

Research Article

Theoretical Study on the Static (Hyper)Polarizabilities of α -*t*-Bu- ω -CN-Poly(methylphenyl)silane

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The static linear and nonlinear optical properties of the σ -conjugated polymer α -*t*-Bu- ω -CN-poly(methylphenyl)silane (PMS) are studied at the Coupled-Perturbed Hartree-Fock (CPHF) level with 6-31+G(d) basis set. The calculated results reveal that the static first hyperpolarizabilities of this system increase with the main chain length and have a good agreement with experiments. The (hyper)polarizabilities per unit cell have been extrapolated to infinite chain limit and a comparison is made to those of polysilane and polyacetylene (PA). Besides, other structural properties depending on the σ -conjugated Si-Si skeleton length are investigated as well. Electron correlation effect is estimated and it turns out that the MP2 static first hyperpolarizability is about 1.5 ~ 2.0 times larger than the corresponding CPHF value for the polymer with $n \leq 6$.

1. Introduction

In recent years, polysilanes have attracted increasingly extensive attention due to their unique physical and chemical properties resulting from σ -electrons delocalized along the silicon backbone. In this regard, they have resulted in a variety of technological applications, such as conductor and semiconductor [1], photoconductive materials [2], organic multilayer, light emitting diodes (LEDs) [3], high-density optical data storage materials [4], electro luminescence (EL) devices [5, 6], and nonlinear optical (NLO) materials [7, 8].

The polysilanes represent a completely new class of potentially interesting nonlinear optical (NLO) materials, and in contrast to the classical π -conjugated polymers, their physical, chemical, and optical properties show significant differences. Polysilanes are linear polymers of silicon, and the σ -electrons of the polymer backbone are delocalized. This σ -conjugation gives rise to electronic properties that allow for possible applications as electroluminescent, nonlinear, optical, lithographic, and semiconductor materials. The σ -electrons delocalization associated with the phenomenon, in which the silicon backbone itself is a chromophore, greatly influences the optical properties of polysilanes. Therefore, in spite of saturation of all the Si atoms on the main chain,

polysilanes have strong absorption in the UV in the region of 250–400 nm, which is attributed to the σ - σ^* transition or the σ^{3d} transition and relevant to the configuration and length of the Si-Si backbone. As NLO materials, in comparison with π -conjugated carbon-backbone polymers, polysilanes own many unique advantages; for example, they have optical transparency in the visible spectrum, their UV absorption peak can be able to be shifted, they are easily to be made into films and applied to optic research, and they are of good thermal and chemical stability [9].

Many substituted polysilanes have been investigated from experimental points of view and the majority of them focus on the third-order optical nonlinear coefficient $\chi^{(3)}$. Shi et al. [10] have synthesized poly(methylphenyl)silane (PMPS) and measured its third-order nonlinear optical susceptibility $\chi^{(3)}$ of 5.8×10^{-12} esu by third harmonic generation (THG) with a pulse laser width at 1064 nm for thin films. Then, Tang and coworkers [11] have explored a novel strategy to develop polysilanes functionalized with a high density of nonlinear optical chromophores and the poled film reveals a resonant d_{33} value of 19 pm/V by second harmonic generation (SHG) measurement at the frequency of 1064 nm. However, what would the situation of the second-order nonlinear optical

susceptibility of PMPS derivatives be? There is little scientific attention from the theoretical point of view.

For an asymmetric molecule, its second-order nonlinear optical susceptibility is nonzero. In this paper, electric properties of PMS are studied in order to assess the trends with increasing Si–Si chain length for the cases $n = 2, 4, 6, 8, 10, 12,$ and 14 . Meanwhile, the mechanism of the variation of the static (hyper)polarizability as a function of chain length is elucidated by analyzing the Si–Si bond lengths and natural population analysis (NPA) charges on Si atoms along the backbone as well as energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

2. Computational Details

All of the calculations have been performed through the following procedures.

