Functionalization of polysilsesquioxanes

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(Received 23 February 1994)

New polysilsesquioxanes are prepared by incorporating tetrahydropyranyl moieties into silsesquioxanes. These polymers, which are soluble in organic solvents, are synthesized by means of HCl-catalysed reactions.

(Keywords: polysilsesquioxanes; tetrahydropyranyl; synthesis)

Introduction

With increasing complexity of VLSI (very large-scale integrated) chips, new techniques and resists are required. One of these new techniques is a double-layer system which has radiation-sensitive polysiloxane films as the top imaging layer[1]. Polysiloxanes and polysilsesquioxanes (ladder polysiloxanes possessing silanol end-groups) appear to be suitable materials because of their very high resistance to RIE in an oxygen plasma[2–4].

Our objective is to prepare a new class of chemically amplified resists based on polysilsesquioxanes by incorporating tetrahydropyranyl (THP) groups[5–7]. Acid-catalysed condensation of protected and unprotected silanol end-groups at high temperatures will generate negative images during lithographic development techniques[8,9]. This paper describes the synthesis and characterization of new silanol-protected polysilsesquioxanes.

Experimental

Materials. All reactions were carried out in an atmosphere of dry nitrogen using standard Schlenck techniques.

Tetrahydrofuran (THF; Janssen) was dried and distilled from sodium benzophenone ketal. Polyphenylsilsesquioxane (**1**) (Petrarch, $\bar{M}_n = 9500$, $D = 3.5$) was used as received. 3,4-Dihydro-2H-pyran (**2**) and 3,4-dihydro-2-methoxy-2H-pyran (**3**) (Janssen) were distilled from CaH_2 and stored under dry nitrogen. Diethyl ether was distilled from $CaCl_2$ and dried over sodium. Dichloromethane, trifluoroacetic acid (Janssen) and HCl (gas) were used as received.

Measurements. ^1H and ^{13}C n.m.r. spectra, internal standard $CDCl_3$, were recorded on a Varian VXR 300 spectrometer operating at 299.9 MHz and 75.43 MHz, respectively. ^{29}Si n.m.r. (59.59 MHz) spectra were recorded on the Varian spectrometer with tetramethylsilane (0.0 ppm) as external standard. In all cases, Fourier transform mode was applied using the ^2H resonance of the solvent as field-frequency lock. Chemical shifts (in ppm) are positive in the low-field direction. Molecular weights were obtained by means of gel permeation chromatography on a Waters ALC/GPC-15-C apparatus equipped with Styragel columns using $CHCl_3$ as eluent and employing the method of universal calibration relative to polystyrene standards. Glass transition measurements were recorded at a heating rate of $10°C\ min^{-1}$ using a Perkin–Elmer DSC7 unit.

Synthesis of protected polysilsesquioxanes. Compound **3** was synthesized as follows. A solution of 5.06 g (3.16 mmol) of **1** and 0.63 g (7.43 mmol) of **2** in 20 ml of THF was added dropwise at 0°C to 6 ml of diethyl ether, saturated with HCl gas. After stirring this solution for 3 days at room temperature, the resulting white suspension was extracted twice with 3% KOH solution. The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. The resulting white solid polymer (**3**) was dried under high vacuum at 60°C; yield 4.35 g (86%). ^1H n.m.r.: 1.4–1.9 (m, 6H, $-CH_2$), 3.5–3.9 (m, 2H, $-CH_2$), 4.9 (m, 1H, –CH), 6.3–7.8 (m, 5H, $H_{arom.}$). ^{13}C n.m.r.: 19.5 ($-CH_2$), 22.7 ($-CH_2$), 31.0 ($-CH_2$), 62.5 ($-O-CH_2$), 94.5 (–O–CH), 127.0–136.2 ($6C-H_{arom.}$). ^{29}Si n.m.r.: broad peaks in the region −78 to −84 ppm.

