

Unusual behavior of silicon oligomers and polymers having functional groups

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Abstract

Synthesis, structures, and electronic properties of silicon polymers and oligomers having hypervalent silicon moieties, polar substituents, or transition metal moieties are reported. UV spectra of pentacoordinate silicon oligomers reveal that the introduction of pentacoordinate silicon moieties into oligosilanes leads to a drastic change of the $\sigma_{\text{SiSi}} \rightarrow \sigma_{\text{SiSi}}^*$ excitation energies. ^{29}Si -NMR spectra have proved that the conformation of pentacoordinate oligosilanes is tightly locked, indicating that free rotation about the Si–Si single bonds is nearly completely inhibited by electrostatic interaction. UV–vis spectra of polysilanes substituted with (alkoxycarbonyl)methyl groups exhibit unusual spectral properties such as long-wavelength absorption above 400 nm, and temperature- or solvent-dependent change of the UV spectra. Effective electron delocalization in Si–Ru–Ru–Si–C₆H₄ polymers was demonstrated by the absorption spectra. Solvent-sensitive skeletal rearrangement of the Si–Ru–Ru–Si moieties gives rise to a remarkable change of the optical properties of the polymers.

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Keywords: Polysilane; σ -Conjugation; Pentacoordinate silicon; Conformational control; Thermochromism; Solvatochromism

1. Introduction

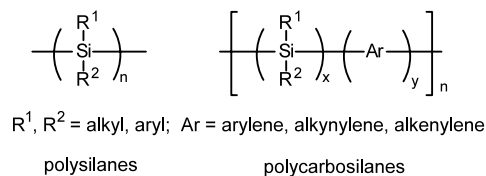
Silicon polymers containing silicon–silicon bonds in the backbones have attracted strong attention due to their unique electronic properties and growing technological importance [1]. The cumulated silicon–silicon bonds in the silicon polymers lead to extensive σ -electron delocalization along the polymer backbones (σ -conjugation). This unusual mobility of the σ -electrons allows the important technological application of polysilanes and polycarbosilanes containing π -conjugated organic moieties, that is, as charge transport materials, conductive and photoconductive materials, or photoresists (Scheme 1) [2]. The electronic and optical properties of the silicon polymers can be modified dramatically by subtle changes in the solid structures, backbone conformations, degree of polymerization, and nature of the substituents attached to the main chains.

Therefore, control of both the solid structures and the conformations of the polymer backbones is essential for realizing the ideal physical properties of the silicon polymers.

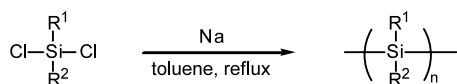
The solid structures and conformational properties of organic and inorganic polymers generally depend on the size and the electronic nature of the side groups attached to the main chains. Over the past decades, a considerable number of studies have been made on the influence of simple aryl- and alkyl-side groups on the polymer properties of polysilanes [3]. However, little is known about the influence of polar substituents such as amide and ester on the properties of silicon polymers, though the introduction of polar substituents into the silicon polymers is expected to cause drastic changes of the physical and chemical properties. The reason for this is that introduction of functional groups into the polysilanes has been strictly limited because of vigorous conditions of sodium condensation reaction usually used in synthesis (Scheme 2) [1a]. Nevertheless, this difficulty can be overcome by the recent development of

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Scheme 1. Silicon-based polymers.



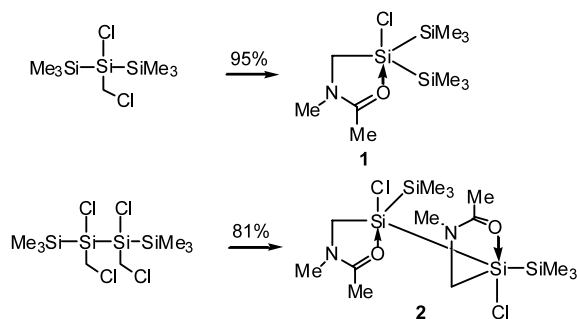
Scheme 2. Synthesis of polysilanes.

new methods allowing the preparation of functionalized silicon polymers [2b].

Recently, we have developed the methods for the synthesis of oligosilanes and polysilanes which have amide or ester moieties in the side groups, demonstrating the unique properties of functionalized silicon polymers. Furthermore, we have found that incorporation of transition metal moieties such as ruthenium clusters into the polycarbosilane backbones cause a dramatic change of photochemical behavior of polycarbosilanes. These results strongly indicate that the conformations of the silicon chains, stereochemistry of the silicon atoms, and the electronic structures of the functionalized silicon polymers are profoundly different from those of conventional silicon polymers with simple aryl- and alkyl-side groups. This article will focus on recent work from our group which illustrates the possibilities for highly functionalized silicon polymers in the area of material chemistry.

2. Synthesis and properties of oligosilanes containing pentacoordinate silicon moieties

The introduction of $\text{Me}(\text{C}=\text{O})\text{N}(\text{Me})\text{CH}_2$ groups into the internal positions of oligosilanes forms pentacoordinate oligosilanes having a $\text{ClSiOC}(\text{Si})_2$ coordination framework with $\text{O} \rightarrow \text{Si}$ bonds (Scheme 3) [4]. Hypervalent silicon moieties in the polysilane backbones are



Conditions: $\text{MeCON}(\text{Me})\text{SiMe}_3$ (1.1 eq.), hexane, r. t., 12 h

