

Synthesis of *N*- β -Aminoethyl- γ -aminopropyl Polydimethyl-*co*-polydiphenylsiloxane and Its Film Morphology and Orientation

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ABSTRACT: A fabric softener, *N*- β -aminoethyl- γ -aminopropyl polydimethyl-*co*-polydiphenylsiloxane (PASO), was synthesized by the polymerization of octamethyl cyclotetrasiloxane with an amino-functional silane and dimethyldiphenylsilane. The chemical structure of the synthesized polysiloxane was characterized by Fourier transform infrared and $^1\text{H-NMR}$ spectra. The morphology, composition, and hydrophobic properties of the PASO film were investigated by X-ray photoelectron spectroscopy, atomic force microscopy, contact angle measurement, and other measurements. The experimental results indicate that on the silicon wafer

surface, PASO formed a hydrophobic, nonhomogeneous structural film. In addition, the atomic force microscopy results show that the PASO film deposited on the silicon wafer seemed to be slightly rougher than the film of the control, the *N*- β -aminoethyl- γ -aminopropyl polydimethylsiloxane. As a result, an orientation model of PASO is proposed on the basis of the characterization of the PASO film properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2715–2719, 2009

Key words: atomic force microscopy (AFM); films; morphology; orientation; polysiloxanes

INTRODUCTION

Aminosilicones have been widely used in the textile industry as softener treatments. In practice, amino-functional silicones provide unique performance properties, such as a soft, smooth, silklike, or cottony hand to fabrics.^{1–3}

Aminosilicones offer unique performance and mechanical properties for textiles, which are attributed to their good film-forming ability.^{4,5} Film-forming ability is one of the characteristic properties of the silicones. Film morphology not only influences the handle and performance of aminosilicone but also can provide information about the configuration and orientation of the film-formed molecule in the absorbed state,⁶ which is favorable for a better understanding of the softening mechanism of the aminosilicone.^{7–10} In previous research,¹¹ we observed the morphology of a series of polysilox-

anes, and the results show that *N*- β -aminoethyl- γ -aminopropyl polydimethylsiloxane (ASO-1) formed a homogeneous hydrophobic film on a cellulose model substrate, and furthermore, the film surface was very even and smooth.

If a polydiphenylsiloxane chain is combined with an aminosilicone backbone, it might improve the heat resistance and antioxidation properties of the aminosilicone as a result restraining yellowness performance of treated fabrics.^{12–15}

In this study, a polydiphenylsiloxane chain grafted onto the backbone of an aminosilicone, *N*- β -aminoethyl- γ -aminopropyl polydimethyl-*co*-polydiphenylsiloxane (PASO), was synthesized by the polymerization of octamethyl cyclotetrasiloxane (D_4) with an amino-functional silane and dimethyldiphenylsilane. The chemical structure of the synthesized polysiloxane was characterized with Fourier transform infrared (FTIR) and $^1\text{H-NMR}$ spectroscopy. The film morphology and the surface properties were investigated with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle measurements, and other measurements.

EXPERIMENTAL

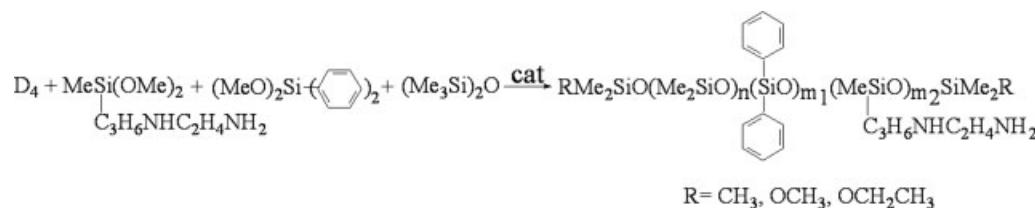
Materials

N- β -Aminoethyl- γ -aminopropyl methyldimethoxysilane (KH-Si-602), diphenyldimethoxysilane, D_4 , and

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**Scheme 1** Synthetic route to PASO.

hexamethyldisiloxane, all industrial grade, were purchased from Lanxing, Inc. (Jiangxi, China), Dadi, Inc., and Shanghai Huarun, Inc. (Shanghai, China), respectively; acetic acid and acetic ether, all analytical-reagent-grade, were from Xi'an Chemicals (Xi'an, China). The basic catalyst was prepared in our laboratory. The diphenyldimethoxysilane was distilled *in vacuo* before use, and the other chemicals were used as received without further treatment.

