



Structural Landscape on the Gas Phase of Novel Aryl-bridging Organosiloxanes†

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Novel aryl-bridging organosiloxanes are modeled and examined theoretically in the gas phase. Three substituents (phenyl, biphenyl and biphenyl ether) are introduced to siloxane to design precursors (Pr1, Pr2 and Pr3) for making polysiloxanes. Pr1 has a very symmetric structure and the aryl ring can help electron transfer through the conjugated bond, Pr2 has a non-conjugated electron delocalized structure, which may reduce the ability of delivering electrons. Despite the non-plane structure, Pr3 is likely to own a favorable structure for electron transferring with the help of oxygen, which may help this type of materials to improve the dielectric properties.

Key Words: Aryl-bridging organosiloxanes, Theoretical investigation, Geometric effects.

INTRODUCTION

With the emerging of 22 nm technology node for ultralarge-scale integrated (ULSI) chips, new low dielectric (low k) materials with dielectric constant below 2.1 are urgently required to minimize the cross-talking and RC delay caused by higher densities of devices and wiring for high performance chips¹. Among many possible candidates for ultra-low k materials, nanoporous organosilicate thin films are one of the most promising materials because of their excellent comprehensive performance, besides their continuously adjustable k value via the incorporation of nanopores within the thin films²⁻⁴. Carbon-bridging organosiloxanes are among those organosilicates, which have undergone intensive studies and proved good ultra-low k materials^{5,6}. However, the relatively low thermal stability of the current alkyl-bridging organosiloxanes has limited their further development. In order to solve this problem, we have designed a series of novel aryl-bridging organosiloxanes, $(\text{EtO})_3\text{Si-R-Si}(\text{EtO})_3$ where R = phenyl, biphenyl or biphenyl ether, which are the precursors for making polysiloxane hybrid network with better thermal stability and other performances. For the purpose of checking the material properties related to the precursor structure, three types of bridge substituents (R1, R2 and R3, Fig. 1) are selected to synthesize the precursor of Pr1, Pr2 and Pr3. The previously available data are not adequate to the structure of precursors, therefore, this consideration led us to a series of theoretical works

carried out to investigate the structure of Pr1, Pr2 and Pr3, results demonstrating in this article will explain the structural effect on the study of designing low k materials in the upcoming publications.

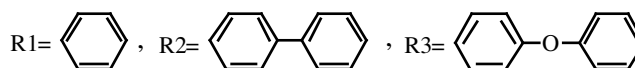
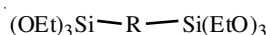


Fig. 1. Schematic structures of modeled precursors

EXPERIMENTAL

The geometric structures of all species are modeled and examined theoretically in the gas phase using the Gaussian03⁷ at the PM3, HF/6-31G(d) and DFT of B3LYP at the 6-31G(d) level. The use of three calculation levels allows a comparison of their optimized molecular structure, thus, another purpose of this work is to find an effective and time-saving theoretical level for investigating on polysiloxane hybrid networks. The nature of the stationary points was confirmed by the harmonic frequency analysis as a minimum with all positive frequencies⁸.

RESULTS AND DISCUSSION

Precursor 1:1,4-bis(trimethylsilyl)benzene: The polysiloxane hybrid network becomes dielectric active when

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linked group can pass electron, therefore, Pr1 is modeled as 1,4-*bis*(trimethylsilyl)benzene and calculated at three levels of theory. As were noted⁹, the commonly used B3LYP density functional with base set of 6-31g* often gives satisfactory results. So, Pr1 is first optimized at B3LYP/6-31g* level of theory, then, the same calculation is performed at PM3 and HF/6-31g* level of theory, the results at the latter two will be compared. All results are shown in Table-1.