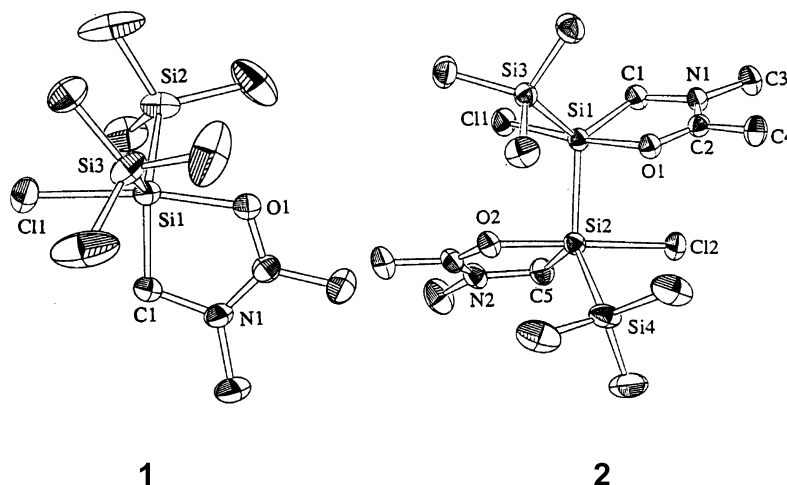
Scheme 3. Synthesis of pentacoordinate oligosilanes.

supposed to cause a strong perturbation to the electronic structures of the polymers. For examples, chemical reactivities of pentacoordinate- and hexacoordinate-silicon compounds are significantly different from those of tetracoordinate counterparts, indicating the variation of the electronic structures with the coordination number of the silicon [5]. However, little attention has been given to the influence of coordination number and valence state on the polymer properties. Although several efforts have been made to introduce hypervalent silicon atoms into disilanes and trisilanes, the synthesis of polysilanes containing pentacoordinate silicon moieties in the internal positions has not been realized yet [6]. We have synthesized trisilane **1** containing a pentacoordinate silicon atom and tetrasilane **2** having two adjacent pentacoordinate silicon atoms at the internal positions to find the unusual spectral properties of these compounds [7].

Pentacoordinate trisilane **1** was prepared in a high yield by the reaction of *N*-methyl-*N*-trimethylsilylacetamide with 2-(chloromethyl)-2-chlorotrisilane (Scheme 3). The similar reaction with 2,3-bis(chloromethyl)-2,3-dichlorotetrasilane (1:1 mixture of diastereomers) stereoselectively gave *dl*-isomer of pentacoordinate tetrasilane **2**; $^1\text{H-NMR}$ analysis of the reaction mixture showed that there was no trace amount of *meso*-isomer. These compounds are colorless crystals and fairly stable in the air.

The X-ray analysis of **1** and **2** revealed the almost ideal trigonal bipyramidal (TBP) structure with the chlorine and the oxygen atoms in the axial positions (Fig. 1). The TBP character of the internal silicon atoms of the pentacoordinate oligosilanes is markedly high; the %TBP_e value for **1** estimated from the three equatorial-to-equatorial angles is 99%, and the %TBP_e value for **2** (average of the two pentacoordinate silicon moieties) is 98% [8]. The Si–Cl bond lengths (2.367(1) Å for **1**, 2.3217(6) and 2.3704(5) Å for **2**) and the Si–O distances (1.947(2) Å for **1**, 1.981(1) and 1.943(1) Å for **2**) are normal as [3+2] TBP coordination. The sum of the three equatorial angles (359.9° for **1**, 360.0° and 359.1° for **2**) indicates almost complete planarity of the equatorial planes in **1** and **2**. The Si₁–Si₂ bond length (2.3362(5) Å) in **2** is comparable to tetrahedral Si(sp³)–Si(sp³) bonds (2.33–2.37 Å), while the bond between the two equatorial silicon atoms can be formally regarded as Si(sp²)–Si(sp²) [7]. The relatively long Si_{eq}–Si_{eq} bond length, however, is quite reasonable in view of the sterically crowded coordination sphere of pentacoordinate silicon species.

The $^{29}\text{Si-NMR}$ spectra of **1** and **2** in C_6D_6 solution showed that the chemical shifts for the internal silicon atoms (–63.71 ppm for **1** and –61.88 ppm for **2**) are markedly upfield shifted by ca. 60 ppm from their tetracoordinate precursors, proving the strong $\text{O} \rightarrow \text{Si}$ coordination [9]. Strong coordination in these molecules

Fig. 1. X-ray structures of **1** and **2**.

is also supported by the IR spectra (in KBr) which exhibited the $\nu(\text{CO})$ bands at 1603 cm^{-1} for **1** and 1607 cm^{-1} for **2**. The $\nu(\text{CO})$ of analogous pentacoordinate ($\text{Me}_2\text{ClSi})\text{CH}_2\text{N}(\text{Me})(\text{C}=\text{O})\text{Me}$ with $\text{O} \rightarrow \text{Si}$ coordination also appeared at the same region (1598 cm^{-1}), indicating that replacement of two equatorial methyl groups by two trimethylsilyl groups has no influence on the strength of the $\text{O}-\text{Si}$ bond [10]. This result is somewhat surprising, because the presence of an electropositive ligand such as silicon in the equatorial position is supposed to weaken the coordination bonds.

The UV spectra of **1** and **2** are shown in Fig. 2, in which the spectrum of 2-chloroheptamethyltrisilane (**3**) is also given for comparison. In isooctane solution, **1** exhibited a strong absorption at 227 nm (Fig. 2a, $\epsilon = 7045\text{ M}^{-1}\text{ cm}^{-1}$), which can be assigned to $\sigma \rightarrow \sigma^*$ transition of the $\text{Si}-\text{Si}$ bond [1a]. It should be noted that the absorption maximum of **1** appears at the longest wavelength among various $\text{Me}_3\text{SiSi}(\text{X})\text{MeSiMe}_3$ (X =

halogen, N, O, S, Me) [11]. For example, compared with the spectrum of **3** (Fig. 2b, $\lambda_{\text{max}} = 215\text{ nm}$, $\epsilon = 7300\text{ M}^{-1}\text{ cm}^{-1}$ in isooctane), the λ_{max} of **1** is red-shifted by 12 nm. This strong bathochromic shift is likely to be a result of electronic perturbation of the $\text{Si}-\text{Si}$ bond by the pentacoordinate moiety. These results strongly suggest that the pentacoordinate silicon moieties can considerably reduce the $\sigma \rightarrow \sigma^*$ transition energies of the $\text{Si}-\text{Si}$ bonds.

