

A Functional Polysiloxane with Benzophenone Derivative Ultraviolet Absorbing Side Groups: Synthesis, Morphology, and its Performance on Fabrics

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ABSTRACT: A novel functional polysiloxane (PSBP) bearing benzophenone derivatives as UV absorbing side groups was synthesized by hydrosilylation of polyhydromethylsiloxane (PHMS) with 2-hydroxy-4-(β -hydroxy- γ -allyloxy)propoxy benzophenone (HHAPB). The chemical structure, film morphology, and the softening fabric property of the synthesized polysiloxane were characterized and investigated by spectrum analysis, atomic force microscope (AFM), and Kawabata evaluation system. The experiment results indicated that PSBP was not only an excellent polymeric UV-absorber, which showed intensive ultraviolet absorptions respectively, at wavelengths of 243.2, 288.2, and 325.4 nm, but could exhibit a nonhomogeneous, some

rough structure film on silicon wafer substrate. In addition, the functional side group, benzophenone derivative as well as its mass ratio to PSBP has an influence on the performance of the synthesized polysiloxane. As the mass ratio decreased from 31.48 to 12.87%, the molar extinction coefficients ϵ_{\max} ($\lambda_{\max} = 288.2$ nm) of the PSBP fluids lowered from 3.4564×10^5 to 1.5763×10^5 , but while the softening fabric properties of PSBP on cotton fabrics increased. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 680–687, 2007

Key words: polysiloxane; benzophenone derivative; ultraviolet absorber; fabrics; film morphology; softness

INTRODUCTION

Polysiloxanes with pending benzophenone derivative side groups are functional ultraviolet absorbing polymeric materials.^{1–3} They have been used as compounding agents for sun screening cosmetics and medicals, or as additives in various plastics, resins, anti-UV coatings, and functional textile finishing to prevent the undesirable photo-oxidation and photo-degradation from the sunlight.^{2–5}

One of the feasible routes to bond benzophenone derivative functional group to the siloxane skeleton is the hydrosilylation of vinyl derivative of benzophenone with Si–H group containing silicone. By means of this method, Riedel and Höcker² successfully synthesized a polysiloxane UV-absorber with pendant benzophenone side groups. Woolen and polyamide fibers finished by the polysiloxane were endowed with an evident anti-UV effect. Moreover, it was discovered that combination of PSBP with cinnamates or

alkoxy-substituted dibenzoylmethane in cosmetics or medicals, could not only absorb UV-A and UV-B lights, but improve the dispersivity and compatibility of the absorbents with oil stuff as well. In addition, Payne and Wang⁵ found that siloxanes functionalized by benzophenone groups, then compounded with UV-radiation screening ingredients, could form a durable and uniform UV absorption coating on glass, especially on the float glass.

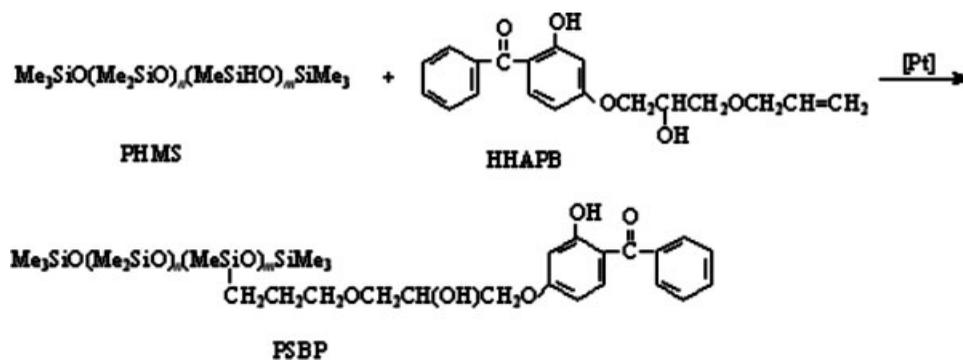
Film-forming ability is one of characteristic properties of polysiloxane. Film morphology not only affects the performance of polysiloxane, but also can provide the information about the orientation, configuration, or conformation of film-forming molecules in absorbed state.^{6–8} Therefore, the researches about morphology of the functional polysiloxanes have attracted more attention recently. PSBP, as one of the most important functional polysiloxanes, has shown a great potential in surface coating and textile finishing, but there are still little data about the morphology of these materials. Thus, a new polysiloxane with pendant 3-[β -hydroxy- γ -(3-hydroxy-4-benzoyl phenoxy)propoxy]propyls (the benzophenone derivative functional groups, as shown in Scheme 1) was synthesized in our research, then the film morphology and the softness of the synthesized polysiloxane on cotton fabrics were investigated by AMF, UV-visible spectrometer, and other instruments.

