

STUDY ON A HYDROPHOBIC-HYDROPHILIC GRADIENT ROD*

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Abstract A hydrophobic-hydrophilic gradient rod with a length of 40 mm and a diameter of 3 mm was prepared by heating a polymethylsilsesquioxane rod in a cylindrical stove with temperature gradient. The rod was thus pyrolyzed under a temperature gradient condition. The organic end of the gradient rod appears hydrophobic with a contact angle of 109.9° while the other end is hydrophilic with a contact angle of 62.4°. The gradient chemical structure and the gradient microstructure along the rod were characterized by FTIR and SEM, respectively.

Keywords Gradient polymer rod, Hydrophobic, Hydrophilic, Polymethylsilsesquioxane

INTRODUCTION

Gradient materials constitute a special case of various materials. The concentration of one of the components of the material, being chemically and/or physically different from other components, is allowed to change as a function of its position in the sample, producing a predetermined gradient profile. The gradient material can be in any shape — *i.e.*, linear, sigmoid, parabolic, flat or rod. Generally, this kind of material should have gradients along one direction in their structures and/or compositions. Gradient polymeric systems are usually prepared by diffusing a guest monomer into the host polymer (matrix) for certain periods of time to establish the predetermined gradient profile, which is then fixed by *in-situ* polymerization of the diffused monomer^[1].

Any solid surface contacted with liquids is either hydrophobic or hydrophilic, which is governed by both the chemical properties and the microstructure of the surfaces. Recent studies have focused on superhydrophobic surfaces defined as surfaces with contact angles greater than 150°. The first research was reported in 1996 with the spectacular example of a water drop with a contact angle of 174° on a surface obtained using alkyl ketene dimer to provide a rough surface^[2, 3]. Since that time various superhydrophobic surfaces have been obtained by using glass beads^[4], sol-gel process to generate a porous and hence rough surface^[5, 6], vacuum deposited PTFE thin films^[7, 8], anodic oxidation of aluminum surfaces^[3], plasma polymerization^[9, 10] and, most recently, lithographic patterning of silicon wafers^[11]. Superhydrophobic organosilica foams with contact angles greater than 150° were prepared using a sol-gel phase-separation process in which a rapid hydrophobic to hydrophilic transition occurred at around 400°C on heating^[12].

In spite of the above research conducted on hydrophobic surface, few investigations on materials with both hydrophobic and hydrophilic moieties have been reported so far. To our knowledge, both natural materials and

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artifacts are either hydrophobic or hydrophilic. In this study, a hydrophobic-hydrophilic gradient rod with a length of 40 mm and a diameter of 3 mm was prepared by pyrolyzing an organosilicon rod in a temperature gradient field. The organic end of the gradient rod is seen to be hydrophobic with a contact angle of 109.9° and the other end is hydrophilic with a contact angle of 62.4° .

EXPERIMENTAL

The sol-gel method, a relatively cheap method of manufacturing complex materials^[13], was used to prepare an organosilica rod from methyltrimethoxysilane. 26 g of methyltrimethoxysilane (monomer), 0.1 g of *p*-toluenesulfonic acid and 20 mL of acetic anhydride were put into a 500 mL three-necked flask equipped with a water knockout drum. 25 mL of acetic acid was slowly dropped into the flask at 130°C over 2 h while vigorously stirring. With the reaction proceeded, some gases were produced and condensed in the water knockout drum. When the amount of condensed liquid had increased to 25 mL or so, heating was stopped, and the reaction system cooled down to room temperature with continuing stirring. Then the silicone gel, polymethylsilsesquioxane (PMSQ), was removed into a plastic tube with one end enveloped and kept at room temperature for a couple of weeks. A sharp razor was used to cut the tube carefully to take out the cured PMSQ rod. Then the rod was sheared into a rod with a length of 40 mm and still left at room temperature for another couple of weeks to make it fully crosslinked. To avoid overheating, cracking and inconsistencies, the rod was heated at a rate of 2.0 K/min in a temperature gradient field from room temperature to 600°C under a nitrogen atmosphere. The temperature gradient field was formed by controlling the heating element density and the heating voltage of our self-made stove.

The molecular weight of polymethylsilsesquioxane (PMSQ) was measured using a Polymer Laboratory Chromatograph GPC 210 in THF at 35°C with PS standards for calibration. Thermogravimetric analysis was conducted in flowing nitrogen ($30\text{ cm}^3/\text{min}$) at a heating rate of 10 K/min using a Perkin-Elmer TGA 7. Contact angles on the rod were measured by using a Dataphysics Contact Angle System.

Changes in the chemical structure of the gradient rod were assessed by FTIR spectroscopy (BIO-RAD FTS6000/UMA500). The spectra were recorded in transmission from $4000\text{--}400\text{ cm}^{-1}$ at 1 cm^{-1} resolution.

