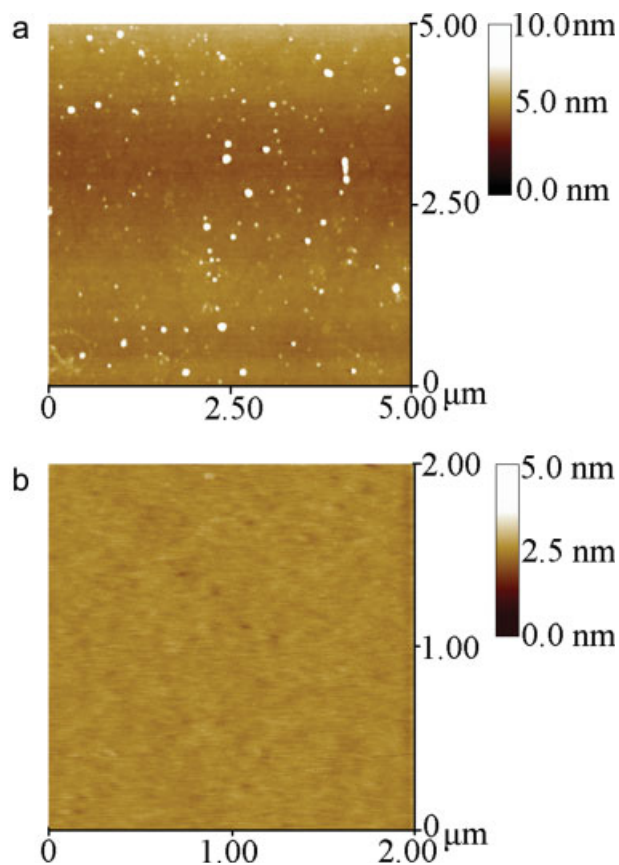


Figure 4 Flattened AFM images of (a) CPES and (b) ASO-1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the region of $\delta 0.45$ to $\delta 6.47$. The weak signal at $\delta 0.45$ (bH) is attributed to the SiCH_2- , whereas the multiplets occurring at $\delta 1.2$ (dH), $\delta 3.3$ (iH), and $\delta 3.7$ (gH) belong to the protons from $\text{C}-\text{CH}_3$, $-\text{OCH}(\text{CH}_3)\text{CH}_2-$, and $-\text{OCH}_2\text{CH}_2-$ groups, respectively. Signals at $\delta 6.15$ and $\delta 6.47$ (jH) demonstrate that the $-\text{CH}=\text{CH}-$ group was successfully bonded in the CPES molecule.

Although the $^1\text{H-NMR}$ signal at $\delta 10.5$ to $\delta 12$ due to $-\text{COOH}$ is not clearly shown in Figure 3 (possibly influenced by a solvent effect or other factors), the spectra from Figures 1–3 still indicate that $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{O}-$, polyether groups such as $-\text{OCH}(\text{CH}_3)\text{CH}_2-$ and $-\text{OCH}_2\text{CH}_2-$, and the conjugated carboxyl ($-\text{CH}=\text{CH}-\text{COOH}$) and conjugated ester ($-\text{CH}=\text{CH}-\text{COOR}$) groups are present in the CPES molecule by hydrosilylation of PHMS with F6 and its subsequent opening cyclic reaction of PESO with MAn.

Morphology of CPES and the superpolysiloxane CPES/ASO-1 film

Film-forming ability is one of the characteristic properties of a polysiloxane.^{7,8,11,13} The film morphology not only affects the performance of a polysiloxane^{1,14}

but also can provide information about the orientation, configuration, or conformation of a film-forming molecule in an adsorbed or an aggregated state and reveal the film-forming mechanism.^{8,11,13}

Figure 4 shows the AFM images and precise microstructures of CPES and ASO-1. CPES forms an inhomogeneous film on the silicon wafer surface, and there are many bright dots randomly scattered on the film surface, especially as the scanning field is $5 \times 5 \mu\text{m}^2$ and the data scale is 10 nm in AFM observations.

As is known, polydimethylsiloxane usually forms a strongly hydrophobic, homogeneous structural