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Scheme 1 The synthesis route of PSBP.

EXPERIMENTAL

Materials

α -Alkenyl derivative of benzophenone, 2-hydroxy-4-(β -hydroxy- γ -allyloxy)propoxy benzophenone (HHAPB, with a formula: $\text{C}_{19}\text{H}_{21}\text{O}_5$), was synthesized by a ring-opening reaction of allyl glycidyl ether with 2,4-dihydroxybenzophenone in the presence of a phase transfer catalyst and an alkaline.³ HHAPB: a viscous liquid, yield 87.10%, n_D^{20} 1.5863. Element Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{O}_5$ (%): C, 69.50; H, 6.14; O, 24.36. Found: C, 69.30; H, 6.21; O, 24.50. UV spectrum, λ_{max} (nm): 239.2, 288.0, 326.6. The molar extinction coefficient ϵ_{max} ($\lambda_{\text{max}} = 288.0\text{nm}$): $9914 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Polyhydromethylsiloxanes (PHMS), selected as starting and skeleton materials, were commercial products obtained from Qinyang Chemical and Lixing Chemical, China. The Si—H contents, expressed by the moles of Si—H groups contained in 100 g of PHMS, was respectively, PHMS-1, 0.14%; PHMS-2, 0.08%; PHMS-3, 0.045%. The number average molecular weight (M_n) and the mass average molecular weight (M_w): PHMS-1, $M_n = 1.78 \times 10^4$, $M_w = 3.91 \times 10^4$; PHMS-2, $M_n = 2.10 \times 10^4$, $M_w = 4.86 \times 10^4$; PHMS-3, $M_n = 2.78 \times 10^4$, $M_w = 7.13 \times 10^4$. All of PHMS were used as received.

Polydimethylsiloxane (PDMS), synthesized by acid catalysis telomerization of octamethyl-cyclotetrasiloxane with hexamethyldisiloxane, and with a dynamic viscosity of 0.645 Pa s, was used as a control film forming material in investigation of the film morphology of PSBP.

Synthesis

In a 250 mL three-neck flask equipped with a mechanical stirrer, a reflux condenser and a thermometer, 16.4 g HHAPB and 30 g PHMS-1 were dissolved in 50 mL toluene solvent. The mixture was stirred and heated to 80–100°C under N_2 , and then a catalytic amount of H_2PtCl_6 in isopropyl alcohol solution was dropped. After the mixture was maintained at 80–100°C to react for 4–6 h, the low boiling point impurities were evaporated under reduced pressure.

Then the remaining product was cooled, washed thoroughly by a mixture solvent of methanol : acetone = 5 : 1 (v/v) and dried at $(80 \pm 2)^\circ\text{C}/0.11033 \text{ MPa}$ for 4 h. Finally, a polysiloxane (PSBP-1) with benzophenone derivative side groups as a viscous liquid was obtained. PSBP-1, its yield was 82.94% (based on the mass consumption of PHMS in reaction); the Si—H conversion, estimated from the integration of $^1\text{H-NMR}$, was 91%; $M_n = 3.07 \times 10^4$, $M_w = 8.26 \times 10^4$.

Reference to the method mentioned earlier, PSBP-2 and PSBP-3 were respectively, synthesized from PHMS-2 and PHMS-3. The Si—H conversion: PSBP-2, 95%; PSBP-3, 96%.

Characterization

Infrared (IR) spectrum was acquired on a Bruker VECTOR-22 spectrometer, KBr liquid film. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded by INOVA-400 spectrometer (Varian), CDCl_3 (Sigma-Aldrich Inc.) as a solvent and tetramethylsilane as an internal standard. The average molecular weight was determined by a Waters GPC instrument, THF (Tianjin Chemical Reagent Co., China) as solvent, polystyrene of narrow average molecular weight used as a reference standard. UV-visible absorption spectrum was recorded on a UV-265FW ultraviolet-visible spectrometer (Shimadzu) using THF as a solvent, the concentration of PSBP in THF was controlled in 30–50mg/L. In addition, the molar extinction coefficient ϵ_{max} ($\lambda = 288.2 \text{ nm}$) of PSBP fluid was determined and calculated as follows: 0.8711 g PSBP dissolved in THF to form a solution of mass concentration about 0.1307 g/L, the absorbance A of the solution was measured by UV-265FW spectrometer, then the ϵ_{max} of PSBP at $\lambda = 288.2 \text{ nm}$ was calculated according to the formula $A = \epsilon_{\text{max}}bc$, where b , representing path length was 1 cm, c stands for the mass concentration/ M_n .

