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Effects of oxygen atom in the side chain on physical and optical properties of dodecapentoxypentasilane

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Abstract

The effects of the alkoxy side chain on the conformation of oligosilane have been studied for perpentoxypentasilane. The UV-absorption maxima shifted extremely to a shorter wavelength than that of peralkyloligosilane. Molecular dynamics and ab initio MO calculations showed that the excitation energy of the twisted structure for peroxyloligosilane (a model of perpentoxypentasilane) was smaller than that of permethyloligosilane, because of the interaction between the n orbital of the oxygen atom and the σ orbital of the Si–Si bond. The Coulomb repulsion energies between the oxygen atoms greatly affect the stability of the twisted conformation of the silicon backbone. © 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Because of the σ electron delocalization on the main chain, polysilane is known as a polymer with unique electronic and optical properties. It has been confirmed that various physical properties of this polymer greatly depend on the main chain structures [1,2], and that it is possible to control the main chain structure by the side chain [3–5]. In order to control the structure of the Si-skeleton, the polysilanes, which have a selective spiral structure, were made by introducing a chiral sub-

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stituent as a side chain [6–10]. In addition, positive trials have been carried out for the polysilanes containing a heteroatom in the side chain, to dissolve in water [11–13], to introduce oxygen or nitrogen atom into the side chain showing unique solvatochromism [14–17], to introduce a chirality and a heteroatom in the side chain [18].

Then a question arises regarding whether the oxygen atom affects the structure of the main chain by electrostatic effects between the oxygen atoms or the interaction between the n orbital of oxygen and σ orbital of the Si–Si bonds. Unfortunately, only poor discussions on this matter are available at present. To understand the effect of oxygen introduced in the side chain on the properties of an oligosilane, we prepared dodecapentoxypentasi-

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lane (POS5) and examined its physical properties by experimental techniques, molecular orbital (MO) calculations, and molecular dynamics (MD) simulations. These approaches clarify the relationship between the physical properties and the structure.

2. Experimental

2.1. Preparation of dodecapentoxypentasilane (POS5)

Decaphenylcyclopentasilane prepared from dichlorodiphenylsilane as reported [19,20] was refluxed in tetrachloroethane for 40-min to give 1, 5-dichlorodecaphenylpentasilane [21]. The dichloropentasilane in dry benzene was introduced HCl gas for 7-h in the presence of AlCl₃. The solution was carefully introduced into 10 ml of n-pentanol under nitrogen, and allowed to stand for 5-h at RT. The solvent was then removed in vacuo. The residue was washed with methanol, filtered, and a viscous colorless residue was obtained. Matrixassisted laser desorption/ionization time-of-flight mass (MALDI-TOF MS) spectral measurement was performed by a Shimadzu/Kratos Kompact-MALDI III with 3-indoleacetic acid used as a matrices. After several times reprecipitation (CHCl₃-methanol), the obtained mass number of the product was appeared as a single peak at 1184, which was assigned to POS5. The NMR spectra were measured in CDCl₃ in the presence of TMS as reference by a JEOL JNM-GSX600 spectrometer (600 MHz). ¹H-NMR δ 3.6–3.8(m, 2H, O-CH₂-), 1.5-1.7(m, 2H, O-CH₂-CH₂-), 1.3-1.5(m, 4H, CH₂-CH₂-CH₃), 0.8-1.1(m, 3H, CH₃). ¹³C-NMR δ 14.0, 14.1(CH₃), 22.8, 22.9(-CH₂ -CH₃), 29.0, 29.1, 29.2(-CH₂-CH₂-CH₃), 37.5, 35.8, 35.9(-O-CH2-CH2-), 65.65, 65.7, 65.8(-O-<u>C</u>H₂–).