- (1) The conformations of the polymers were optimized for all-trans conformation, which was assumed to be the ground state geometry, at the B3LYP/6-31G(d) level of theory. We constrained the Si–Si skeleton in a zigzag plane and assumed syndiotactic structure throughout the polymers. The longitudinal z -axis was set by the line connecting the first and second to last silicon atoms of the main chain. With the optimized geometries, NPA charges of the polymers were investigated at the same level as B3LYP/6-31G(d).
- (2) MP2 method was employed for calculating shorter chains of PMS to estimate the electron correlation effects on NLO properties of PMS as it is known that conventional DFT method is unsuitable for describing the chain length dependence of the hyperpolarizability in conjugated systems [12, 13]. Thus, CPHF method has been employed to compute the static polarizability and first hyperpolarizability.

In the presence of an electric field, energy can be expressed as

$$E = E^0 - \mu_i F_i - \frac{1}{2!} \alpha_{ij} F_i F_j - \frac{1}{3!} \beta_{ijk} F_i F_j F_k \cdots, \quad (1)$$

where E^0 is the energy without the applied electrostatic field, F_i is the component of the field along the i th Cartesian direction, and μ_i , α_{ij} , and β_{ijk} may be called a component of dipole, polarizability, and the first-order hyperpolarizability tensor, respectively. Based on the computed tensor components, we focus on μ_0 , α_0 , and β_0 . Their expressions are written as follows:

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}, \quad (2)$$

$$\alpha_0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (3)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}, \quad (4)$$

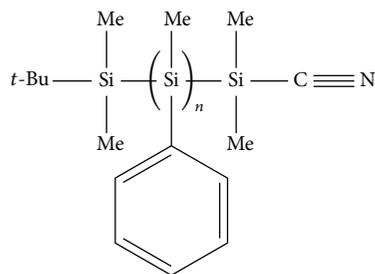


FIGURE 1: Schematic illustration of structure of α - t -Bu- ω -CN-poly(methylphenyl)silane.

where

$$\beta_i = \frac{3}{5} (\beta_{iii} + \beta_{ijj} + \beta_{ikk}), \quad i, j, k = x, y, z. \quad (5)$$

All calculations were performed with the GAUSSIAN 03 [14] program package. Net atomic charges were obtained using the NPA included in the natural bond orbital (NBO) algorithm [15, 16]. The plots of molecular orbitals were generated with the GaussView program (Gaussian, Inc., Wallingford, CT, USA) [17].

3. Results and Discussion

3.1. Conformations. The schematic illustration of optimized conformations of PMS is shown in Figure 1. The important geometrical parameters for $n = 2, 4, 6, 8, 10, 12,$ and 14 are listed in Table 1. As seen in Table 1, for a certain polymer molecule, the longest Si–Si bond is always in the central part of it. Meanwhile, from $n = 2$ to $n = 14$, with the increase of Si main chain length of the system, one can find that the Si–Si bond length is increased. The variation tendency of the central Si–Si bond length is depicted in Figure 2. The central Si–Si bond length ranges from 2.393 to 2.411 a.u., and it is almost convergent when n is greater than 10. From this tendency, one can deduce that the Si–Si bond dissociation energies are getting smaller and smaller; consequently the σ - σ^* transitions become easier as the Si skeleton length increases. However, the bond lengths between substituents and Si atoms at both edges of the backbones (t -Bu–Si, Si–CN) are barely changed. Compared with polysilanes, whose Si–Si bond length is around 2.36 Å, PMS polymer exhibits relatively longer Si–Si bond lengths (2.38–2.41 Å), because its main Si–Si chain is positively charged by the influence of the larger electron affinity of phenyls.

The Si–Si–Si bond angles of the PMS polymer are ranging from 112.5 to 113.8 degree. At the two ends of the chain, the bond angles become a little bit smaller.