Observation of the film morphology of PSBP by AFM

Considering three polysiloxane products were synthesized in our experiment, and to obtain a clear, charac-

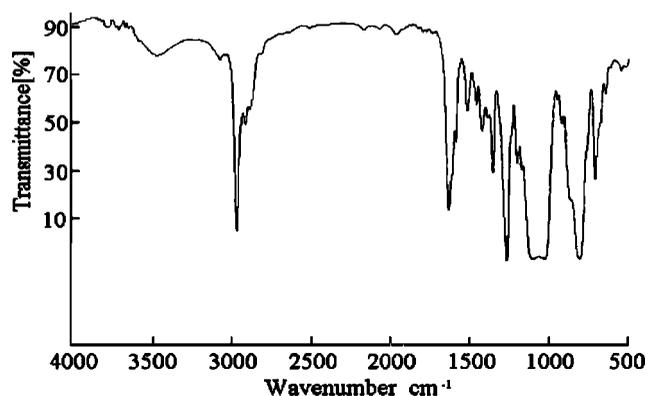


Figure 1 Infrared spectrum of PSBP-1.

teristic morphology of the synthesized polysiloxane, PSBP-1, with more functional side groups, was chosen as a representative sample and PDMS (with the same main chain as PSBP-1) used as a control to investigate the morphology of PSBP. And moreover, a polished silicon wafer was applied as a rigid substrate to prepare the tested polysiloxane film. The detail procedure is shown as follows.

Pretreatment of silicon wafer

A polished silicon wafer was cut into 0.5 cm × 1 cm tablets, immersed in a mixed solution of 98% H₂SO₄ : 27% H₂O₂ = 4 : 1 (w/w) at room temperature for 20 h, then washed by distilled water and dipped in 2% Na₂CO₃ aqueous solution for another 1 h, then rinsed thoroughly by distilled water and dried.

Sampling

Reference to Langmuir film preparation technique and literature methods,^{6,9} 0.03 g PSBP-1 or PDMS (accurate to 0.0001 g) was respectively, dissolved in 100 g of secondary distilled analytical ethyl acetate to form a 0.03% polysiloxane solution. The dried silicon

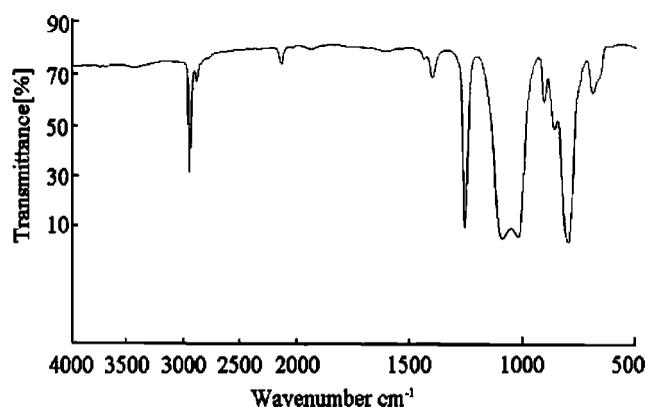


Figure 2 Infrared spectrum of PHMS.

wafers were covered with a thin film of the polysiloxane, PSBP-1 or PDMS, by vertically dipping these wafers in the different polysiloxane solutions for a couple of seconds. Then the coated silicon wafers were drawn out, dried at 100°C for 5 min and cured at 160°C for 2 min, then balanced in a desiccator for 24 h under a nitrogen atmosphere.

Morphology observation

The surface morphology of the silicon wafer coated with different polysiloxanes were observed by Nano-scope IIIA atomic force scanning microscope (Digital Instruments) in air at 26.6°C and 48.6% relative humidity. All the scanning was performed in the tapping mode.

Measurement of the softening fabric property of PSBP on cotton fabrics

In textile industry, the softening fabric property (in short, the softness) of polysiloxane was usually evaluated by the bending rigidity of the treated fabrics.¹⁰ The bigger the bending rigidity of the treated fabrics, the smaller the softness of polysiloxane on fabrics will be.

Polysiloxane fluid is not suitable for directly treating the fabrics, it is often used in emulsion or in solution. Thus in the experiment, 0.3% PSBP in ethyl acetate solution was applied to treat the tested fabric sample.