Synthesis (Scheme 1)

A round-bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser was charged consecutively with 60 g (0.2027 mol) of D_4 , 3.2 g (0.0108 mol) of KH-Si-602, 1.4 g (0.0057 mol) of diphenyldimethoxysilane, 1.2 g (0.0074 mol) of hexamethyldisiloxane, and 0.2 g of basic catalyst. The reaction mixture was slowly heated to 115°C, kept at this temperature for 4 h, and then continually heated to 130°C for the equilibrium reaction for 2 h. The silicone product with a low boiler was separated at 90°C under reduced pressure (6.67 kPa) from the crude products for 30 min. A colorless transparent liquid, namely, PASO, was obtained with an amount of 62.7 g (the theoretical value was 65.8 g), a yield of 95.3%. The PASO amino content was 0.5025 mmol NH/g of PASO, the phenyl content was 0.1214 mmol/g of PASO, the number average relative molecular weight was 12,143, and the weight-average relative molecular weight was 18,830 (determined by a Waters (USA) gel permeation chromatograph with tetrahydrofuran as an eluant and polystyrene as a reference sample).

With reference to the aforementioned method, ASO-1 was prepared and used as a control to research the film morphology of PASO.

Characterization

Samples were cross-examined with different instruments combined with a chemical analysis method. Infrared spectra were recorded on a Bruker Vector-22 FTIR spectrometer (Ettlingen, Germany). 1H -NMR spectra were recorded at 26°C on a Varian Inova 400 with $CDCl_3$ as a solvent and tetramethylsilane ($\delta = 0$ ppm) as an internal standard. Gel permeation

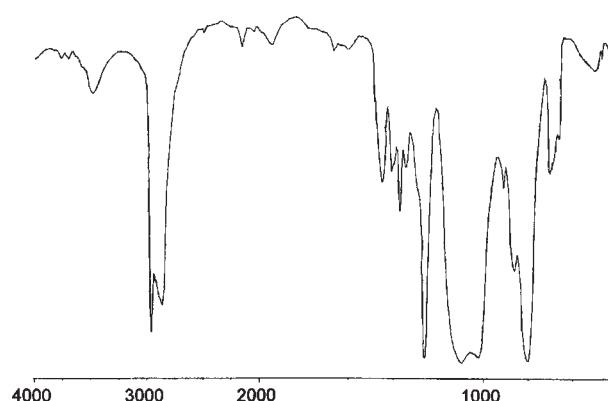
chromatography was performed with a Waters 1525 binary high-performance liquid chromatography pump; a Waters 2414 refractive-index detector; Styragel HT2, HT3, and HT4 columns; and tetrahydrofuran as an eluant.

Investigation of the film morphology

Because the natural fibers were difficult to fix in AFM observation and, moreover, a flat wafer surface allows for better morphological characterization of the coating on the nanoscale than the rugged surface of a fiber, a polished silicon wafer was used as a rigid substrate to research the film morphology and the microstructure of the PASO. To obtain a substrate surface similar to the natural cellulose fiber, with many hydroxyl groups and carrying negative charges on its surface, the silicon wafer was pre-treated as follows.

Pretreatment of the silicon wafer

A polished silicon wafer was cut into $0.5 \times 1\text{ cm}^2$ strips, washed with distilled water, immersed in a mixed solution of 98% H_2SO_4 and 27% H_2O_2 [4 : 1 (w/w)] at room temperature for 20 h, then rinsed with pure distilled water, and treated with a 2% Na_2CO_3 aqueous solution for another 1 h. After washing with large amounts of pure distilled water, the silicon wafer was dried at 100°C and then kept in a desiccator until use.

