SYNTHESIS OF SILOXANES AND SILSESQUIOXANES FOR 157 NM MICROLITHOGRAPHY

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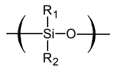
Introduction

A large amount of effort is devoted to designing high-resolution single-layer resists suitable for 157 nm exposure using an F_2 excimer laser light source. Since air, water, and most hydrocarbons are strongly absorbing at this wavelength, designing resists that have adequate transparency at 157 nm poses a difficult challenge. Current resist platforms used for 193 nm and 248 nm exposure have also been found to be too absorbing at reasonable thicknesses. However, spectroscopic studies have revealed that fluorinated polymers and siloxane/silsesquioxane polymers are sufficiently transparent at this wavelength to be considered possible candidate platforms from which to design new resists[1]. Our group has made significant progress in designing transparent polymers based on fluorinated acrylates and fluorinated norbornenes[2]. Here we report our progress in designing polysiloxanes and polysilsesquioxanes for 157 nm microlithography. This paper presents the synthesis of several new siloxanes and silsesquioxanes along with their properties based on classical characterization together with gas phase and VUV film measurements. The goal is to design imageable materials that are transparent at 157 nm, are resistant to attack by reactive plasmas, and are soluble in both organic solvents and aqueous base. The polymers must also have excellent mechanical properties, tenacious adhesion to metals, common insulators, and semiconducting surfaces. Although there are no known materials at present that meet all of these requirements, we are pleased to report our progress in developing such materials.

Results and Discussion

Polysiloxanes in general have very low glass transition temperatures (**Table 1**)[3]. Poly(dimethylsiloxane), for example, is one of the most flexible chain molecules known, with a Tg of approximately -125°C (one of the lowest recorded for any common polymer). This flexibility arises from the unusually long Si-O skeletal bond and the more open Si-O-Si bond angle (143°). This is not encouraging news when one wants to design resists based on this platform. A closer look at the data in **Table 1**, however, reveals that the Tg's can be considerably increased when bulky side groups such as phenyl are used or when fluorine is incorporated into the side chains. In addition, the Tg's of polysilsesquioxanes are improved a little because of their crosslinking nature. In our own laboratories we have determined that the glass transition temperature of polymer **1** is approximately 90°C (**Figure 1**). This fact has encouraged us to pursue this platform, and we next investigated the transparency of these types of polymers at 157 nm.

Table 1. Tg Data for Some Polydiorganosiloxanes


$-(\mathrm{Si}(R_1)(R_2)-O)-$

R_1	R_2	Tg/°C
CH_3	H	-138
CH_3	CH_3	-125
CH_3	Phenyl	-90 to -75
CH_3	CH_2CH_3	-135
CH_3	$CH_2CH_2CH_3$	-120
CH_3	$CH_2CH_2CF_3$	-70
Phenyl	Phenyl	50 to 100

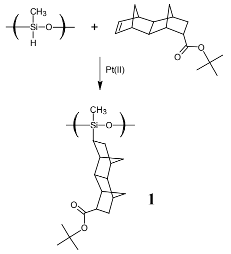
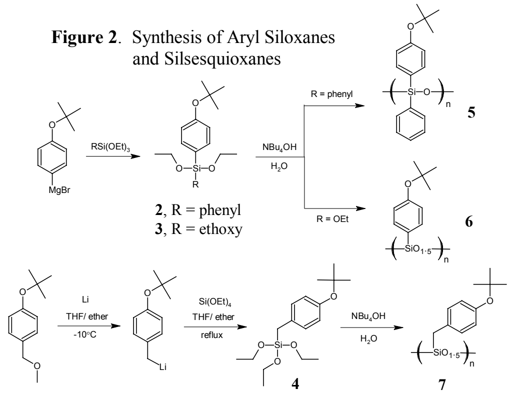


Figure 1. Synthesis of a dinorbornylmethylsiloxane

Our gas phase VUV spectroscopy measurements of diphenyldiethoxysilane, which is less absorbing at 157 nm than initially thought, encouraged us to pursue siloxane and silsesquioxane polymers based on this monomer. Hence, the polymers shown in **Figure 2** were prepared by base-catalyzed (NBu_4OH/H_2O) condensation of the corresponding monomers. Monomer **2** was prepared by the Grignard addition of 4-*t*-butoxyphenylmagnesium bromide to phenyltriethoxysilane using THF as the solvent. Similarly, monomer **3** was prepared using tetraethoxysilane. Monomer **4** was synthesized by the addition of 4-*t*-butoxyphenylmethyllithium to tetraethoxysilane. The Tg's of the three polymers **5**, **6**, and **7** are 56°C, 111°C, and 95°C, respectively. These polymers were spun into thin films and their absorbances at 157 nm were measured by Variable Angle Scanning Ellipsometry (VASE) under vacuum (**Figure 3**).

Figure 2. Synthesis of Aryl Siloxanes and Silsesquioxanes



2, R = phenyl
3, R = ethoxy

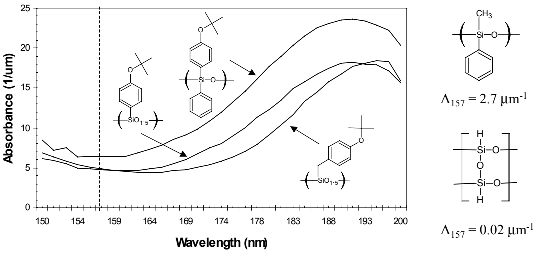


Figure 3. Absorbances of Aryl Siloxanes and Silsesquioxanes

The absorbances of these polymers are too high for use as a resist for 157 nm exposure. The aromatic groups contribute too much to the absorbance of these polymers, so other side units must be considered or fluorine must be introduced into the aromatic ring. It is interesting to note that adding a methylene unit between the aromatic ring and silicon atom does not affect the absorbance significantly. The Tg is somewhat lowered, however.

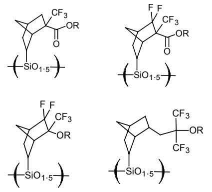


Figure 4. Transparent Silsesquioxanes

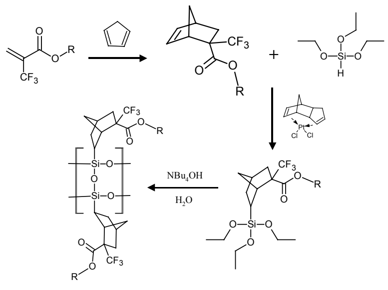


Figure 5. Synthesis of Norbornyl Silsesquioxanes

Currently under investigation is the synthesis of polysilsesquioxanes that contain several of our transparent fluorinated norbornene derivatives (**Figure 4**)[2]. These polymers are prepared from the acid-catalyzed (oxalic acid/H_2O) or base-catalyzed (NBu_4OH/H_2O) condensation of the corresponding monomers. The monomers are made from a hydrosilylation reaction of one of our norbornene analogues to triethoxysilane using cyclopentadienyldichloroplatinum (II) as catalyst (**Figure 5**). The results of these studies will be reported elsewhere.

References

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