100% woven cotton fabrics, with yarn counts of 474 × 235 (the number of warp and filling yarns, 10 × 10 cm), were impregnated in 0.3% (by mass) PSBP in ethyl acetate solution for several seconds, padded with a roller to wet pick-up at about 70% on the weight of the dry fabrics. The padded fabrics were dried at 100–105°C for 3–5 min, cured at 160°C for

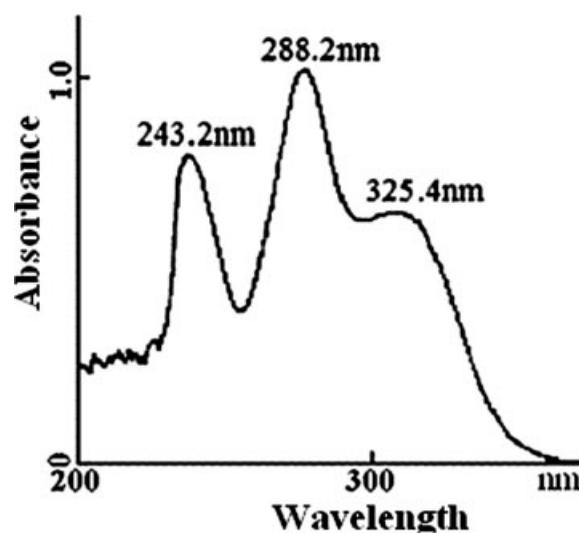


Figure 3 Ultraviolet spectrum of PSBP-1.

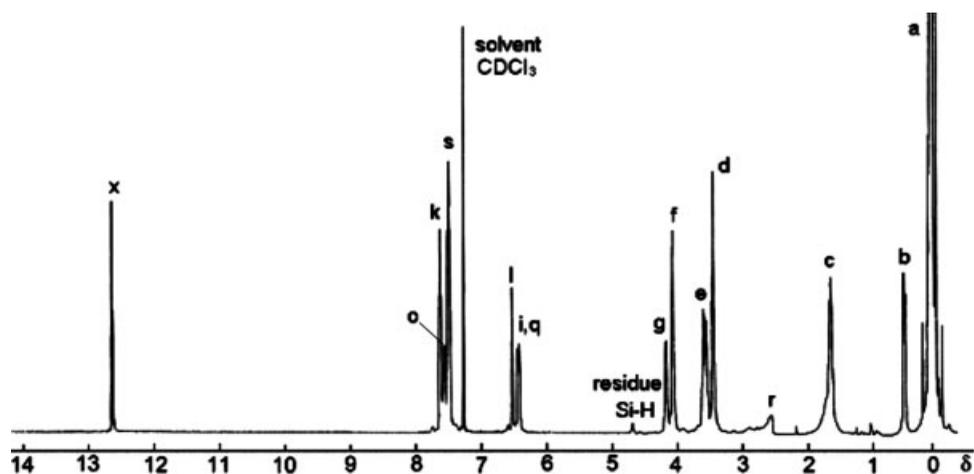


Figure 4 $^1\text{H-NMR}$ spectrum of PSBP-1.

30 s, then air-conditioned at $(20 \pm 2)^\circ\text{C}$ and 65% relative humidity for 24 h.

The bending rigidity of the cotton fabrics treated by PSBP was measured with a Kawabata evaluation system instrument.

RESULTS AND DISCUSSION

Structure Characterization

In this procedure, PSBP-1 was used as an example to illustrate the characterization results.

Figure 1 is the IR spectrum of PSBP-1. Comparing Figure 1 with Figure 2, the IR spectrum of the PHMS-1, it was clearly discovered that the absorption band due to residue Si-H groups at 2150 cm^{-1} faded away from IR spectrum of PSBP-1, and a series of new absorption bands separately emerged at $3300\text{--}3458$, 3080 , 1626 , $1580\text{--}1447\text{ cm}^{-1}$. The broad, weak absorption band in the $3300\text{--}3458\text{ cm}^{-1}$ region should be arisen from the O—H stretching vibration of hydroxyl in PSBP-1. The sharp, moderately intense absorption band at 1626 cm^{-1} was due to the C=O stretching

vibration from the conjugate aromatic ketone, while the other new absorption bands at 3080 , 1580 , 1505 , and 1447 cm^{-1} illustrated the presence of the conjugate substituted aromatic rings in PSBP-1.

Figure 3 is the ultraviolet spectrum of PSBP-1. Obviously there were three strong ultraviolet absorptions separately occurred at 243.2 , 288.2 , and 325.4 nm , which coincided with those of starting material, HHAPB, in positions and intensity.