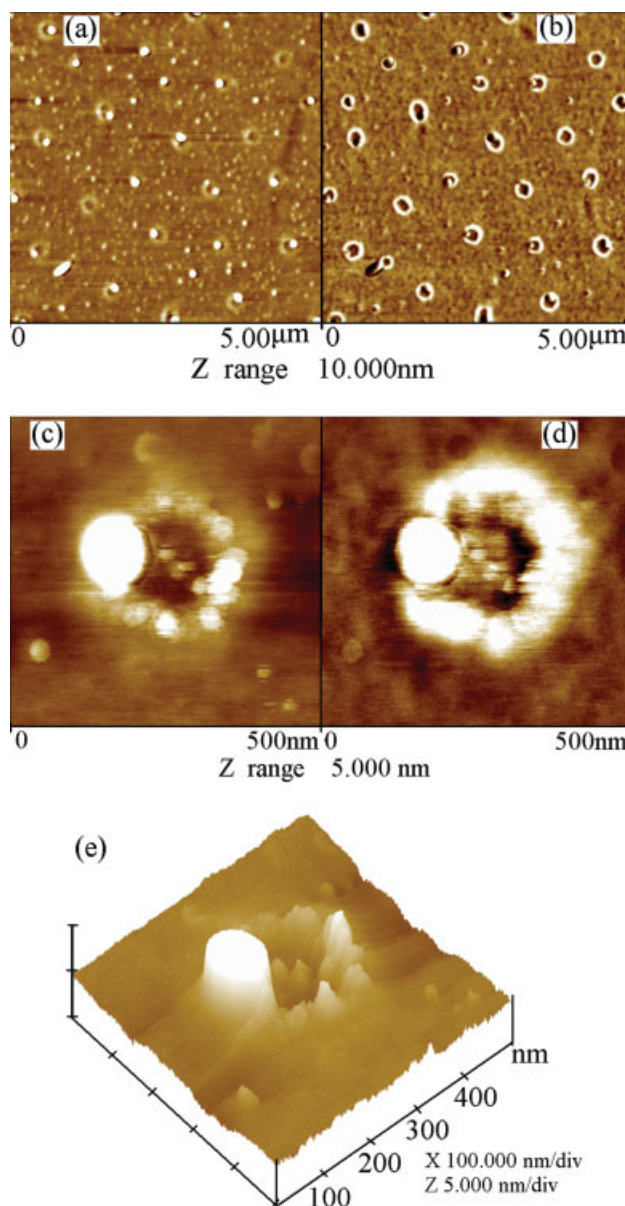


Figure 5 AFM images of CPES/ASO-1: (a) flattened image, (b) phase image, (c) amplified aggregate image, (d) phase image of an amplified aggregate, (e) and three-dimensional AFM image of an aggregate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

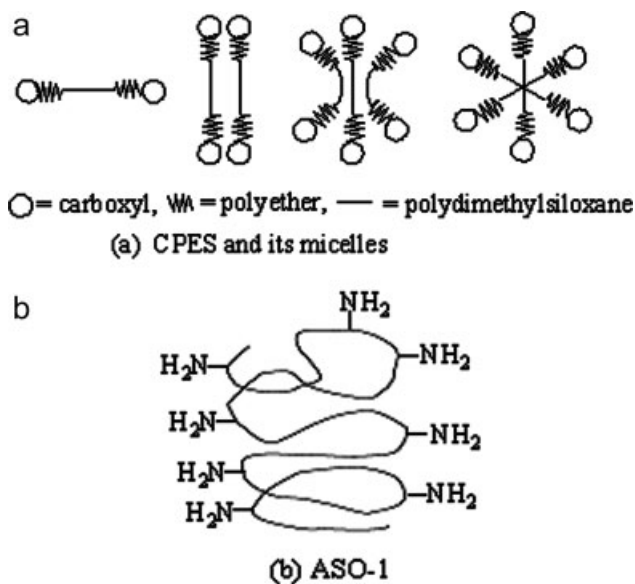


Figure 6 Schematic states of (a) CPES and (b) ASO-1 in diluted ethyl acetate solutions.

film on a silicon wafer surface.^{13,15} By a comparison of the AFM image of CPES with those reported,¹³ the bright dots in Figure 4(a) are deduced to result from the carboxyl polyether groups bonded at the end of CPES molecules and their aggregates among the different molecules.

Figure 5(a–e) shows a series of AFM images of the supermolecule, CPES/ASO-1. Clearly, the film morphology of CPES/ASO-1 is very different from that of CPES [Fig. 4(a)] or ASO-1 [Fig. 4(b)]. There are

not only many bright dots scattered on the film surface [Fig. 5(a,b)] but also some big and marvelous dots circled by a series of dots [Fig. 5(c–e)] uniformly located on the CPES/ASO-1 surface.

Chemical structures and states of architectural units can affect the characteristic and ordered morphology of supermolecular aggregates as well as their surface properties.¹⁶ From the point of view of the chemical structure, CPES is a typical, amphiphilic carboxyl polyether-block-polydimethylsiloxane-block-carboxyl polyether, that is, an ABA triblock copolymer. This particular, characteristic structure of CPES makes the molecule very similar to a surfactant in behavior and properties. Therefore, in a diluted polar ethyl acetate solution, the hydrophilic carboxylated polyether groups bonded at the end of the CPES molecule must spontaneously curl into capsules,¹⁴ distribute at the two ends or on the two sides of the polydimethylsiloxane backbone [Fig. 6(a)], and then aggregate into micelles because of the strong influence of the hydrophilic ends and the hydrophobic main chain. ASO-1 has been reported to be a curled thread [Fig. 6(b)] dispersed in a polar ethyl acetate solution.¹⁵

When CPES and ASO-1 coexist in a diluted ethyl acetate solution, acidic carboxyl groups of CPES react with the basic primary and secondary amino groups of ASO-1. In this way, some carboxylic and amino-functional groups are converted into anionic carboxylate (COO^-) and cationic NH_2^{2+} or NH_3^+ , which lead to micelles of CPES adsorbed onto the curled ASO-1 interface and aggregated as shown in Figure 7.