3.2. Charge Distribution. In order to understand the electronic properties of PMS, atomic charges were calculated by means of NPA at B3LYP/6-31G(d) level. Table 2 shows the atomic charges of Si atoms and the group charges of t -Bu and –CN of the PMS. From the data in Table 2, one can see that regardless of the chain length, the atomic charges of Si on one end of the Si–Si backbone, which is connected to the t -Bu

TABLE 1: Optimized geometrical parameters of Si–Si bond lengths (in Å) and Si–Si–Si bond angles (in degree) of all-trans α -*t*-Bu- ω -CN-poly(methylphenyl)silane.

n	2	4	6	8	10	12	14
Bond length							
Si(1-2)	2.393	2.398	2.400	2.400	2.401	2.402	2.402
Si(2-3)	2.393	2.399	2.402	2.403	2.404	2.404	2.404
Si(3-4)	2.393	2.397	2.403	2.405	2.406	2.405	2.405
Si(4-5)		2.395	2.405	2.408	2.409	2.409	2.409
Si(5-6)		2.379	2.400	2.408	2.410	2.409	2.409
Si(6-7)			2.396	2.406	2.410	2.411	2.411
Si(7-8)			2.379	2.401	2.409	2.410	2.411
Si(8-9)				2.397	2.407	2.410	2.411
Si(9-10)				2.380	2.402	2.408	2.410
Si(10-11)					2.397	2.405	2.410
Si(11-12)					2.380	2.401	2.408
Si(12-13)						2.396	2.406
Si(13-14)						2.379	2.401
Si(14-15)							2.396
Si(15-16)							2.379
Bond angle							
Si(1-2-3)	110.8	110.8	110.7	110.7	110.7	110.5	110.4
Si(2-3-4)	111.3	113.5	113.7	113.6	113.6	113.8	113.9
Si(3-4-5)		112.8	112.6	112.7	112.8	112.7	112.7
Si(4-5-6)		110.3	112.9	112.9	112.9	113.0	113.1
Si(5-6-7)			112.7	112.6	112.8	112.8	112.9
Si(6-7-8)			110.5	112.7	112.8	113.0	113.0
Si(7-8-9)				112.7	112.7	112.8	112.9
Si(8-9-10)				110.5	112.8	113.0	113.0
Si(9-10-11)					112.7	112.7	112.8
Si(10-11-12)					110.5	112.9	113.0
Si(11-12-13)						112.5	112.7
Si(12-13-14)						110.6	112.9
Si(13-14-15)							112.5
Si(14-15-16)							110.9

group, are near 1.41 a.u., and while the atomic charges of Si on the other end, which is connected to the –CN group are near 1.25 a.u., the latter is smaller than the former. A proper explanation of this result could be given that the charge transfer from electron-donating group to electron-accepting group along the Si–Si backbone has taken place so that the atomic charges of Si connecting to the electron-donating group *t*-Bu are more positive than those of Si connecting to the electron-accepting group –CN. In the central region of the chain, there is a concentration of charge distribution and the curve of the average charges of the middle two Si atoms is shown in Figure 3. The values are ranging from 0.84 to 0.88 a.u., and it is almost convergent when n is greater than 6. On the other hand, charges on the both groups of *t*-Bu and –CN are getting more and more negative with n increasing; however, charges on –CN are always more negative than those of *t*-Bu and their differences of $|\Delta q|(|q(-CN)-q(t-Bu)|)$ are decreased.

3.3. The Frontier Orbital Energies. The frontier orbital energies of PMS were evaluated by B3LYP method with the 6-31G(d) basis set and listed in Table 3. With the increase of repeating unit, the energies of HOMO are increased and the energies of LUMO are decreased; thus the energy gaps ($\Delta\epsilon$) between LUMO and HOMO are decreased. From the schematic illustration of HOMO and LUMO as shown in Figure 4, one can see that the HOMO is localized on both the main chain and phenyls and is combined of σ and π type; while the LUMO is antibonding σ^* orbital. Therefore, it is expected that when the Si–Si main chain gets longer, the σ - σ^* conjugation along the Si–Si backbone will be stronger.