Figures 4 and 5 are respectively, the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of PSBP-1 along with their analysis. These results further indicated that functional groups such as Si-CH₃, SiCH₂CH₂CH₂O-, C₆H₅, C₆H₃, conjugate carbonyl group C=O, phenolic hydroxyl really existed in PSBP-1 molecule.

Therefore, combination of these spectra demonstrates that PSBP-1 possesses the expected structure as shown in Scheme 2.

Film morphology

Functional polysiloxanes possess different film-forming capacity and can give varying morphology in

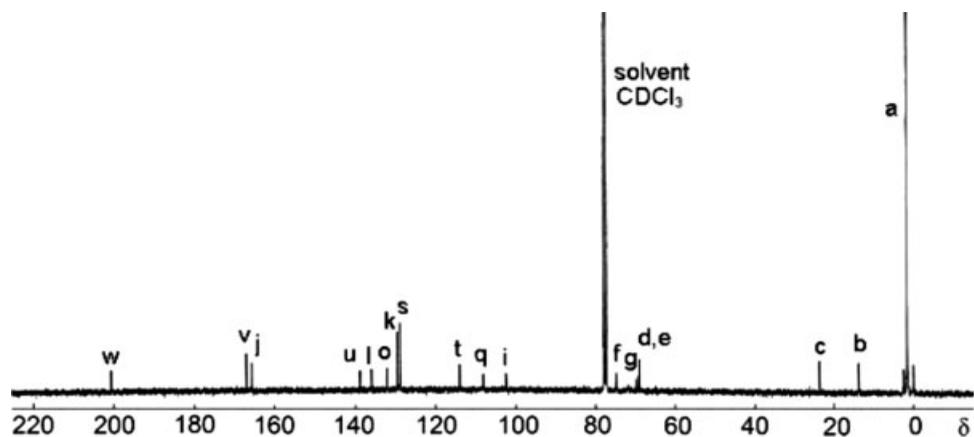
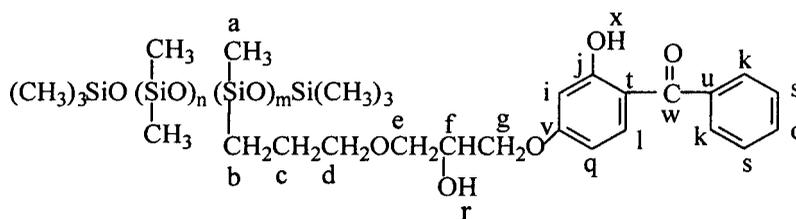


Figure 5 $^{13}\text{C-NMR}$ spectrum of PSBP-1.



Scheme 2 The chemical structure of PSBP-1.

atomic force microscope (AFM) observation. But which morphology fashion should PSBP behave in?

AFM is a powerful instrument in observation of film morphology of polymer and their blends. It also provides a possible way to observe the film morphology of functional polysiloxane on molecular scale. Therefore, AFM was utilized in our research to investigate the morphology of PSBP, and the results are shown in Figure 6. In addition, to determine whether the pinnacles or mountains in the topography of PSBP generated from functional groups, the PDMS with the same

main chain as PSBP-1 was used as a control in the experiment, and its AFM images are shown in Figure 7.

Comparing Figure 6 with Figure 7, it was clearly observed that PSBP-1 formed a nonhomogeneous structure film on the silicon wafer surface. The film seems to be rougher, as compared with the control, PDMS. There are many bright, discrete pinnacles, or mountains in its topography. As a result, the root mean square roughness (R_q) of PSBP-1 film reaches to 0.257 nm in $2 \mu\text{m}^2$ scanning field. And the height of the largest peak to lowest valley (LPVH) achieves