2.2. MD and MO calculations

All calculations were performed by a general molecular mechanics program Cerius 2 (Accelrys Inc.). In this study, MD calculation was chosen as the method of conformational analysis, because of the model compounds have many rotationable dihedral angles. In this simulation, long-range non-bonded forces were cut off between 9 Å. MD calculations were carried out using the PCFF force field, which was optimized by Sun et al. [22] for organosilicon compounds. The calculations were performed for decapentoxytetrasilane (POS4), POS5 and decahexyltetrasilane (HS4), respectively. The atomic partial charges were calculated at every 10 fs by the QEQ method [23]. In the calculations, the central Si-Si bonds were set at given dihedral angles, at every 5° or 10°. In the simulation, side chains are changed their conformation freely. To determinate the initial structures for the simulation, the geometric parameters were optimized by force field calculations. The initial temperature was set at 600 K for 1 ps and then decreased to 298.15 K. After 30 ps, the system was assumed to have reached equilibrium. The total energies, recorded for 100 ps at 20 fs intervals, were averaged. For pentasilanes, near the energy minimum, the dihedral angle was changed at each 5°.

Ab initio MO calculations were carried out using the GAUSSIAN 98 program on IBM-RS6000. Because POS5 was too large to perform the calculations, peroxyloligosilanes (decahydroxyltetrasilane, OHS4 and dodecahydroxylpentasilane, OHS5) were used as model compounds. In order to discuss the effects of oxygen atoms on the silicon chain, permethyloligosilanes were also calculated. The geometries were fully optimized at the B3LYP/6-31G** level. Using the geometries as such determined, CIS calculations were performed at the CIS/6-31G* level. In these calculations, the dihedral angles of the central Si–Si bonds were set at given dihedral angles at every 10° or 30°.

3. Results and discussion

3.1. Thermochromic properties of POS5

Fig. 1 shows the UV absorption spectra of POS5 in 3-methylpentane in the range between 298 and 80 K. These spectra have three remarkable characteristics. First, the band maxima in this temperature range were observed at shorter



Fig. 1. UV absorption spectra of POS5 in 3-methylpentane as a function of temperature.

wavelengths compared to those of peralkylpentasilanes. This characteristic will be discussed after this session. Second, it was shown that the absorption spectra were broad, having a shoulder up to 290 nm. Third, the change in the band maxima on decreasing the temperature was very small. These tendencies were also observed for HS5.

3.2. Result of MD simulation

The calculated potential energy distribution curves as a function of the dihedral angles of each tetrasilane; HS5 and POS5, are shown in Figs. 2a and b, respectively. The curve of the solid line is the potential energies obtained from MD calculations. Another two curves, the dotted line and the broken line, are extracted from the potential energies to the Coulomb energies and van der Waals energies, respectively. It was observed that the energy distribution curves of two kinds of tetrasilanes had two similar energy minima; trans (around 170°), and ortho (85°), respectively. However, there are remarkable differences in that HS5 is stabilized at a trans conformation, while POS5 has an energy minimum in the ortho conformation. The reason for these phenomena is explained by the Coulomb and the van der Waals energies for each conformer. The Coulomb energy is a dominant factor in determining the potential energy of POS5. However, for HS5, the two energy



Fig. 2. Calculated ground state conformational energies of HS4 (a) and POS4 (b) as a function of ϕ_1 and ϕ_2 . Potential energies (squares), Coulomb energies (triangles), and van der Waals energies (circles). (c) Potential energies (kcal/mol, relative to the lowest minimum) of POS5 as a function of ϕ_3 and ϕ_4 .

distribution curves are quite similar to the potential energy curve. Columbic repulsion between oxygen atoms makes the conformation twisted, and the population of the twisted conformation is larger than that of HS5.

The potential energy map of POS5 is shown in Fig. 2c as functions of the dihedral angles ϕ_3 and ϕ_4 . The complete ranges of possible dihedral angles are covered in this diagram. The lowest energy minimum of the energy surface is 'ortho-ortho' conformation; therefore, this figure also proves that the twisted conformation is the most stable.

3.3. Result of ab initio MO simulation

Fig. 3a shows the results of CIS/6-31G* calculations of singlet excitation energies (E_S) as a function of dihedral angles ϕ for OHS4. The cor-



Fig. 3. Calculated (CIS/6-31G*) E_s (a) and f (b) of OHS4 as a function of ϕ . 1A (circles), 1B (squares), 2A (triangles), 2B (rhombus), see in text.

responding oscillator strengths (*f*) at the same level calculations are shown in Fig. 3b. Because of a large number of transitional states, the results of only the four lowest excited states are shown in the figure. Four states are called A and B due to the symmetry of the orbital and numbered 1 and 2 from the low-lying excited singlet states, respectively. These results are similar to the previously reported results for Si₄H₁₀ [24] and decamethyl-tetrasilane (MS4) [24–26].