3.4. Static Electronic (Hyper)Polarizabilities

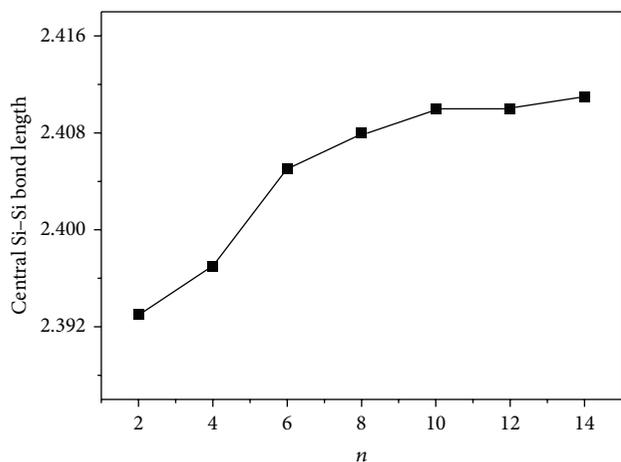
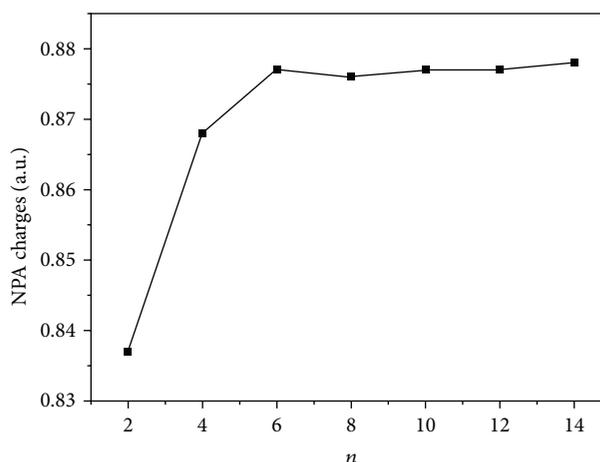
3.4.1. Basis Sets Effect. Different basis sets were chosen as following: 3-21G, 6-31G, 6-31G(d), 6-31G(d, p), 6-31+G(d), 6-31+G(d, p), 6-31++G(d, p), and 6-311++G(d, p), to study the

TABLE 2: NPA charges on *t*-Bu, -CN, and Si atoms on the backbone of α -*t*-Bu- ω -CN-poly(methylphenyl)silane. All quantities are in a.u.

n	2	4	6	8	10	12	14
Si ₁	1.409	1.407	1.406	1.406	1.406	1.405	1.406
Si ₂	0.819	0.831	0.832	0.832	0.832	0.832	0.832
Si ₃	0.855	0.872	0.870	0.870	0.870	0.870	0.869
Si ₄	1.248	0.864	0.877	0.878	0.878	0.878	0.878
Si ₅		0.859	0.876	0.876	0.876	0.876	0.875
Si ₆		1.247	0.864	0.876	0.877	0.877	0.878
Si ₇			0.860	0.878	0.877	0.877	0.877
Si ₈			1.247	0.863	0.876	0.877	0.878
Si ₉				0.860	0.878	0.878	0.877
Si ₁₀				1.248	0.864	0.876	0.877
Si ₁₁					0.860	0.879	0.877
Si ₁₂					1.248	0.864	0.876
Si ₁₃						0.860	0.878
Si ₁₄						1.248	0.864
Si ₁₅							0.860
Si ₁₆							1.248
<i>t</i> -Bu	-0.4604	-0.4622	-0.4637	-0.4643	-0.4647	-0.4649	-0.4654
-CN	-0.4697	-0.4704	-0.4710	-0.4715	-0.4718	-0.4719	-0.4722
$ \Delta q $	0.0093	0.0082	0.0073	0.0072	0.0071	0.0070	0.0068