Two triethylsilyl substituents of Pr1 are distributed symmetrically along the benzene ring. This suggests that the poly hybrid network started from Pr1 will have a symmetrical and regular structure. The geometry optimized at level of HF/6-31g(d) is essentially unchanged, the deviations is smaller than 0.05 Å on bond length and 0.01° on bond angle. However, the deviations become large, somehow unacceptable at PM3 level,

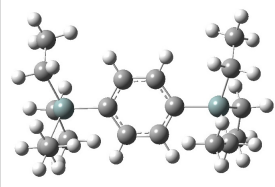
Precursor 2: 4,4'-*bis*(trimethylsilyl)biphenyl: To understand how substituents alter the polysiloxane hybrid network and influence the dielectric activity, it is necessary to analyze the substituent effects on the precursor. R group is extended to more complex one, Pr2 is then modeled as 4,4'-*bis*(trimethylsilyl) biphenyl (Table-2). The structure of Pr2 is significantly different from its of Pr1, the torsion angle of two aryl rings is

about 37° (at level of B3LYP/6-31g(d)), the relatively large torsion angle show that this is not a conjugated electron delocalized structure, so electrons have to overcome barrier to transfer through molecules, this structure may cause a lower dielectric activity. The non-conjugated structure also suggests that the polysiloxane hybrid network started from Pr2 may be a fixable network.

The calculations at level of HF/6-31g(d) get a very close results comparing with those at the level of B3LYP/6-31g(d). The deviation at PM3 level is also unacceptable.

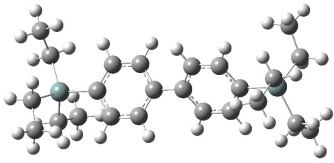
Precursor 3: 4,4'-*bis*(trimethylsilyl)biphenyl ether: The biphenyl ether is the most interesting of the substituent group, the lone pair electrons of bridging oxygen play an important role on the electron transfer process, the precursor participated by biphenyl ether is modeled as 4,4'-*bis*(trimethylsilyl)biphenyl ether. The torsion angle of two aryl rings of biphenyl ether is about 66° (Table-3, at level of B3LYP/6-31g(d)), the pretty large torsion angle provides enough space to expand two aryl ring and the lone pair electrons of oxygen, electrons can easily transfer through molecule by crossing oxygen, this effect can enhance dielectric activity. The results at HF/6-31g(d) also show a good agreement at all respects.

TABLE-1
SELECTED GEOMETRIC PARAMETERS OPTIMIZED FOR Pr1

	PM3	HF/6-31g(d)	B3LYP/6-31g(d)
			
Si-C(B) ^{a,b}	1.849	1.903	1.900
Si-C(B)-C(B) ^c	122.1,118.5	122.6,120.9	122.6,120.8
Si-C(B)-C(B)-Si ^c	88.5	0.0	11.4

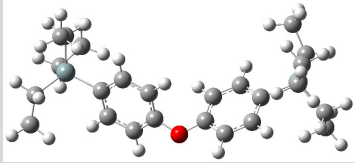
a: Carbon atom in benzene ring. b: in Å. c: in degree.

TABLE-2
SELECTED GEOMETRIC PARAMETERS OPTIMIZED FOR Pr2

	PM3	HF/6-31g(d)	B3LYP/6-31g(d)
			
Si-C(B) ^{a,b}	1.849	1.902	1.899
Si-C(B)-C(B) ^c	118.6,122.0	120.9,122.6	121.3,122.5
C(B)-C(B)-C(B)-C(B) ^c	46.6,47.2	43.7,44.1	36.9,37.3

a: Carbon atom in benzene ring. b: in Å. c: in degree.

TABLE-3
SELECTED GEOMETRIC PARAMETERS OPTIMIZED FOR Pr3

	PM3	HF/6-31g(d)	B3LYP/6-31g(d)
			
Si-C(B) ^{a,b}	1.848	1.900	1.900
C(B)-O ^b	1.388	1.364	1.380
Si-C(B)-C(B) ^c	118.4,122.0	121.0,122.6	121.0,122.5
C(B)-C(B)-C(B)-C(B) ^c	63.9	73.7	65.6

a: Carbon atom in benzene ring. b: in Å. c: in degree.

Conclusion

With three substituent, polysiloxane precursor is modeled as 1,4-*bis*(trimethylsilyl) benzene (Pr1), 4,4'-*bis*(trimethylsilyl) biphenyl (Pr2) and 4,4'-*bis*(trimethylsilyl) biphenyl ether (Pr3) in this work. Pr1 has a symmetric structure, Pr2 has a non-conjugated electron delocalized structure, which may reduce the ability transferring electron. Pr3 has a very interesting configuration, the presence of bridging oxygen is significantly reduce the repulsion energy, the lone pair electrons of oxygen can help electron transfer from one aryl ring to another aryl ring, which is favorable to the material dielectric properties. The results at level of HF/6-31g* can reproduce the results at higher level.

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