RESULTS AND DISCUSSION

GPC characterization shows that M_n and M_w of PMSQ are 6000 and 50200, respectively. Our studies on pyrolysis of polysilsesquioxanes have been reported in the literature^[14, 15, 16]. Figure 1 shows the typical mass loss of the PMSQ rod in this work from room temperature to 800°C in flowing nitrogen at a heating rate of 10 K/min. There existed three main regions where changes occurred, *i.e.* $50\text{--}200^\circ\text{C}$, $200\text{--}600^\circ\text{C}$ and $600\text{--}750^\circ\text{C}$. In the first region, no obvious weight loss was found, implying that the PMSQ had already been fully crosslinked or condensed before heating. This is different from our previous research on non-fully crosslinked material with an obvious weight loss in this region^[15]. In the range from 200 to 600°C , obvious weight loss was observed, which might be due to the low molecular weight ($M_n = 6000$) of PMSQ before crosslinking. The weight loss occurs due to dehydrogenation and evaporation of the low molecular weight components, such as H_2O and CH_3OH . As a reference, a high molecular weight PMSQ ($M_n = 730700$) was prepared and characterized by TGA. In Fig. 1, the weight loss of the high molecular weight PMSQ was only 6.5% in the whole temperature range. The comparison might mean that higher molecular weight corresponds to higher thermal stability. In the last region, the weight percentage of the rod sample decreased sharply, meaning that the material decomposed severely. The excessive weight loss should be attributed to the redistribution of the Si—O bond and the C—H bonds in Si—CH₃ according to our previous studies.

After the PMSQ rod was heat-treated in a temperature gradient stove under nitrogen, a gradient rod was obtained as shown in Fig. 2. The right end of the rod still retains its original color after the treatment. From right end to left end along the rod, the color becomes darkened gradually due to the increased temperature of treatment in that direction. Obviously, the left rod end shows the color of carbon.

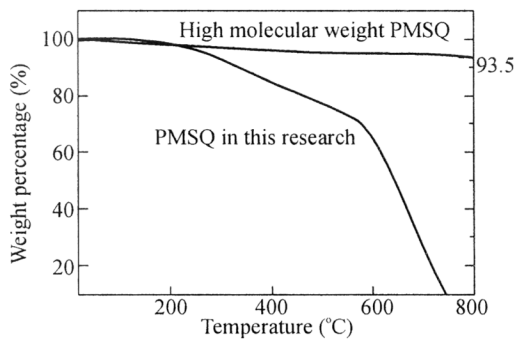


Fig. 1 TGA analysis of PMSQ samples

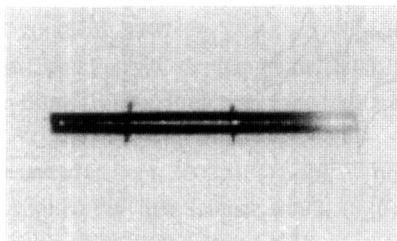


Fig. 2 The gradient rod after heat-treatment in a temperature gradient stove under nitrogen

The contact angles of the gradient rod with water at intervals of about ten millimeters along the longitudinal direction of the gradient rod are shown in Fig. 3. The organic end retained its original PMSQ crosslinked structure as this end was in room temperature during the heat-treatment. The farther from the organic end, the higher the temperature is and the lower the contact angle is, implying that the heat treatment reduced the hydrophobicity of the PMSQ sample.

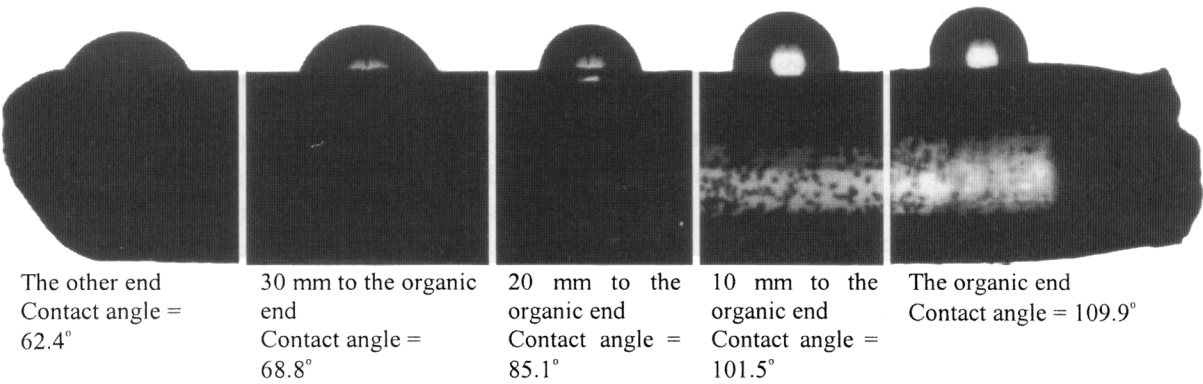


Fig. 3 The contact angles along the longitudinal direction of the gradient rod

Infrared spectra over the wave number range from 750 to 3000 cm^{-1} of the gradient rod heat-treated in N_2 are shown in Fig. 4. The methyl group (CH_3) is characterized by an absorption band of 1275 cm^{-1} . With increasing heat-treatment temperature along the rod, the $\text{Si}-\text{CH}_3$ band intensity decreases. The other characteristic absorption bands at 1030 and 1130 cm^{-1} are attributed to the $\text{Si}-\text{O}-\text{Si}$ stretching vibration. At the organic end, the intensity of 1130 cm^{-1} band is larger than that of the 1030 cm^{-1} band. With the increase of temperature, the intensity of the 1130 cm^{-1} band decreases and the intensity of the 1030 cm^{-1} band increased.