To gain an insight of this point, ab initio calculations (CIS/6-31G**) were carried out on model compounds, tetracoordinate ($\text{H}_3\text{Si})_2\text{Si}(\text{Cl})\text{CH}_3$ (**4**) and pentacoordinate ($\text{H}_3\text{Si})_2\text{Si}(\text{Cl})\text{CH}_2\text{NHCHO}$ with $\text{O} \rightarrow \text{Si}$ coordination (**5**), where the structures were optimized at the B3LYP/6-31G** level (Scheme 4) [12]. The calculated λ_{max} of **5** was red-shifted by 6.2 nm from that of **4**, and the strongest absorption was mainly originated by the $\sigma_{\text{SiSi}} \rightarrow \sigma_{\text{SiSi}}^*$ transition in both compounds. Compared with the corresponding orbitals of **4**, the σ_{SiSi} orbital (HOMO) of **5** is substantially destabilized, whereas the σ_{SiSi}^* orbital (LUMO) of **5** is slightly destabilized. The lone pair orbital of the oxygen shifts up the σ_{SiSi} orbital of **5** in energy, while it does not affect the σ_{SiSi}^* orbital of the different symmetry. Thus, the red-shift in the absorption spectra of **5** is theoretically explained as the result of an interaction between the oxygen lone pair orbital and the σ_{SiSi} orbital. These results predict that pentacoordinate polysilanes with high molecular weights will have narrower band gaps and more useful electronic properties based on smaller excitation energies, compared with tetracoordinate polysilanes.

In striking contrast, the λ_{max} of **2** (Fig. 2c, 207 nm, $\epsilon = 8400\text{ M}^{-1}\text{ cm}^{-1}$ in isooctane) appeared at the shorter-wavelength region relative to **1**, although the presence of the two pentacoordinate silicon moieties are expected to be more effective in destabilizing the σ_{SiSi} . We attribute this unexpected spectral property of **2** primarily to a conformational effect on the electronic

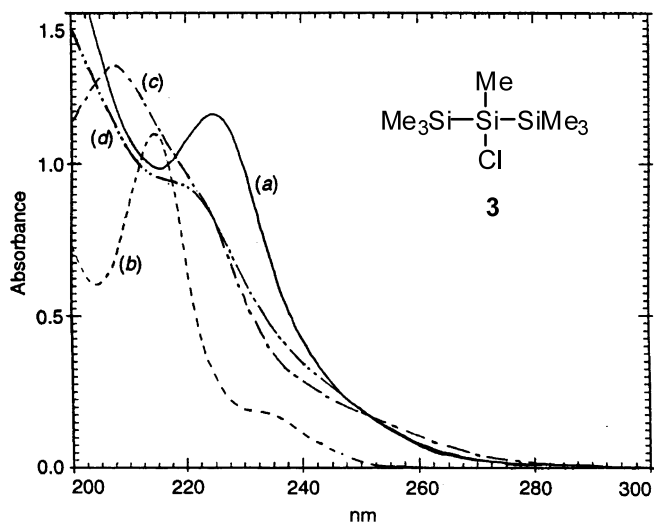
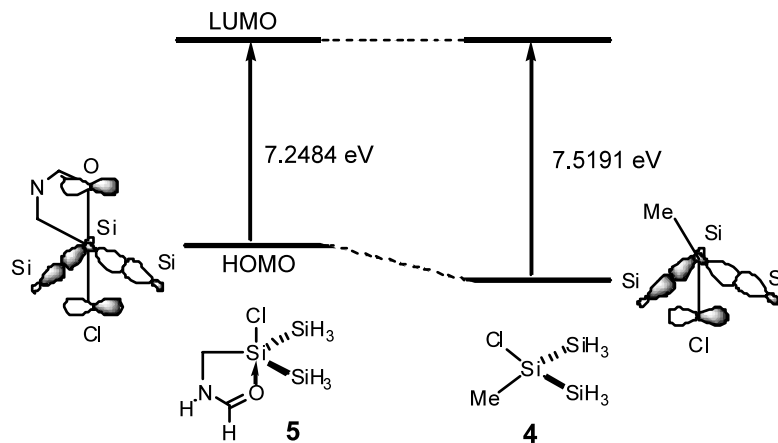


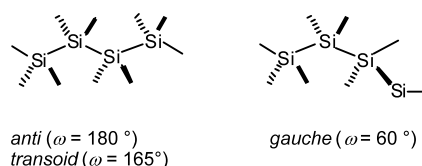
Fig. 2. UV spectra of (a) **1**; (b) 2-chloroheptamethyltrisilane (**3**); (c) **2** in isooctane solution and (d) **2** in acetonitrile solution.

Scheme 4. MO energy levels calculated for ground states of model compounds **4** and **5**.

structure. As suggested by the crystal structure of **2** (the Si–Si–Si–Si dihedral angle (ω) = 57.14(4)°), the lowest energy conformation of **2** in solution seems to be pseudo-gauche; this conformation would be responsible for the disappearance of the absorption in the longer-wavelength region (see next section). Our hypothesis is strengthened by the observation that the UV spectrum of **2** displayed a solvent-sensitive red-shift of the λ_{max} in polar solvent such as acetonitrile (Fig. 2d), suggesting that greater contribution of conformers other than gauche in polar solvent gave rise to the observed red-shift.