TABLE 3: The energies of the frontier orbitals of α -*t*-Bu- ω -CN-poly(methylphenyl)silane. All quantities are in eV.

n	2	4	6	8	10	12	14
ϵ (HOMO)	-5.995	-5.609	-5.395	-5.257	-5.161	-5.092	-5.044
ϵ (LUMO)	-0.642	-0.681	-0.808	-0.891	-0.943	-0.976	-1.000
$\Delta\epsilon$	5.353	4.928	4.587	4.366	4.218	4.116	4.044

FIGURE 2: The central Si-Si bond length (in Å) of α -*t*-Bu- ω -CN-poly(methylphenyl)silane versus n .FIGURE 3: NPA charges of the average of the middle two Si atoms of α -*t*-Bu- ω -CN-poly(methylphenyl)silane.

effect of basis sets on dipole μ_0 , polarizability α_0 , and the first hyperpolarizability β_0 . The results are listed in Table 4.

From the data, one can see that the choice of basis sets has a great influence on the results. For μ_0 and α_0 , with the increase of the size of basis set, both of them become bigger. For β_0 , however, three basis sets 6-31+G(d), 6-31+G(d, p), and

6-31++G(d, p) provide nearly the same results. Comparing basis sets 6-31G and 6-31G(d) with 6-31G(d, p), we find that β_0 becomes larger when polarization functions are introduced, but the second polarization function has little effect on it. Comparing basis sets 6-31G(d) with 6-31+G(d) and 6-31+G(d, p) with 6-31++G(d, p), it is found that β_0 becomes smaller

TABLE 4: The basis set effects on the electric properties of α -*t*-Bu- ω -CN-poly(methylphenyl)silane ($n = 2, 4, 6$). All quantities are in a.u.

	$n = 2$			$n = 4$				$n = 6$	
	μ_0	α_0	β_0	μ_0	α_0	β_0	μ_0	α_0	β_0
3-21G	1.86	311.06	85.9	1.91	485.99	158.5	1.94	662.21	225.6
6-31G	1.99	322.50	83.1	2.04	502.80	152.9	2.08	684.28	220.1
6-31G(d)	1.88	321.36	98.9	1.92	500.31	175.1	1.95	679.68	233.5
6-31G(d, p)	1.88	324.46	104.6	1.92	338.02	175.1	1.95	685.32	227.8
6-31+G(d)	1.95	354.10	77.2	2.00	553.67	139.7	2.03	754.27	197.7
6-31+G(d, p)	1.96	356.88	77.2	2.00	557.54	139.6	2.04	759.13	197.6
6-31++G(d, p)	1.96	358.43	74.1	2.01	559.32	134.8	2.04	761.38	195.1
6-311++G(d, p)	1.97	361.80	73.8	2.02	564.25	130.0	2.05	767.64	187.7