**Figure 1** FTIR spectrum of PASO.

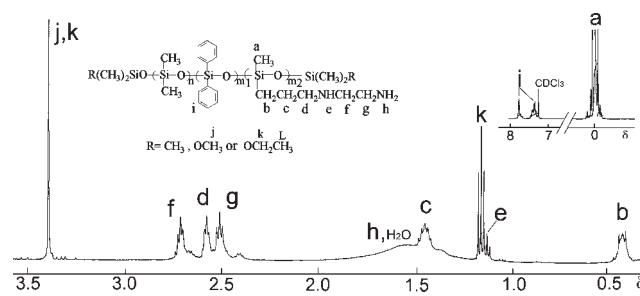


Figure 2 ^1H -NMR spectrum of PASO.

Preparation and observation of the PASO film on the silicon wafer

Emulsion is not suitable for the formation of a polysiloxane film on a silicon wafer because the residual emulsifier deposited on the silicon substrate could contaminate the probe of the atomic force microscope and interfere with the AFM image. Thus, an organic solution of functional polysiloxane was used to coat the silicon wafer. Meanwhile, to avoid a multilayer of polysiloxane softener deposited on the silicon substrate, a thoroughly diluted polysiloxane in ethyl acetate solution was used in the following procedure, and the film formation on the silicon wafer surface was performed with reference to Langmuir film preparation and literature methods.¹⁰

PASO and ASO-1 (0.03 g, accurate to 0.0001 g) were respectively placed in two beakers and then dissolved in an ethyl acetate solvent (analytical reagent, redistilled before use) to form a 0.03% polysiloxane solution. The dried, clean silicon wafer was vertically dipped in the polysiloxane solution for several seconds, then drawn out, immediately dried at 100°C for 10 min, cured at 160°C for 2 min, and then conditioned in a desiccator for 24 h at room temperature.

The topographic images of the polysiloxane films immobilized on the silicon substrates were observed with a Nanoscope IIIA atomic force microscope (Digital Instruments, USA) at 22°C in air at a relative humidity of 48%, and all of the scanning was performed in tapping mode.

The characterization of the PASO film chemical structure was developed with an Axis Ultra XPS instrument made by Kratos (Manchester, United Kingdom). This system was equipped with a single-anode ($\text{Al K}\alpha$) X-ray source and a hemispherical analyzer. The X-ray source had a power and full width at half-maximum of 1486.6 and 0.7 eV, respectively. The sample was introduced into the main analyzing chamber through a prevacuum buffer chamber of 5×10^{-8} Torr pressure. The analyzing chamber pressure fluctuated between 10^{-8} and 10^{-9} Torr. The core-level spectra were referenced to a C1s line taken at 284.8 eV.

The contact angle of $\text{H}_2\text{O}/\text{PASO}$ on the silicone wafer was measured by a JC2000 angle contact measurement made in Powereact (Shanghai, China).

RESULTS AND DISCUSSION

Chemical structure of PASO

The chemical structure of PASO was principally characterized by FTIR and ^1H -NMR. Figures 1 and 2 show the typical FTIR and ^1H -NMR spectra, respectively.

Figure 1 clearly shows that typical absorption bands appeared separately at 3350, 2960–2820, 1595–1420, 1260, 1100–1020, and 801 cm^{-1} , which indicated functional groups such as $-\text{NH}_2$, $-\text{Ph}_2\text{SiO}-$, and $-\text{Me}_2\text{SiO}-$ combined in the PASO molecule.

Furthermore, from the ^1H -NMR spectrum and peak assignments analysis, it was clear that there were functional groups such as $-\text{SiCH}_3$, $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, $\text{Ph}-$, and residual $-\text{SiOCH}_3$ and $-\text{SiOC}_2\text{H}_5$ in the PASO molecule.

In conclusion, from the combined the results of the FTIR and ^1H -NMR analysis, it was obvious that the product had the expected chemical structure, and in its backbone, the phenyl and N - β -aminopropyl groups were bonded. The PASO molecule was as follows.