3. Conformational locking of silicon chains by pentacoordinate silicon moieties

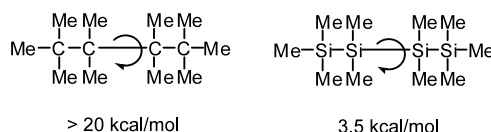
Conformations of flexible linear chains are of fundamental importance in determining the physical properties of organic and inorganic polymers. Over the past decade, a great deal of effort has been made on conformational control of polysilanes [1,13], because electronic and optical properties of σ -conjugated silicon polymers are highly sensitive to subtle change in the backbone conformations [14]. In this regard, conformational locking of the silicon chains into an *all-transoid* form is essential for realizing the useful physical properties of polysilanes [15], since *all-transoid* conformation allows effective σ -conjugation along the silicon chains, whereas gauche conformation interfere the σ -conjugation. For example, recent studies on conformationally constrained tetrasilanes have demonstrated that the *transoid*-conformation (the Si–Si–Si–Si dihedral angle (ω) = 165°) leads to intense absorption at 229 nm, while pseudo-gauche conformation (the Si–Si–Si–Si dihedral angle = 55°) causes a significant decrease of absorbance in the longer-wavelength region above 220 nm (Scheme 5) [16].

Scheme 5. Conformation of silicon chains; ω indicate Si–Si–Si–Si dihedral angles.

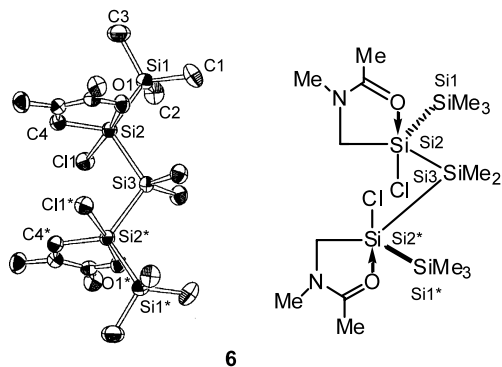
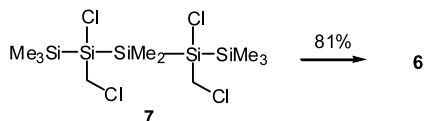
However, conformational control of silicon chains is extremely difficult, since the rotational barriers about Si–Si single bonds are so small that essentially free rotation occurs at room temperature. For instance, the energy barrier to the rotation about the Si2–Si3 bond of decamethyltetrasilane is predicted to be only 3.5 kcal mol⁻¹, which is significantly smaller than that of the corresponding C3–C4 bond of octamethylhexane (> 20 kcal mol⁻¹), revealing the greater flexibility of silicon chains compared with carbon chains (Scheme 6) [17].

We have found unusual locking of silicon chains into *all-transoid* conformation by pentacoordinate silicon moieties [18]. Thus, the internal rotation about the Si–Si single bonds of pentacoordinate pentasilane **6** was found to be nearly completely inhibited even in a room-temperature solution, although there are no significant steric interactions between the substituents (Fig. 3).

Pentacoordinate pentasilane **6** was prepared by the reaction of *N*-methyl-*N*-trimethylsilylacetamide with tetracoordinate pentasilane **7** (1:1 mixture of diastereomers) in hexane at room temperature. The reaction stereoselectively gave the *dl*-isomer of **6**, which was recrystallized from hexane/benzene to give analytically pure **1** in 81% yield as colorless crystals (Scheme 7).



Scheme 6. Energy barrier to rotation.

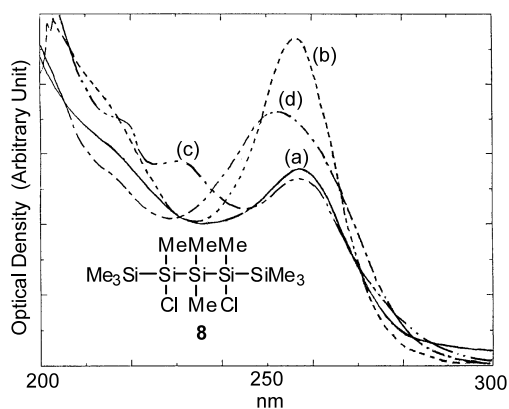
Fig. 3. X-ray structure of pentacoordinate pentasilane **6**.

Conditions: MeCON(Me)SiMe₃ (1.1 eq.), hexane, r. t., 12 h

Scheme 7. Synthesis of pentacoordinate pentasilane **6**.

X-ray analysis of **6** revealed that strong intramolecular O→Si coordination led to the almost undistorted TBP structure of **6** as indicated by the high %TBP_a and %TBP_c values for the pentacoordinate silicon atoms (89 and 99%, respectively). The most remarkable feature of the crystal structure of **6** is the *all-transoid* conformation of the silicon backbone. Thus, pentacoordinate pentasilane **6** has a stretched silicon chain; the Si–Si bond lengths (2.3353(8), 2.3480(9) Å), Si–Si–Si bond angles (113.50(3), 111.66(4)°), and Si–Si–Si–Si dihedral angle (163.61(3)°) meet expectation for the *all-transoid* conformation.

The solid-state UV spectrum of the thin film of **6** exhibited an intense absorption at 257 nm, which is attributed to the $\sigma_{\text{SiSi}} \rightarrow \sigma_{\text{SiSi}}^*$ excitation of the silicon backbone with the *all-transoid* conformation (Fig. 4a). A weak absorption around 220 nm is assignable to the amide chromophore. To our surprise, the UV spectrum

Fig. 4. UV spectra of (a) thin film of **6**; (b) **6** in ether solution; (c) thin film of **8** and (d) **6** in acetonitrile solution.

of **6** in ether solution was essentially similar to the solid-state spectrum, showing an intense absorption at 257 nm ($\epsilon = 22\,000\text{ M}^{-1}\text{ cm}^{-1}$) (Fig. 4b). The obvious similarity between the solid state and the solution spectra reveals that the most stable conformation of **6** is *all-transoid* even in a room-temperature solution, because UV spectra of oligosilanes are highly sensitive to the conformational change of the silicon backbones [14a]. In sharp contrast, the conformational properties of tetracoordinate oligosilanes are strikingly different from those of **6**. For instance, the UV spectrum of the thin film of analogous tetracoordinate pentasilane **8** (viscous liquid) showed three absorption maxima at 215, 230 and 255 nm (Fig. 4c), indicating that **8** exists as a mixture of several conformers in liquid state [19]. These results imply that the pentacoordinate silicon moieties effectively hinder the segmental motion of the silicon chains to stabilize *all-transoid* conformation.