As seen in Fig. 3b, the f to the states, 1B and 2B are calculated to be very strong and dependent on the ϕ , while 1A and 2A are very weak in all ranges of the angles. These phenomena are reasonable, because the transitions to the B state mostly consist of symmetry-allowed transitions. It is also confirmed that the f's of 2B were higher than those of 1B when dihedral angles were <120°, however, their orders were changed at 120°. This angle agreed with the results for MS4, but not for Si_4H_{10} . This showed that there are no effects of the substituents, even the oxyl or methyl groups, on the change in f due to the conformation of the Siskeleton. The two transitions to 1B and 2B are dependent on the angle, and they have large f in the trans and cis conformations, respectively. The $E_{\rm S}$ at those conformations are determined to be 6.7 and 7.7 eV, respectively. We have done also the ab initio MO calculations for MS4 on an equal basis in order to compare the equal order of the $E_{\rm S}$ with OHS4. It was calculated that the excitation energies of MS4 needed 6.7 and 8.0 eV in the *trans* and cis conformations, respectively. The $E_{\rm S}$ were different between the oligosilanes with hydroxyl and methyl groups, especially in the region near cis conformations. It can also be predicted that the $E_{\rm S}$ in the twisted structure of OHS4 has a lower value than that of MS4. The difference in the $E_{\rm S}$ is explained by the molecular orbitals. For MS5, the MO coefficients of the silicons are large and the connecting carbons have the opposite phase; therefore, they are localized in each atom in HOMO. In LUMO, the coefficients of silicons are delocalized along the silicon chain. For POS5, molecular orbitals have a similar character to MS5, except that oxygen atoms have large n-orbital coefficients that the carbons do not have in HOMO. However, the difference is more remarkable in LUMO, where the molecular orbital consists of vacant silicon and oxygen orbitals, and the coefficients of the silicons are delocalized along the silicon chain and also delocalized on the oxygen atoms. Therefore, the coefficients did not change due to the rotation of the dihedral angle in HOMO; however, the coefficients on the oxygen atoms became larger by twisting in LUMO. This difference in the molecular orbital affected the energy of LUMO and thus the transition energies of these oligosilanes. This result is fully consistent with the explanation of the long wavelength shift of the absorption spectrum of the polysilane having oxygen in the side chain [17]. The twisting of silicon main chain is not significantly influenced to the delocalozation in LUMO, therefore, reported alkoxypolysilanes have absorption maxima at longer wavelength than those of simple alkylpolysilanes even they take both twisted and extended conformations in random coil structure in solution. In addition, their small temperature dependence and shift to the shorter wavelengths by decreasing temperature are reasonably matched above discussions.

We also carried out CIS/6-31G* calculations of $E_{\rm S}$ as a function of the dihedral angles (ϕ_6 and ϕ_7) of OHS5. Calculated $E_{\rm S}$ and the oscillator strengths of the four lowest singlet excitation states are shown in Figs. 4a-c. At this time, we assumed three conformational models. First, extended states is consist of conformers which have dihedral angles between 180° and 150°, and twisted states consist of those which have dihedral angles between 90° and 60°. The three conformers of extended-extended, extended-twisted, and twisted-twisted are defined as follows, extendedextended correspond to $T_{\pm}-T_{\pm}$, $T_{\pm}-D_{\pm}$, and D_{\pm} - D_{\pm} ; extended-twisted correspond to T_{\pm} - O_{\pm} , $T_{\pm}-G_{\pm}$, $D_{\pm}-O_{\pm}$, and $D_{\pm}-G_{\pm}$; twisted-twisted correspond to $O_{\pm}-O_{\pm}$, $O_{\pm}-G_{\pm}$, and $G_{\pm}-G_{\pm}$, where T, D, O, and G indicate transoid, deviant, ortho, and gauche conformation, respectively, as shown by Michl and West [27]. The obtained spectra have been resolved into these three conformers as shown in Figs. 4a-c. The theoretically obtained absorption spectra composed of the three conformers are similar to those of MS5 calculated by us and MS4 reported [25].