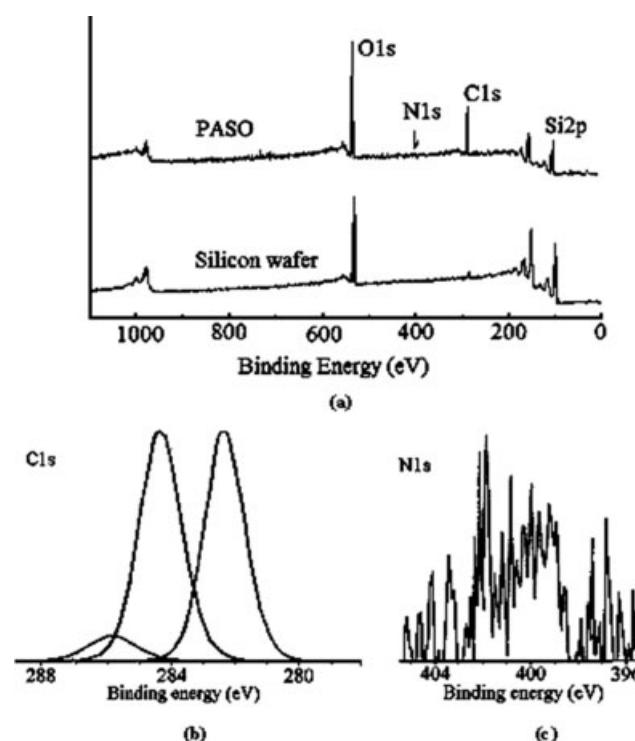


Figure 3 XPS spectrum of PASO and high-resolution C1s and N1s spectra.

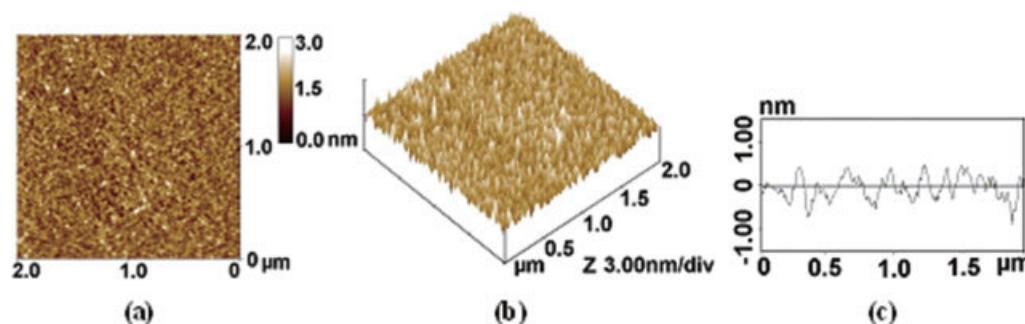


Figure 4 AFM images of PASO with an R_q value of 0.228 nm: (a) flattened image, (b) three-dimensional image, and (c) surface profile along a line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Film property and surface XPS analysis

Film-forming capabilities are one merit of silicones, which are derived from the low strength of the intermolecular binding force, which results in low surface tension. So, in the silicone film covered with the substrate, the surface performance of the substrate certainly changed.

Young¹⁶ proposed an equation (Young's equation):

$$\sigma(s/g) = \sigma(s/l) + \sigma(l/g) \cos \theta$$

where θ is the contact angle and $\sigma(s/g)$, $\sigma(s/l)$, and $\sigma(l/g)$ are the solid-gas, solid-liquid, and liquid-gas interface tensions, respectively. Thus, the hydrophilicity or hydrophobicity of the silicone film on the silicon wafer could be detected by the measurement of the contact angle, which provided favorable information about the orientation of the PASO molecule spreading out onto the silicon wafer surface.

The contact angle of the silicon wafer surface was 31.2° (detected as H₂O touched the silicon wafer surface between 2 and 6 s); however, the contact angle of the PASO film surface on the silicon wafer was 94.9° actually. Furthermore, after the bead water was on the wafer surface for 2 min, the contact angle

was still 94.0°. Obviously, the PASO film surface on the silicon wafer was strongly hydrophobic.