²⁹Si-NOE (nuclear Overhauser effect) experiments in C₆D₆ solution have provided conclusive evidence for the conformational rigidity of **6** in room-temperature solution. The negative NOE η values of ²⁹Si nucleus are correlated to the segmental motion of the silicon chains in solution [20]. The silicon atoms with limited mobility relax predominantly via a dipole–dipole mechanism (DD relaxation) as shown by large $-\eta$ values, while more mobile silicon atoms tend to relax via a spin-rotation mechanism (SR relaxation) as indicated by smaller $-\eta$ values. The $-\eta$ value of the central Si3 atom of **6** (−24.89 ppm) comes close to the limit, that is, 2.37 (94% DD relaxation), indicating that the segmental motion of the Si2–Si3–Si2* skeleton is nearly completely hindered. Thus, it is clear that the rotation about the Si2–Si3 bonds is completely inhibited in NMR timescale in ether and benzene solutions. In contrast, ²⁹Si-NOE experiment in CD₃CN revealed a marked decrease in the $-\eta$ value of the central Si3 atom (−11.75 ppm; $-\eta = 1.86$; 74% DD relaxation), indicating that the rotation about the Si2–Si3 bond is allowed in polar solvent. Consequently, the UV spectra of **6** in acetonitrile solution displayed a broadening of the band with a significant decrease of the intensity ($\lambda_{\text{max}} = 253\text{ nm}$, $\epsilon = 7500\text{ M}^{-1}\text{ cm}^{-1}$) (Fig. 4d), apparently due to the conformational lability of **6** in polar solvent.

The origin of the conformational locking by the pentacoordinate silicon moieties is profoundly interesting. The relatively short Si2–Si3 bond length of **6** (2.3353(8) Å), which is comparable to that of Me₃Si–SiMe₃ (2.340(9) Å) [21], suggests that there is no appreciable steric interaction between the Si2 and Si3 atoms. Therefore, the conformational rigidity of **6** cannot be explained by the steric interference alone. In order to gain an insight into the nature of the rotational barriers about the Si2–Si3 bonds, potential energy profile for the rotation was calculated by freezing the Si1*–Si2*–Si3–Si2 dihedral angle at 160° and optimiz-

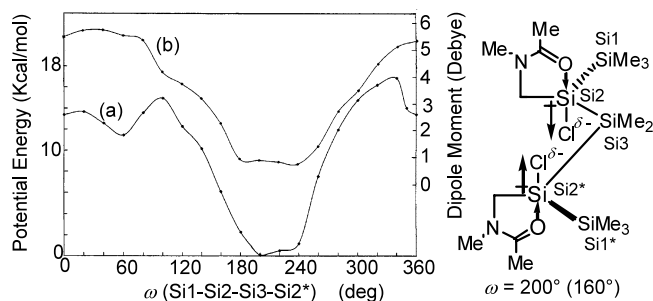


Fig. 5. (a) Potential energy of **6** as a function of the dihedral angle ω (Si1–Si2–Si3–Si2*). For the rotation around the Si2–Si3 bond, change of the ω is positive for counterclockwise rotation when viewed from the side of the Si1 atom. (b) Change of dipole moment of **6** as a function of the ω (Si1–Si2–Si3–Si2*).

ing all other coordinates (Fig. 5). Although this method does not yield all conformational minima of **6**, it is sufficient for quantitative understanding of the nature of the rotational barriers. The energy curve calculated by semiempirical PM3 method [22] are essentially consistent with the experimental observations: for example, the presence of *all-transoid* minimum at 200° [160° as ω (Si1–Si2–Si3–Si2*)] and two energy maxima at 100° and 340° which are 14.9 and 16.8 kcal mol⁻¹ higher in energy than *all-transoid* minimum, respectively.

In Fig. 5, calculated dipole moments of pentasilane **6** as a function of the dihedral angle ω are also shown. It is obvious that the change of the dipole moments of **6** is closely similar to the potential energy curve. Moreover, the hypervalent Cl–Si–O bonds should have large dipole moment as a result of donor–acceptor O → Si interaction involving charge transfer [5a]. All these things make it clear that electrostatic interactions between the strongly polarized Cl–Si–O bonds play a critical role in hindering the rotation about the Si2–Si3 bonds. Thus, the *all-transoid* conformer seems to be effectively stabilized by cancellation of the bond dipole moments, whereas other conformers would be significantly destabilized by unfavorable alignment of the bond dipoles. The conformational lability of **6** in highly polar solvents such as acetonitrile, which weakens electrostatic interactions between the two bond dipoles to allow conformations other than *all-transoid*, is entirely consistent with this speculation.