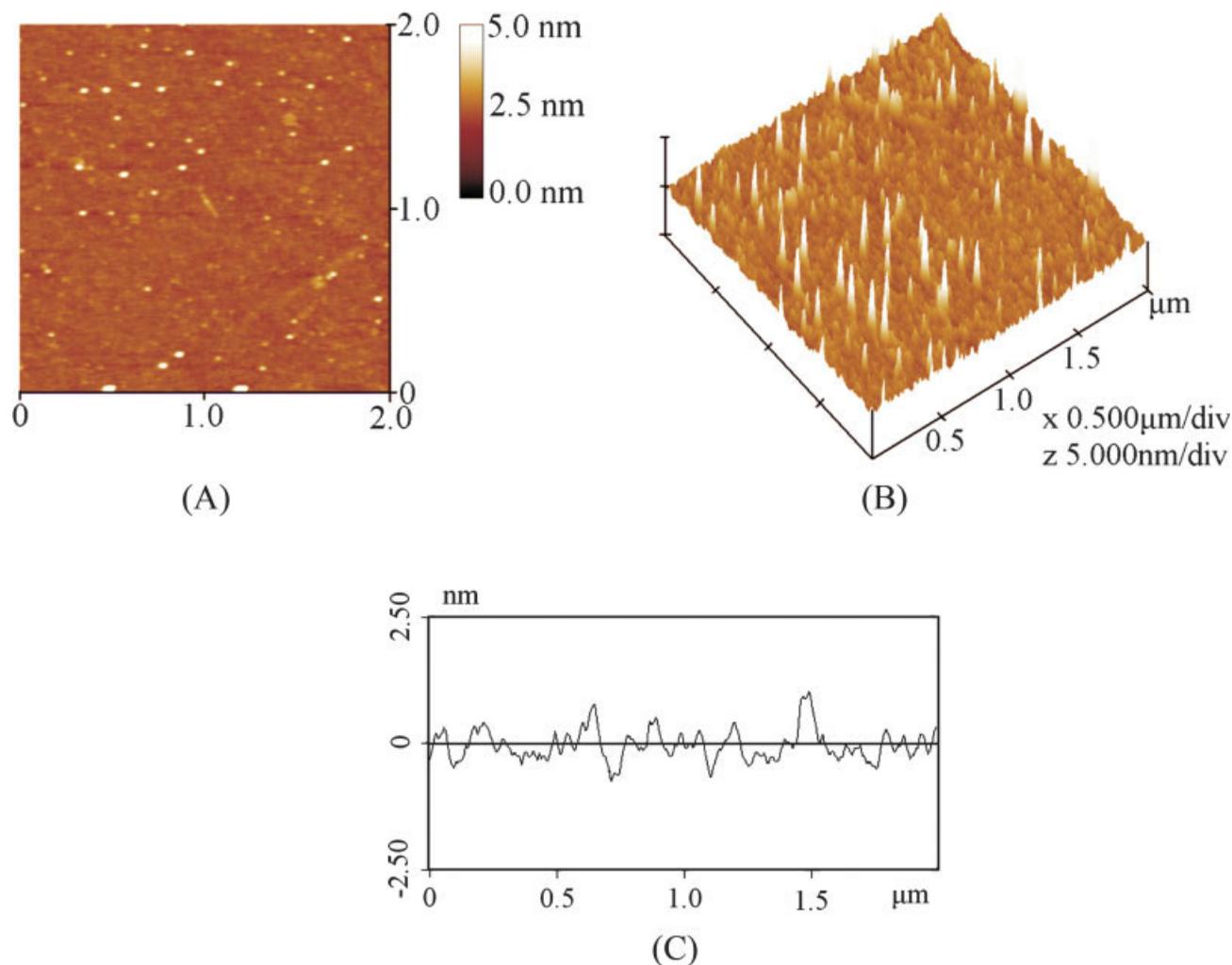


Figure 6 AFM images of PSBP-1 film with a R_q of 0.257 nm. (A) Flatten, (B) three-dimensional, (C) the surface profile along a line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