Compound **4** was synthesized in the same way as compound **3**, resulting in a cream-coloured solid polymer with a yield of 84%. ^1H n.m.r.: 1.4–2.0 (m, 6H, $-CH_2$), 3.5 (m, OCH_3), 4.6–4.8 (m, 1H, –CH), 4.9 (m, 1H, –CH), 6.3–7.8 (m, 5H, $H_{arom.}$). ^{13}C n.m.r.: 17.2 ($-CH_2$), 29.8 ($-CH_2$), 42.0 ($-CH_2$), 55.2 ($-O-CH_3$), 98.8 (CH), 99.4 (CH), 126.0–132.0 ($6C-H_{arom.}$). ^{29}Si n.m.r.: broad peaks in the region −78 to −84 ppm.

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0032-3861/94/14/3131–02
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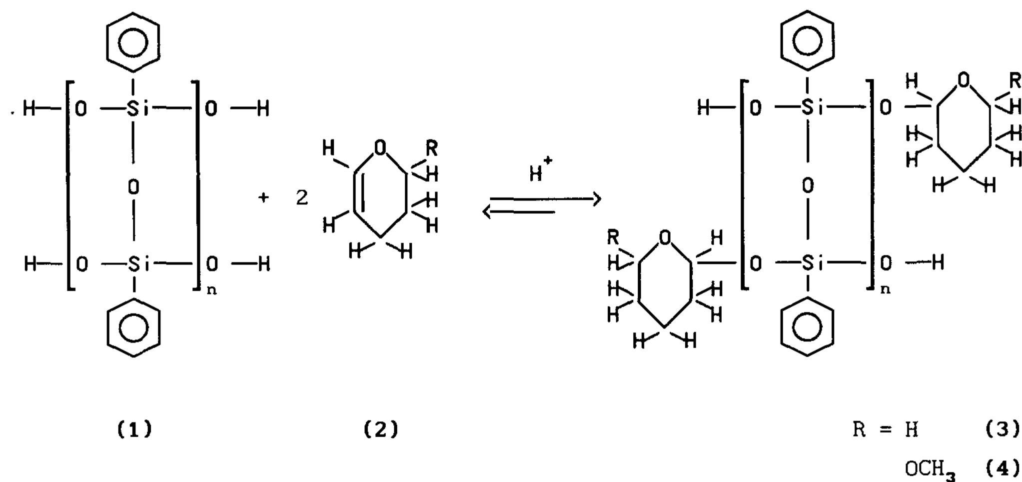
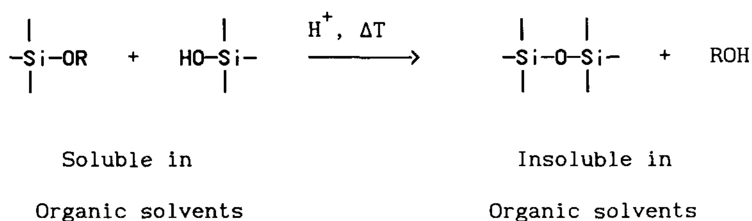


Scheme 1



Scheme 2

Results and discussion

Scheme 1 shows the synthesis of the protected polysilsesquioxanes, which takes place in high yields (70–90%). The molecular weights of the polysilsesquioxanes (**3** and **4**) are around 13 000, with a dispersion degree of 2.1. The synthesized polymers showed no distinctive glass transition temperatures and appeared to be stable up to 150°C.

The temperature at which the THP group is added is important for the acid-catalysed reaction. It was observed that above room temperature the reaction is strongly favoured to the left, resulting in a low degree of protection and subsequent crosslinking. At temperatures below 20°C the equilibrium shifts to the right, and the desired degree of protection is achieved. This temperature-dependent equilibrium — both reactions are based on acid catalysis — gives us the opportunity to protect the silanol groups of these polymers at low temperatures and to unprotect them at temperatures above room temperature. For application as negative resists based on chemical amplification, the polymers need to be highly sensitive to acids. A photoacid generator is often added. Upon exposure, an acid is generated which will lead to a crosslinked product at high temperatures (*Scheme 2*)[10,11].

In addition to the observed results, we tested the acid sensitivity in solution by dissolving the polymers in dichloromethane. Trifluoroacetic acid was added and the solution was refluxed for 10 min. A white residue was formed in all cases, which appeared to be insoluble in organic solvents. These results show an acid sensitivity suggesting that the polymers are suitable candidates for application as negative resists in microlithography. Lithographic studies are currently underway.

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