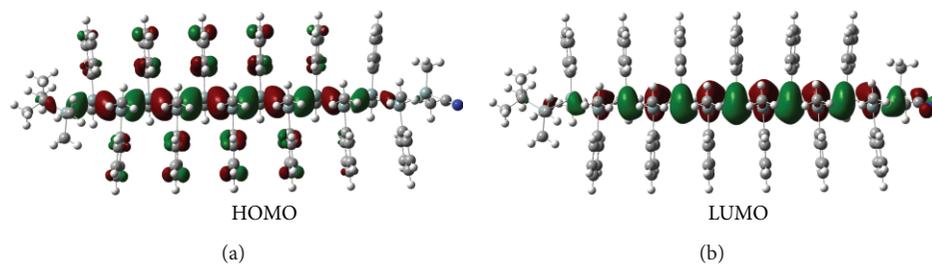
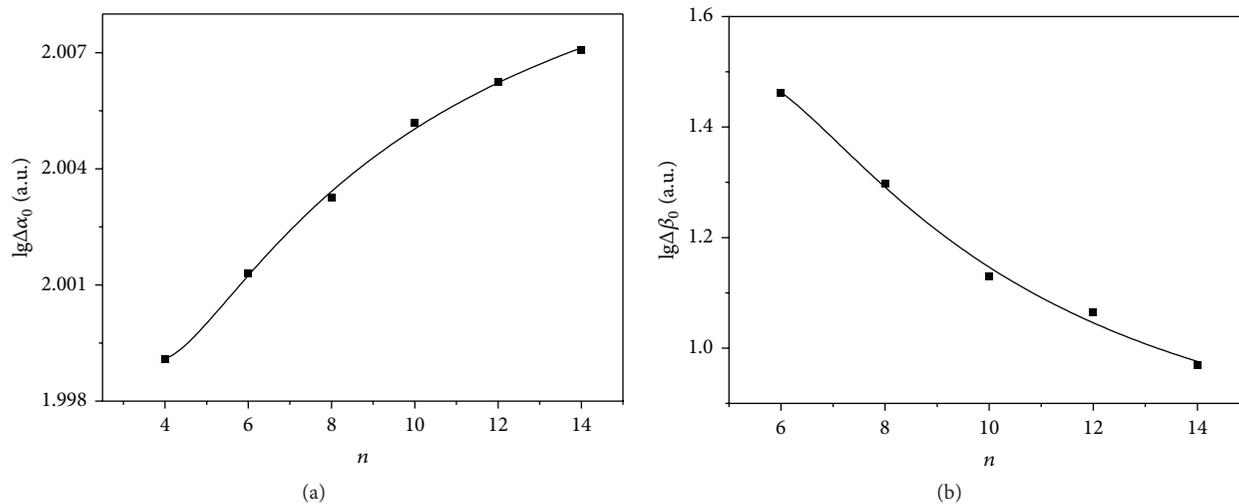
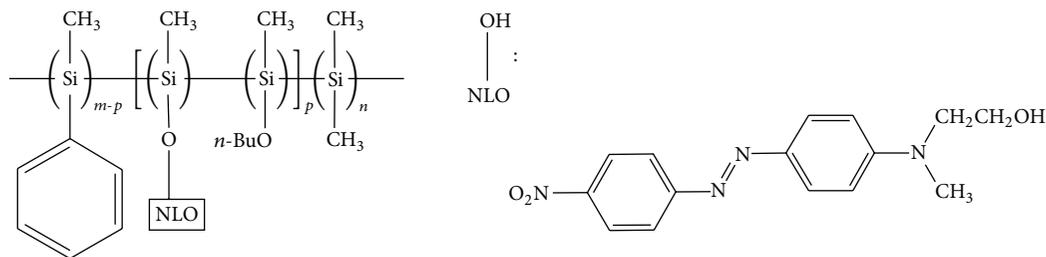
FIGURE 4: The schematic illustration of HOMO and LUMO of α -*t*-Bu- ω -CN-poly(methylphenyl)silane ($n = 12$).FIGURE 5: Plots of $\lg\Delta\alpha_0$, $\lg\Delta\beta_0$ versus n . n is the number of repeating unit cells. (a) $\lg\Delta\alpha_0$ versus n and (b) $\lg\Delta\beta_0$ versus n .

FIGURE 6: Schematic illustration of structure of the functionalized polysilanes PII-1.

TABLE 5: The electron correlation effect of α -*t*-Bu- ω -CN-poly(methylphenyl)silane ($n = 2, 4, 6$). All quantities are in a.u.

n	CPHF	MP2	MP2/CPHF
2			
μ_0	1.95	1.86	0.95
α_0	354.10	376.09	1.06
β_0	77.2	111.0	1.43
4			
μ_0	2.00	1.91	0.96
α_0	557.54	590.66	1.06
β_0	139.7	250.2	1.79
6			
μ_0	2.03	1.94	0.96
α_0	754.27	807.87	1.07
β_0	197.7	405.1	2.05

when diffuse functions are added; however, the second diffuse function also has little effect on β_0 . This implies that basis sets of H atoms contribute only a bit to the first hyperpolarizability β_0 . Based on these analyses, the basis set of 6-31+G(d) was chosen, which could be a good one for less time consuming and relatively reliable results.