Figure 3 shows a typical XPS survey spectra for the clean silicon wafers and those with deposited PASO layers. For the clean silicon wafer, only Si and O were observed, but for the PASO film, four elements, O, C, N, and Si, were detected.

The details of the high-resolution C1s peak of PASO shown in Figure 3(b) indicated that there were three different kinds of carbon particles derived from alkyl groups. The binding energy of C1s appeared at 282.3, 284.3, and 285.8 eV, and the corresponding peak areas were 46.0, 48.4, and 5.5%, respectively. Compared with the normal spectra of $-[\text{PhSi}(\text{CH}_3)\text{O}]_n-$, it was affirmed that there were three kinds of groups, PhSi, SiCH₃, and C—CH₂, in the PASO/silicon surface layer. Moreover, for high-resolution N1s spectra analysis, there were two kinds of nitrogen particles, which presented as NH or NH₂ and $-\text{NH}_2^-$ or $-\text{NH}_3^+$, and their corresponding energy peaks appeared at 399.7 and 401.9 eV, respectively. In addition, from the XPS spectra of PASO [Fig. 3(a)], it was obvious that the peaks of the binding energy of O1s (532.2 eV) and Si2p (99.4 eV) were fairly strong, which may have been due to the oxidized silicon wafer because the X-ray hit through the PASO film and the substrate was

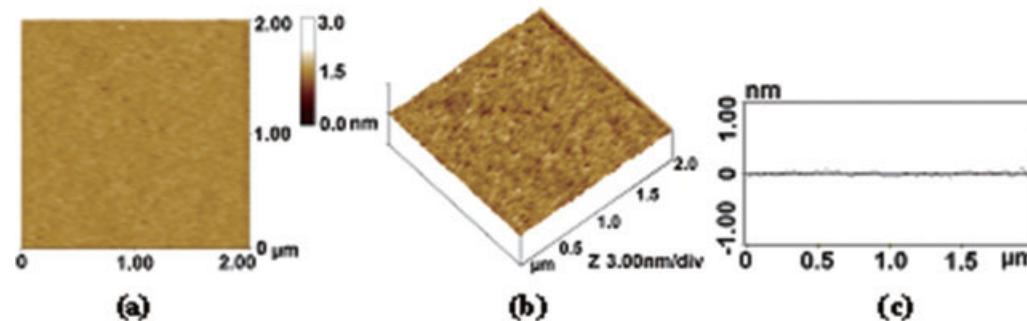


Figure 5 AFM image of ASO-1 with an R_q value of 0.084 nm: (a) flattened image, (b) three-dimensional image, and (c) surface profile along a line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

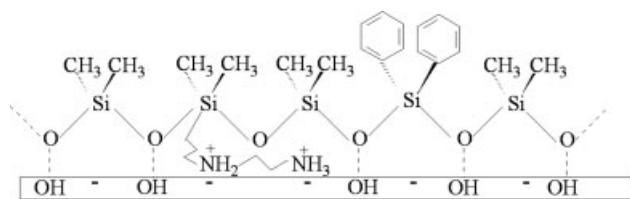


Figure 6 Orientation of the PASO molecule on the silicon wafer surface.

exposed. Despite the flaw, however, the results of XPS could still indicate that ASO-1 formed a film on the substrate wafer.

Film morphology and orientation of the PASO molecule

The films morphologies of PASO and ASO-1, which was used as a control in the experiment, were observed by AFM, and the AFM images are shown in Figures 4 and 5, respectively.

Figure 4 shows that PASO formed an inhomogeneous structure film on the silicon surface, and the film seemed to be rougher compared with the control, ASO-1. Obviously, this was attributed to the bigger groups of Si—Ph combined with the main chain of PASO.