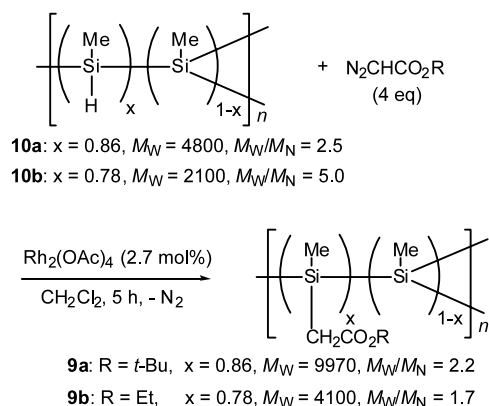
These results can be sharply contrasted with the situation in tetracoordinate peralkylated silicon chains, where the contribution of electrostatic interactions to the rotational barriers is negligible [17]. Thus, it is concluded that retardation of the free rotation about Si–Si bonds by pentacoordinate silicon moieties is most practical method for locking the conformations of silicon chains. Although conformational control of oligosilanes by steric interactions between the bulky substituents [23] or conformationally rigid cyclic systems [19a,24] have been recently reported, this is the first

example where hypervalent silicon atoms exert a strong influence on the backbone conformation. This strategy will stimulate the development of useful organic materials with unique electronic and optical properties which cannot be realized by tetracoordinate silicon compounds. For example, emission property of **6** is vastly different from those of tetracoordinate oligosilanes. Thus, **6** exhibited fluorescence emission at 283.4 nm when excited at 260.0 nm in isoctane at room temperature. The observed Stokes shift (3175 cm⁻¹) is markedly small, compared to tetracoordinate oligosilanes such as Me₃Si(Me₂Si)₃SiMe₃ which shows the emission at 370 nm with a large Stokes shift (13000 cm⁻¹) [19b].

4. Synthesis and electronic properties of polysilanes bearing ester functionality

The electronic properties of silicon polymers are extremely sensitive to the electronic nature of the substituents on the silicon [1]. Above results indicate that introduction of amide moieties into oligosilanes leads to a remarkable change of the $\sigma_{\text{SiSi}} \rightarrow \sigma_{\text{SiSi}}^*$ excitation energies and conformational properties of the silicon chains. These observations have given an impetus to the studies of polysilanes having other functional groups. In order to reveal the influence of highly polar substituents on the electronic properties of polysilanes, we have synthesized polysilanes **9** bearing (alkoxycarbonyl)methyl substituents (Scheme 8).

Functionalized polysilane **9a** was synthesized by the Rh-catalyzed carbenoid insertion [25] into the Si–H bonds of partially branched poly(methylsilylene) **10a** containing 14% methylsilyne (MeSi) units and 86% methylsilylene (MeSiH) units ($M_W = 4800$, $M_W/M_N = 2.5$). Thus, in the presence of catalytic amount of [(CH₃CO₂)₂Rh]₂, **10a** smoothly react with *t*-butyl diazoacetate in dichloromethane to give partially branched



Scheme 8. Synthesis of (alkoxycarbonyl)methyl-substituted polysilanes.

polysilanes **9a** having $\text{CH}_2\text{CO}_2t\text{-Bu}$ substituents as an air-stable yellow solid.

Analysis of **9a** by GPC using polystyrene standards indicated that M_W was 9970 and polydispersity (M_W/M_N) was 2.2. Functionalized polysilane **9a** was soluble in toluene, methanol and chloroform, and moderately soluble in isooctane. The ^{29}Si -NMR spectrum of **9a** in C_6D_6 displayed two broad peaks at -35 and -70 ppm, which are assignable to the silylene ($\text{MeSiCH}_2\text{CO}_2t\text{-Bu}$) and the silyne (MeSi) moieties, respectively [26]. ^1H -NMR spectroscopy also supported the polysilyne–polysilylene network structure containing 14% methylsilyne branching moieties, revealing that almost all the Si–H bonds of **10a** were converted to Si– $\text{CH}_2\text{CO}_2t\text{-Bu}$ moieties. Under the similar conditions, partially branched polysilane **9b** having $\text{CH}_2\text{CO}_2\text{Et}$ substituents ($M_W = 4100$; $M_W/M_N = 1.7$; 22% branching) was prepared from **10b** ($M_W = 2100$; $M_W/M_N = 5.0$) and ethyl diazoacetate.

The solid state UV–vis spectra of a thin film of **9a** (4.5 μm thick) are shown in Fig. 6, where the spectrum of a thin film (4.9 μm thick) of *n*-octyl-substituted polysilane with same degree of branching, $[(\text{CH}_3\text{Si})_{0.14}(\text{n-C}_8\text{H}_{17}\text{SiCH}_3)_{0.86}]_n$ **11** ($M_W = 7780$; $M_W/M_N = 2.0$), is also given for comparison (Fig. 6b). The spectrum of **9a** at 25°C exhibited a monotonously decreasing broad band and a shoulder peak around 300 nm (Fig. 6a), which is assignable to $\sigma_{\text{SiSi}} \rightarrow \sigma_{\text{SiSi}}^*$ transition of the linear silylene moieties [1]. Both spectra of **9a** and **11** display similar featureless broad bands, which are characteristic of branched polysilanes [27]. However, functionalized polysilane **9a** showed broader absorption extending to visible region (≤ 480 nm), while *n*-octyl-substituted polysilane **11** exhibited absorption in the near UV region (≤ 350 nm) (Fig. 6b). The remarkable red-shift of the absorption edge of **9a** relative to **11**

indicate that the $\text{CH}_2\text{CO}_2t\text{-Bu}$ substituents in **9a** effectively promote the σ -conjugation and hence reduce the band gap (E_g) from 3.54 to 2.58 eV [28].

The spectrum of thin film of **9** displayed a reversible temperature-dependent change. When the film of **9a** was heated at 100°C for 15 min, the absorption edge significantly blue-shifted from 480 to 350 nm (Fig. 6c). This absorption, however, was not retained upon cooling at room temperature and the original spectrum (Fig. 6a) slowly returned after 5 h via transient spectrum (Fig. 6d). This thermochromic behavior of **9a** can be explained by assuming that the blue-shift of the absorption edge at 100°C is caused by thermally induced conformational change of the silyne moieties, since the long-wavelength absorption above 400 nm is attributable to the silyne moieties. It is well known that linear poly(dialkylsilylenes) do not exhibit UV absorption above 400 nm in both solid state and solution [29], while polysilynes usually show the absorption edge above 400 nm [27]. The thermochromism of **9a** can be sharply contrasted with the fact that conformationally rigid polysilynes with simple alkyl side groups such as methyl do not display thermochromic change of the absorption spectra [30]. Thus, it seems likely that the $\text{CH}_2\text{CO}_2t\text{-Bu}$ substituents exert a strong influence on the conformation of the silyne moieties, although these groups are bonded to the silylene moieties.