3.4.2. Electron Correlation Effect. The first hyperpolarizabilities of PMS ($n = 2, 4, 6$) were calculated by both CPHF and MP2 method, using 6-31+G(d) basis set to discuss the electron correlation effect. The results are listed in Table 5. From Table 5, one can see that the electron correlation effect has much significant influence on the first hyperpolarizability compared with basis sets effect. When $n = 2$, MP2 β_0 is 1.44 times larger than that of CPHF; when $n = 4$, the multiple rises to 1.79; and when $n = 6$, the corresponding multiple becomes 2.05. So one can estimate that the electron correlation effect on the first hyperpolarizability β_0 is about 1.5~2.0 times larger than that of CPHF for polymer $n \leq 6$.

3.4.3. Static (Hyper)Polarizabilities. The CPHF/6-31+G(d) static first hyperpolarizabilities of PMS ($n = 2, 4, 6, 8, 10, 12, 14$), as calculated for different chain lengths, are given in Table 6. From this table it can be seen that (i) β_z component, which represents for the value in the longitudinal direction of the Si-Si skeleton, makes the dominant contribution to β_0 and increases much faster than the others; (ii) μ_0 , α_0 , and β_0 increase as the chain length elongated; however, the amount of increase for each component is discriminating. Among them, α_0 has the biggest rate of increase, which ranges from 354.10 to 1564.33 a.u. from $n = 2$ to $n = 14$; β_0 is ranging from 77.2 to 306.0 a.u.: it first increases quickly and then slow down when n increases. The μ_0 's increase is the minimum, rising from 1.95 to 2.09 a.u.

The polarizability and first hyperpolarizability per unit cell of all-trans PMS were evaluated as $\Delta p(n) = [p(n) - p(n-2)]/2$ with $p = \alpha_0$ or β_0 . Thus $\Delta\alpha_0$ or $\Delta\beta_0$ represents the α_0 or β_0 of each unit cell of $-(\text{SiCH}_3\text{C}_6\text{H}_5)-$. They were extrapolated to the infinite chain limit. Assuming asymptotic

limit as n approaches infinity, the values of $\Delta\alpha_0$ and $\Delta\beta_0$ have been fitted to

$$\lg \Delta p(n) = \alpha + \frac{b}{n} + \frac{c}{n^2} + \frac{d}{n^3}, \quad (6)$$

where a , b , c , and d are the fitting parameters. The extrapolated value for infinite polymer is thus $\Delta p(\infty) = 10^a$.

For a physical quantity and a certain fitting function, there might be different fitted limiting value when different fitting data ranges are chosen. The optimal fitting data ranges for $\Delta\alpha_0$ are chosen from 4 to 14, whereas it is chosen from 6 to 14 for $\Delta\beta_0$. The fitting parameters and extrapolated values are listed in Table 7. The corresponding fitting curves of $\Delta\alpha_0$ and $\Delta\beta_0$ can be found in Figure 5. The fitting limit (coefficient of a) for $\Delta\alpha_0$ and $\Delta\beta_0$ is approximately equal to 103.1 a.u. and 5.3 a.u., respectively. To make a comparison, Kirtman and Hasan [18] have calculated the linear polarizabilities of all-trans polysilane with 6-31 G basis set at CPHF level and it was found that the longitudinal linear polarizability per SiH_2 unit is 65.6–65.8 a.u. In addition, Hurst et al. [19] have researched on large π -conjugated organic molecule PA at the level of CPHF/6-31G(d, p), and the corresponding value is 60.8 per CH unit. The polarizability of $-(\text{SiCH}_3\text{C}_6\text{H}_5)-$ unit is greater than that of SiH_2 unit and CH unit.