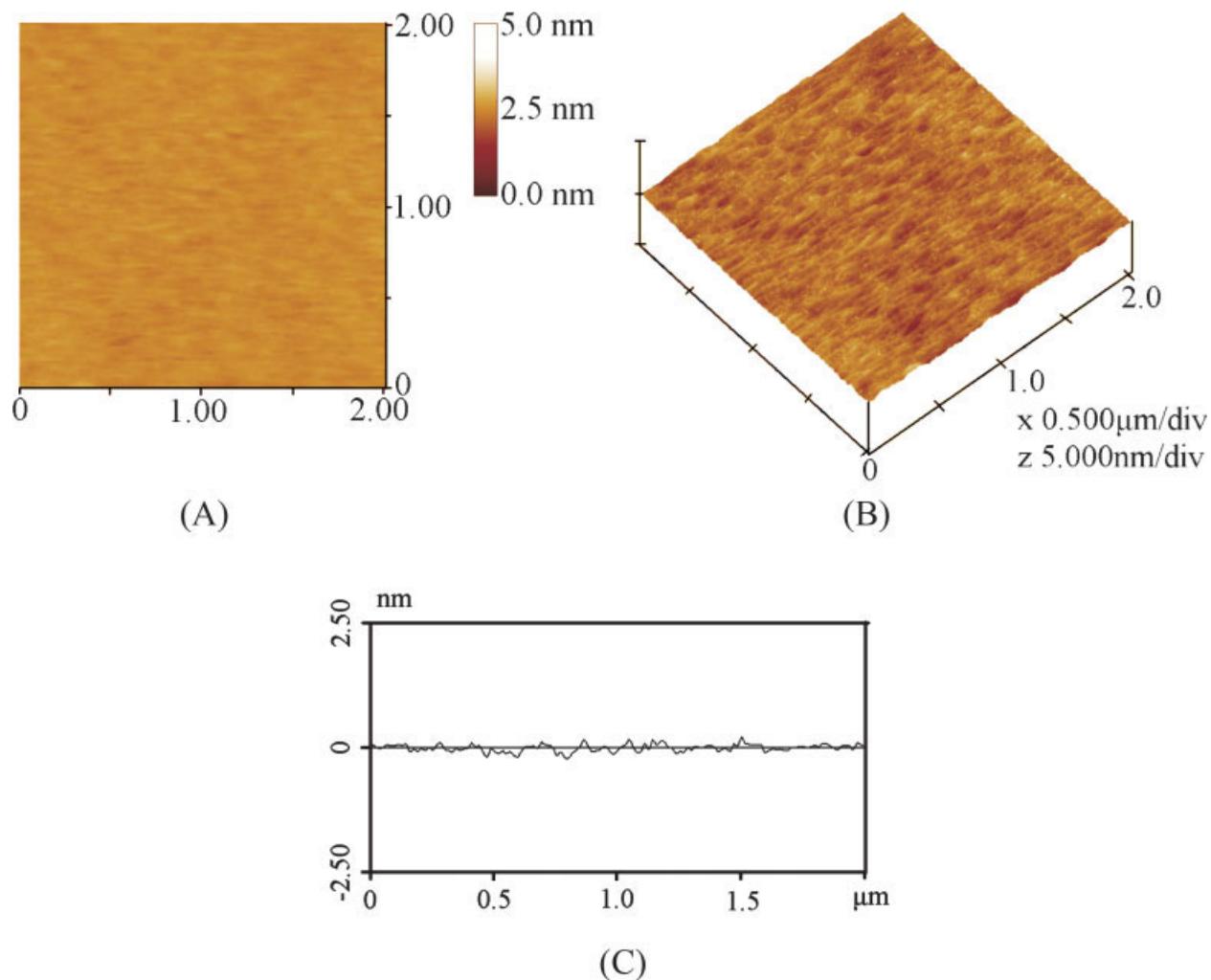


Figure 7 AFM images of PDMS film with a R_q of 0.081 nm. (A) Flatten, (B) three-dimensional, (C) the surface profile along a line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

2.673 nm. Whereas, the control, PDMS film is very uniform and homogenous. In $2 \mu\text{m}^2$ scanning field, the R_q of PDMS film is only 0.081 nm, and the LPVH is 0.198 nm.

From the point of the view of the chemical structure, PSBP is a nonionic polysiloxane with PDMS skel-

eton and pendant benzophenone derivative side groups, 3- $[\beta$ -hydroxy- γ -(3-hydroxy-4-benzoylphenoxy)propoxy]propyls. It is well known that PDMS is a low energy material, easily spread on the solid surface to form a strong hydrophobic film of molecular dimension. This gives us a suggestion that PDMS

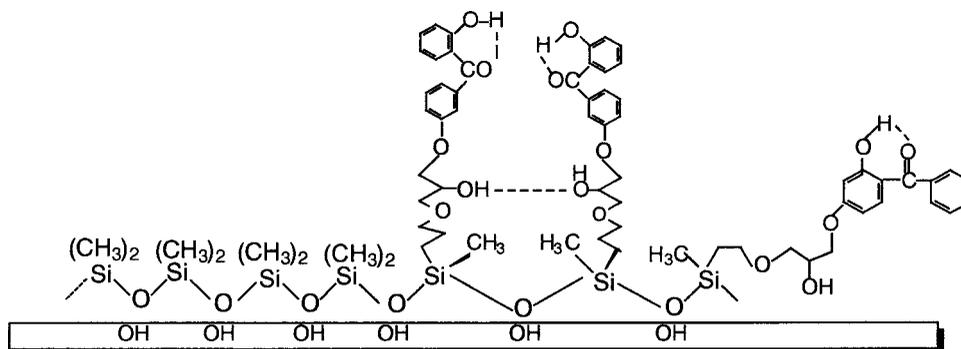


Figure 8 Schematic orientation of PSBP on silicon substrate.