Fig. 4. Calculated (CIS/ $6-31G^*$) wavelength (scaled by 0.78) [29] for OHS5 of three conformational models, (a) extended–extended, (b) extended–twisted, and (c) twisted–twisted. Spectra estimated by (a)–(c) and Boltzmann distribution for POS5 (d).

3.4. Comparison between calculated data and observed spectra

By combining the data of Figs. 2c and 3a-c, it is possible to predict the spectrum in the gas state. Assuming that a Boltzmann distribution is estab-

lished, the abundance ratio of each conformation, p, is obtained according to Eqs. (1)–(3)

$$E'_{\phi 1\phi 2} = \exp\left(-E_{\phi 1\phi 2}/RT\right),$$
 (1)

$$Z = \sum E'_{\phi 1 \phi 2},\tag{2}$$

$$p_{\phi 1\phi 2} = E'_{\phi 1\phi 2}/Z.$$
 (3)

In the equation, R is a gas constant and T is the temperature in equation.

The apparent oscillator strength was synthesized by the superposition of the oscillator strength obtained for each conformer using its population as in Eq. (4)

$$f_{\lambda} = \sum f_{\lambda,\phi 1\phi 2} p_{\phi 1\phi 2}. \tag{4}$$

The obtained spectrum is shown in Fig. 4d. This agrees well with the experimentally obtained spectrum of POS5 in 3-methylpentane as shown in Fig. 1. This indicates that the calculated results (oscillator strength and potential energy) are reproducible of the experiment, i.e., the result that the twisted conformation is stabilized by the Coulomb repulsion between the oxygen atoms for POS5 is reasonable. In the spectra in Fig. 1, the 200-240 nm region was strongly temperature-dependent, however the 260-280 nm region was weakly temperature-dependent. This is explained by the potential energy surface in Fig. 2c. The equilibrium shifted from unstable twisted-extended conformer to the most stable twisted-twisted conformer, but increase of intermediate extendedextended conformer was small.

3.5. Solvent effect on the conformation of POS5

Fig. 5a shows the UV absorption spectra in acetonitrile/alcohol mixtures. The spectral was changed with increase of shoulder at 230 nm and decrease at 210 nm according to the increase in the polarity of the solvent having an isosbestic point at 220 nm. The samples were not changed after the measurements, therefore, three spectral changes were not due to the exchange alkoxy side chains by the solvent. This is explained by the simple extended-twisted model. At first, the observed spectrum was separated into three Gaussian functions



Fig. 5. (a) UV absorption spectra of POS5 in different solvents. (b) Observed UV spectrum resolved into three model conformers. (c) Relative population of conformers.

as shown in Fig. 5b. Those have a maximum at 210, 230, and 260 nm, and their half-widths at half-height were 3410, 4100, and 7470 cm⁻¹, respectively. These functions were tentatively assigned to twisted–twisted, extended–twisted, and extended–extended conformers, respectively. This assumption is reasonable according to the above discussions. The increase in solvent polarity led decrease of the twisted–twisted and increase of the

extended-twisted form as shown in Fig. 5c. This spectral change must be explained as follows. An alcoholic solvent stabilizes the conformer by hydrogen bonding or by protonation when the acidity of the solvent is high. In the former case, it also contains the steric effect of solvation [13], and/or the molecular structure is changed due to the polarity of the solvent atmosphere [28,29]. In addition, the molecular dipole moment of the extended-twisted conformer (5.4 D) is higher than those of the other conformers. The direction of the pentoxy substituent is isotropic; therefore, the dipole moments compensate each other in the cases of extended-extended (2.3 D) and twisted-twisted (1.8 D) conformers. Actually, the extended-twisted conformer has a higher dipole moment than other conformer, and stabilized in the polar solvent. These factors may govern the relative stability of each conformer.

4. Conclusions

POS5 takes a twisted conformation in 3-methylpentane. The σ - σ * transition energy in the Si-Si main chain of the *cis* conformation decreases on the substitution of oxygen because the excitation energy is delocalized along the main chain and oxygen atom in the side chain. This might be a factor in the long wavelength shift of the absorption spectrum of the polysilane having oxygen in the side chain. The longer wavelength absorption shift of the oligosilane in a polar solvent is explained by an increase in the extended-twisted conformer.

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