For experiments, Li et al. [20] have successfully synthesized several kinds of functionalized polysilanes based on PMPS and containing NLO chromophores in the side chain. One of the synthesized structures PII-1 (see in Figure 6) has some similarity to that of PMS polymer because both of them have the $-(\text{SiCH}_3\text{C}_6\text{H}_5)-$ unit. The macroscopic second-order nonlinear susceptibility d_{33} for PII-1 was measured by SHG experiments and its value is 13 pm/V (31.0×10^{-9} esu) at 1064 nm fundamental wavelength, which is about 9 times larger than the experimental measurement for urea crystal (3.4×10^{-9} esu) [21]. β_0 of urea crystal as calculated by Wu et al. [22] is about 27.4×10^{-32} esu by TD-CPHF method with 6-31+G basis set. In our system, when $n = 14$, β_0 is 2.6×10^{-30} esu, which is around 9 times larger than that of urea. Therefore, our calculated β_0 value should be close to the magnitude of the experimental result. If one considers the electron correlation effect, β_0 is estimated around 8.0×10^{-30} esu, which is more than 30 times larger than that of urea.

4. Conclusions

In this work, we present a quantum-chemical theoretical analysis of the static first hyperpolarizabilities of a series of α -*t*-Bu- ω -CN-poly(methylphenyl)silanes at the level of *ab initio* CPHF method. The effects of basis sets and electron correlation on the first hyperpolarizability are discussed. The basis set, 6-31+G(d), is chosen for the CPHF calculation. The calculated results are also sensitive to electron correlation effect; the MP2 results are about 1.5~2.0 times larger than those of CPHF for polymer $n \leq 6$.

Dependences of NLO properties on polymer chain length are considered. It turns out that in the donor-bridge-acceptor structure, there is a concentration of charge distribution in the central region of the chain and the atomic charge on Si

TABLE 6: Electronic dipole moment μ_0 , static average polarizability α_0 (see (3)), and static first hyperpolarizability β_0 (4), as well as the individual components that contribute to the latter property. All quantities are in a.u.

n	μ_0	α_0	$\Delta\alpha_0^a$	β_{xxz}	β_{yyz}	β_{zzz}	β_z	β_0	$\Delta\beta_0^b$
2	1.95	354.10		-27.0	-6.5	125.0	54.9	77.2	
4	2.00	553.67	99.79	-25.4	-7.3	244.0	126.8	139.7	31.3
6	2.03	754.27	100.30	-29.7	-7.7	352.6	189.1	197.7	29.0
8	2.06	955.77	100.75	-31.1	-9.1	423.0	229.6	237.3	19.8
10	2.07	1158.17	101.20	-34.3	-10.1	472.9	257.1	264.3	13.5
12	2.08	1361.06	101.45	-33.2	-9.8	511.0	280.8	287.4	11.6
14	2.09	1564.33	101.64	-39.6	-8.5	550.7	301.6	306.0	9.3

$$^a \Delta\alpha_0 = [\alpha_0(n) - \alpha_0(n-2)]/2; \quad ^b \Delta\beta_0 = [\beta_0(n) - \beta_0(n-2)]/2.$$

TABLE 7: Fitting parameters for (6).

$\Delta p(n)$	a	b	c	d	$\Delta p(\infty)$
$\Delta\alpha_0$	2.01340	-0.09687	0.11375	0.17916	103.1
$\Delta\beta_0$	0.72515	0.14550	63.17173	-224.89603	5.3

at the end of acceptor is smaller than that of donor. With the increase of polymerization degree, the average values of Si-Si bond length are increased and the energy gaps between LUMO and HOMO are decreased; so the σ - σ^* conjugation effect is gradually enhanced. When $n = 14$, the β_0 value reaches to 2.6×10^{-30} esu at CPHF level (about 8.0×10^{-30} esu after MP2 correction), which should be close to the magnitude of the experimental result.

Conflict of Interests

All the authors do not have conflict of interests with the mentioned commercial identities as confirmed.

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