The hypothesis is strengthened by the solvent-dependent change of the solution spectra of **9a** (Fig. 7). In aqueous methanol solution, **9a** exhibited broad absorption extending to 485 nm, which is essentially similar to the solid-state spectrum (Fig. 7a). The intensities of the absorbance at 350 and 440 nm are 1289 and $352 \text{ M}^{-1} \text{ cm}^{-1}$ per Si–Si bond, respectively. In contrast, in nonpolar solvent such as isooctane, the long-wavelength absorption completely disappeared (Fig. 7b). This solvatochromic change of the spectra strongly suggests

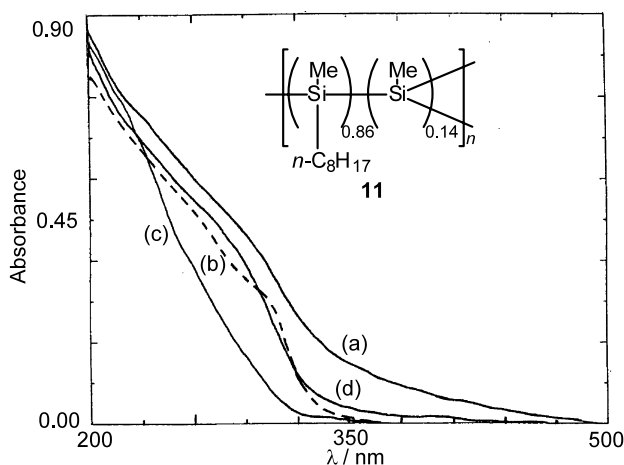


Fig. 6. UV–vis spectra of (a) thin film of **9a** at 25°C ; (b) thin film of **11** at 25°C ; (c) thin film of **9a** at 100°C and (d) after heating at 100°C , thin film of **9a** was cooled at 25°C for 2 h and then spectrum was recorded.

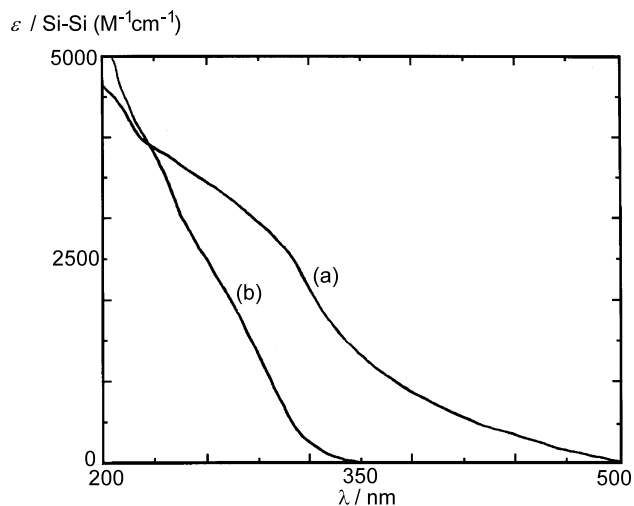


Fig. 7. UV–vis spectra of (a) **9a** in aqueous methanol ($\text{MeOH}:\text{H}_2\text{O} = 500:1$) and (b) **9a** in isooctane.

that conformational change of the silyne moieties is responsible for the disappearance of the long-wave-length absorption, since the absorption above 400 nm possibly arises from the silyne moieties of **9a** [27].

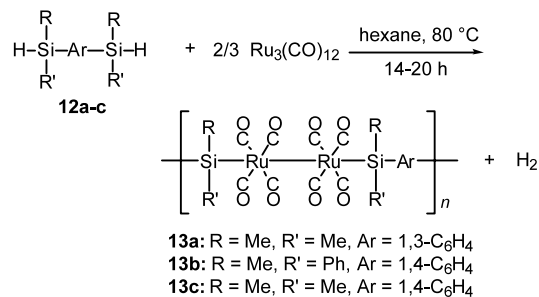
Therefore, it is reasonable to consider that the polar $\text{CH}_2\text{CO}_2\text{R}$ substituents involved in silylene moieties can promote the σ -conjugation through the influence on the backbone conformation of the silyne moieties. The origin of this remarkable promotion of σ -conjugation by polar substituents is not clear. The polarization of the silicon chains is supposed to be enhanced with increasing σ -conjugation length [31]. Thus, delocalized electronic state of the polysilanes can be stabilized by electrostatic, dipole–dipole interaction between the polar ester moieties and polarizable silicon chains, resulting in promotion of the σ -conjugation [31]. Therefore, the $\text{CH}_2\text{CO}_2\text{R}$ substituents in **9** seem to stabilize the backbone conformations of the silyne moieties which allow the effective electron delocalization, whereas conformational change at high temperatures results in the blue-shift of the absorption edge (Fig. 6c). The solvatochromic behavior of **9a** is also consistent with this proposal. Thus, in highly polar aqueous methanol, strong electrostatic interaction between the solvent molecules and polarizable silicon chains can greatly promote the σ -conjugation.

Although precise mechanism which explains the influence of polar substituents on the electronic structure of polysilanes is not clear, above observations clearly illustrate that introduction of polar substituents into the polysilanes effectively reduces the band gaps. It can reasonably be expected that linear polysilanes substituted with various polar groups will exhibit useful physical properties based on small excitation energies.

5. Synthesis and spectral properties of Si–Ru–Ru–Si– C_6H_4 polymers

Organometallic polymers in which metal fragments are linked with conjugated organic groups have attracted considerable attention due to the unique electronic properties [32]. However, little attention has been given to the synthesis of organometallic polymers which have the metal–metal bonds between the main group elements and transition elements in the polymer backbones. We have synthesized organometallic polymers containing tetranuclear Si–Ru–Ru–Si units bridged by phenylene groups to find their unique optical properties such as solvent-dependent change of the UV–vis spectra (Scheme 9) [33].