TABLE I
Mass Ratio of Functional Side Groups and Their Effects on the Performance of PSBP

	MR (%)	Average molecular weight		UV absorption	BR	
		M_n (10^{-4})	M_w (10^{-4})	ϵ_{\max} (10^{-5} L mol $^{-1}$ cm $^{-1}$)	Warp (g cm 2 /cm)	Fill (g cm 2 /cm)
PSBP-1	31.48	3.07	8.26	3.4564	0.0698	0.1316
PSBP-2	20.80	2.75	7.42	2.2837	0.0690	0.1260
PSBP-3	12.87	3.42	12.48	1.5763	0.0673	0.1018

MR, the mass ratio of benzophenone side groups to PSBP. The ϵ_{\max} ($\lambda_{\max} = 288.0$ nm) of HHAPB: 9914 L mol $^{-1}$ cm $^{-1}$. BR, the bending rigidity of cotton treated by PSBP. Control, the untreated cotton fabrics with a warp (w) bending rigidity of 0.0785 g cm 2 /cm and filling (f) bending rigidity of 0.2260 g cm 2 /cm.

chain is adsorbed and preferentially forced into an orientation such that the siloxane dipoles point to the phase boundary of the substrate while the free surface is covered by methyl groups in close packing.¹¹ Substitution methyl with bulky benzophenone derivative imparted PSBP with excellent UV absorbing capacity, but disordered the molecule orientation, especially when PSBP was fixed on the surface of silicon wafer. In addition, the interference from the gigantic and adjacent benzophenone derivative side groups as well as their changeable configurations in space also had an apparent influence on the orientation (as shown in Fig. 8) and film morphology of PSBP on the substrate.

Consequently, a nonhomogenous, rough structure film was clearly observed in 3D AFM images of PSBP-1. The brighter pinnacles are deduced to result from the benzophenone derivative side groups linked to the polysiloxane backbone, while the dim surrounding regions are possibly arisen from the PDMS main chains.

Effect of mass ratio of functional side group on the performance of PSBP

Polysiloxanes have been widely used as effective lubricants and softeners in textile industry for years.^{10,12} At the molecule level, the softening fabric properties of polysiloxane are believed to be derived from the flexibility of the siloxane backbone and the low interaction energy of the methyl groups.¹³ Introduction of the bulk and rigid functional groups, benzophenone derivatives, into polysiloxane skeleton makes PSBP possess a satisfactory UV absorbing capacity, but give rise to somewhat rough structure film on substrate, which may have an influence on the tactile and softness of PSBP on fabrics. In addition, the modification of mass ratio of benzophenone derivatives to PSBP can also influence the UV absorbing capacity and other performance of PSBP. Therefore, it is necessary to investigate how functional groups as well as their mass ratios affect the performance of PSBP. The experiment results are shown in Table I.

Table I showed that as the mass ratio of the functional groups, benzophenone derivatives to PSBP

decreased from 31.48 to 12.87%, the extinction coefficients ϵ_{\max} ($\lambda_{\max} = 288.2$ nm) of PSBP fluids were reduced from 3.4564×10^5 to 1.5763×10^5 L mol $^{-1}$ cm $^{-1}$, and while the warp and fill bending rigidities of the finished cotton fabrics lowered respectively, from 0.0698 (w) and 0.1316 (f) to 0.0673 (w) and 0.1018 (f). Obviously, along with the mass ratio of benzophenone derivative side groups to PSBP decrease, the UV-absorbing capacity of PSBP fluids become less, but the softness of the polysiloxane on the treated fabrics will increase.

It was also discovered from Table I that the molar extinction coefficients of three PSBP were very different, they were bigger than that of the precursor, HHAPB. However, the ϵ_{\max} divided by the moles of benzophenone functional groups contained in PSBP clearly became roughly constant and was approximate to the ϵ_{\max} of HHAPB, 9914 L mol $^{-1}$ cm $^{-1}$. This result indicates that the ϵ_{\max} of PSBP is dominantly determined by benzophenone functional groups along with their contents, and the value of ϵ_{\max} could reflect the contents of benzophenone UV-absorbing groups in PSBP.

CONCLUSIONS

Introduction of the bulky functional groups, benzophenone derivative side groups into polysiloxane skeleton could impart PSBP with excellent UV absorbing capacity, but leads to the resulting polysiloxane to give an unhomogenous, rough structure film on silicon wafer substrate. In addition, the functional side group, benzophenone derivative as well as its mass ratio to PSBP affected the polysiloxane performance. As the mass ratio decreased from 31.48 to 12.87%, the mole extinction coefficients ϵ_{\max} ($\lambda_{\max} = 288.2$ nm) of the PSBP fluids lowered from 3.4564×10^5 to 1.5763×10^5 , but while the softening fabric properties of PSBP on cotton fabrics increased.

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