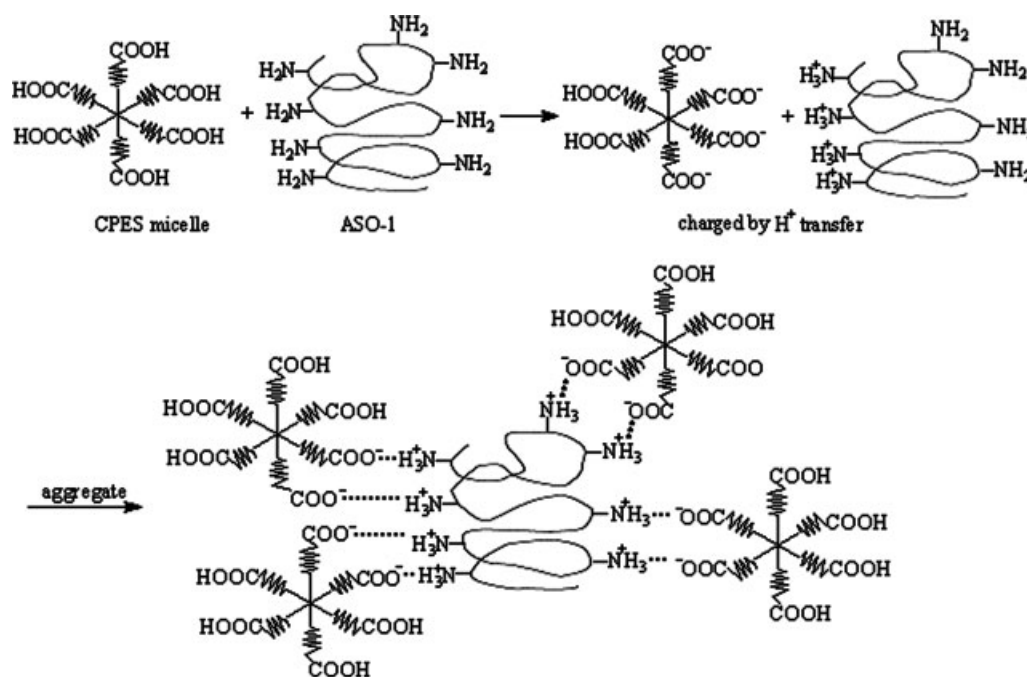


Figure 7 Schematic illustration of the self-assembly of CPES/ASO-1.

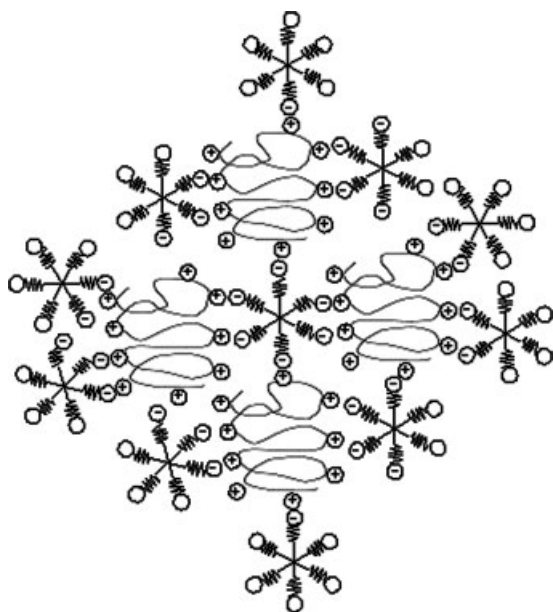


Figure 8 CPES/ASO-1 supermolecular aggregate of the multilayer structure.

Therefore, when such supermolecular aggregates are further transferred and adsorbed to a silicon wafer surface, a marvelous morphology different from that of CPES or ASO-1 can be clearly observed, as shown in Figure 8. Big bright dots are circled by a series dots. We suppose that this morphology is derived from the aggregates of the anionic CPES micelles (formed by H^+ transfer) adsorbed around the cationic ASO-1 molecules or their alternate adsorptions between the two molecules.

CONCLUSIONS

With PHMS and F6 as raw materials, an intermediate polyether-*block*-polydimethylsiloxane (PESO) was synthesized by hydrosilylation, and then a carboxylated polyether-*block*-polydimethylpolysiloxane

(CPES) was synthesized through the reaction of PESO with MAN.

Based on CPES as an architectural unit, a novel superpolysiloxane molecule (CPES/ASO-1) self-assembled from CPES and ASO-1 was obtained in this research. AFM observations indicated that the superpolysiloxane possessed a film morphology very different from that of CPES or ASO-1. On the film surface, in addition to bright dots, some much bigger and nicely circled dots were also observed. The particular morphology of dots circled by dots was estimated to result from the aggregation of different anionic CPES micelles adsorbed onto the curled cationic ASO-1 molecule interface.

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