It is known that a silicon wafers is a very smooth rigid material, which carries much hydroxide and negative charges on its surface after oxidation treatment. However, PASO is a polydimethyl-co-polydiphenylsiloxane grafted N - β -aminoethyl- γ -aminopropyl group in the side chain, carrying positive charges after protonation. Hence, we concluded that PASO oriented in such a way that, in the main chain, the silicone methyl and phenyl groups projected outward toward the air interface and the Si—O dipole bonds projected inward toward the silicone surface to decrease the system's energy and that, in the side chain, the cationic amino groups (expressed as $-\text{NH}_2^+$, $-\text{NH}_3^+$ groups), which were constrained by electrostatic forces and hydrogen bond forces, oriented toward the substrate surface. This orientation reduced the surface energy and made the finished substrate more stable (Fig. 6).

This orientation mode of PASO not only caused the film to be hydrophobic on the silicon wafer but also made the film surface relatively rougher. Thereby, in the $2\text{-}\mu\text{m}^2$ scanning field, the average surface roughness (R_q) of the PASO film reached

0.228 nm, which was 2.71 times coarser than the control ASO-1 film ($R_q = 0.084$ nm).

CONCLUSIONS

A fabric softener (PASO) was synthesized, and the chemical structure of the polysiloxane was characterized by FTIR and $^1\text{H-NMR}$. The contact angle measurement results indicated that on the silicon wafer surface PASO formed a hydrophobic, nonhomogeneous structural film, on which the static water contact angle reached 94.9° . XPS analysis suggested that C1s, N1s, O1s, and Si2p peaks derived from the PASO film occurred at binding energies of 284.3, 399.7, 532.2, and 99.4 eV, respectively. In addition, the AFM results showed that the PASO film deposited on the silicon wafer seemed to be slightly rougher than the film of the control, ASO-1. There were a lot of high or low peaks in the PASO dimensional topography. According to the orientation of ASO-1, we concluded that PASO oriented in such a way that in the backbone the silicone methyl and phenyl groups projected outward toward the air interface but that the Si—O dipole bonds projected inward toward the substrate surface to decrease the system's energy and that, in the side chain, the cationic amino groups (expressed as $-\text{NH}_2^+$ and $-\text{NH}_3^+$ groups), which were constrained by electrostatic forces and hydrogen bond forces, oriented toward the substrate surface.

References

1. Sabia, A. J. *Text Chem Color* 1995, 27, 79.
2. Tae, J.-K.; Min, S.-K. *Text Res J* 2001, 71, 295.
3. Joyner, M. M. *Text Chem Color* 1986, 18, 34.
4. An, Q.; Li, L.; Lu, D.; Huang, L. *J Appl Polym Sci* 2007, 104, 680.
5. Micheal, W. S.; Caibao, Q.; Stelian, G. *Text Res J* 1999, 69, 935.
6. Michael, C. B.; Matthew, D. B.; Daniel, D. *Appl Surf Sci* 2004, 227, 3.
7. Bereck, A.; Riegel, D.; Weber, B. *Textilveredlung* 1997, 32, 138.
8. Riedel, J. H.; Höcker H. *J Appl Polym Sci* 1994, 51, 573.
9. An, Q.; Cheng, G.; Li, L. *J Appl Polym Sci* 2006, 101, 4480.
10. Helmy, R.; Alexander, Y. F. *Langmuir* 2002, 18, 8924.
11. An, Q.; Li, L.; Huang, L.; Chen, K. *AATCC Rev* 2006, 6, 39.
12. Mabry, J. M.; William, P. *J Polym Sci Part A: Polym Chem* 2004, 42, 5514.
13. Song, X. Y.; Zhai, J.; Wang, Y. L.; Jiang, L. *J Phys Chem (China)* 2005, 109, 4048.
14. Harada, Y.; Girolami, G. S.; Nuzzo, R. G. *Langmuir* 2004, 20, 10878.
15. Noll, W. *Chemistry and Technology of Silicones*; Academic: New York, 1968: pp 443 and 587.
16. Young, T. *Philosophical Translation of the Royal Society of London*; 1805; Vol. 95, p 84.