The transition for the ratio of the two band intensities takes place in the range from 10 cm to 20 cm to the organic end. At the other end, the intensity of the 1130 cm^{-1} band is much smaller than the other band intensity. Previous reports show that these two bands' intensity ratio probably represents the regularity in structure of polysilsesquioxane^[17]. In this research, the two bands' intensity ratio changes from the organic end to the other end due to the gradually increased temperature that induces the rearrangement or cleavage of bonds'. We also found slight changes for the two band positions. As shown in Fig. 5, a slight shift of the two bands can be observed from the organic end to the other end.

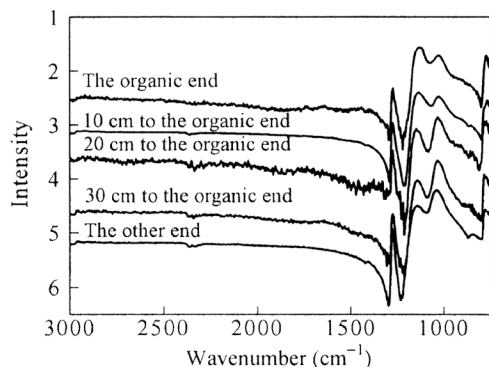


Fig. 4 FTIR spectra along the longitudinal direction of the gradient rod

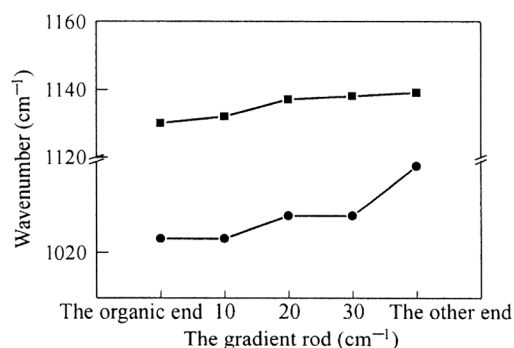


Fig. 5 Changes of peak positions of 1030 cm^{-1} and 1130 cm^{-1} absorption bands along the rod

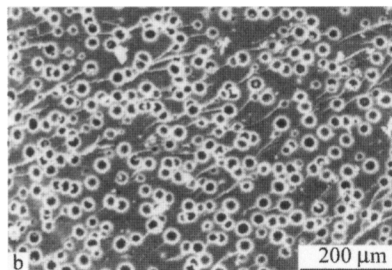
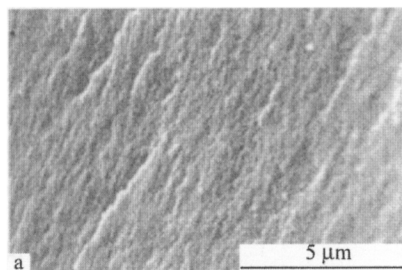


Fig. 6 SEM characterization of the gradient rod
a) Fracture surface of the organic end; b) Fracture surface of the other end

With the hope of gaining an insight into the hydrophobic-hydrophilic gradient rod, SEM investigation was employed to ascertain the difference in the microstructures of the two ends of the gradient rod heat-treated at different temperatures under flowing nitrogen. Fractured surfaces of the rod were observed by SEM. Figure 6(a) shows the surface of the organic end treated at room temperature. It is found that the sample has a solid structure without any holes or particles. Figure 6(b) shows the surface of the other end treated at 600°C . It was found that there are many spherical holes on the surface with diameters of approximately 10–20 microns. This is expected because some gases, such as CH_4 , H_2O and CH_3OH , are given off during the pyrolysis. It is well known that wettability of solid surfaces with liquids is governed by both the chemical properties and the microstructure of the surfaces. As far as the microstructure of a surface is concerned, fine roughness is known to enhance the hydrophobic and hydrophilic properties^[18]. Wenzel pointed out that surface roughness produces a physical enhancement of hydrophobicity into superhydrophobicity. Wenzel's equation predicts that the basic wetting behavior of a surface will be enhanced by roughness so that creating roughness on a flat surface with an equilibrium contact angle more than 90° will increase the contact angle, while the same roughness on a surface with contact angle less than 90° will decrease the contact angle^[18]. Therefore, the spherical holes with a diameter of about 10–20 microns shown in Fig. 6(b) could make a necessary contribution to the hydrophilicity of the other end.

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