Our synthetic strategy to prepare these polymers involves dehydrogenative coupling of bis(hydrosilyl)benzenes **12** and $[\text{Ru}_3(\text{CO})_{12}]$ [34]. Treatment of $[\text{Ru}_3(\text{CO})_{12}]$ with 1,3-bis(dimethylsilyl)benzene (**12a**) in hexane gave $[-\text{SiMe}_2-\text{Ru}(\text{CO})_4-\text{Ru}(\text{CO})_4-\text{SiMe}_2-1,3-$



Scheme 9. Synthesis of $(-\text{Si}-\text{Ru}-\text{Ru}-\text{Si}-\text{Ar}-)_n$ polymers.

$\text{C}_6\text{H}_4-]_n$ (**13a**) in 24% yield as an air-stable yellow solid. Analysis of **13a** by GPC using polystyrene standards revealed that M_W was 15 000 and polydispersity (M_W/M_N) was 2.5. Polymer **13a** was soluble in THF and chloroform, and moderately soluble in acetonitrile and cyclohexane. The ^{29}Si -NMR spectrum of **13a** in CDCl_3 exhibited a single peak at 5.43 ppm. A broad intense CO stretching band at 2004 cm^{-1} in the IR spectrum of **13a** (in KBr) was indicative of $\text{Ru}(\text{CO})_4-\text{Ru}(\text{CO})_4$ units in the polymer chains. These spectral data are nearly identical with those of model complex $[\text{PhMe}_2\text{SiRu}(\text{CO})_4\text{Ru}(\text{CO})_4\text{SiMe}_2\text{Ph}]$ (**14**) ($\delta^{29}\text{Si} = 5.28$; $\nu(\text{CO}) = 2000 \text{ cm}^{-1}$), which is regarded as an unit of the polymer backbones.

The linear geometry of the metal units in **13a** was unequivocally confirmed by the X-ray structure of **14** (Fig. 8). Although each Ru atom in **14** is coordinated by four CO ligands, disorder effect in the region of CO ligands provides eight equidistant CO positions [35].

Similar reaction of 1,4-bis(methylphenylsilyl)benzene (**12b**) with $[\text{Ru}_3(\text{CO})_{12}]$ afforded the desired polymer $[-\text{SiMePh}-\text{Ru}(\text{CO})_4-\text{Ru}(\text{CO})_4-\text{SiMePh}-1,4-\text{C}_6\text{H}_4-]_n$ (**13b**) ($M_W = 11\,000$, $M_W/M_N = 2.6$) in 36% yield as a yellow solid. Polymer **13b** showed higher solubility than **13a** in organic solvents like THF, cyclohexane and acetonitrile; however, an attempt to prepare $[-\text{SiMe}_2-\text{Ru}(\text{CO})_4-\text{Ru}(\text{CO})_4-\text{SiMe}_2-1,4-\text{C}_6\text{H}_4-]_n$ (**13c**) by the reaction of 1,4-bis(dimethylsilyl)benzene (**12c**) with $[\text{Ru}_3(\text{CO})_{12}]$ gave polymeric materials insoluble in common organic solvents.

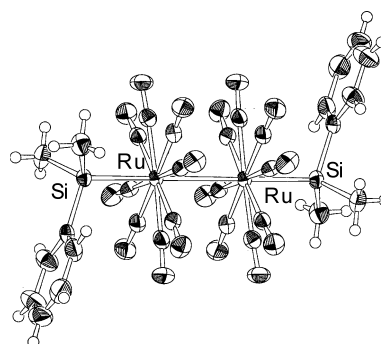


Fig. 8. X-ray structure of $[\text{Me}_2\text{PhSiRu}(\text{CO})_4\text{Ru}(\text{CO})_4\text{SiPhMe}_2]$ (**14**).

The UV–vis spectra of the obtained polymers are shown in Fig. 9, in which the spectra of the model complex **14** (dotted line) are also given for comparison. Polymer **13a** exhibited an intense absorption maximum at 385 nm in cyclohexane (Fig. 9a, $\epsilon = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ per repeat unit) which is assignable to the $\sigma \rightarrow \sigma^*$ transition of the Ru–Ru bonds [36]. Compared with the spectrum of complex **14** (Fig. 9c, $\lambda_{\text{max}} = 362 \text{ nm}$, $\epsilon = 2.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), the position of the λ_{max} of **13a** was found to be markedly red-shifted by 23 nm. The observed red-shift can be ascribed to an electronic perturbation of the Ru–Ru bonds caused by the elongation of the polymer chains, demonstrating a decreased $\sigma \rightarrow \sigma^*$ excitation energy of the Ru–Ru bonds in the polymers. In contrast, polymer **13b** exhibited slight red-shift of the λ_{max} relative to **14** in cyclohexane (Fig. 9b, $\lambda_{\text{max}} = 367 \text{ nm}$, $\epsilon = 1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ per repeat unit), presumably due to the presence of the bulky phenyl groups on the silicon atoms which can interfere the effective interaction between the Si–Ru bonds and the phenylene moieties.

These polymers exhibited a reversible spectral change with variation of solvents (solvatochromism). As shown in the UV–vis spectrum of **13a** in acetonitrile solution (Fig. 9d), an intense band grew at 262 nm ($\epsilon = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ per repeat unit) at the expense of a longer wavelength absorption at 385 nm when the solvent was changed to acetonitrile from cyclohexane. After evaporation of the acetonitrile solution, the absorption at 385 nm returned on addition of cyclohexane to the residue.

Complex **14** displayed similar solvatochromic change of the absorption spectra in cyclohexane and acetonitrile (Fig. 9c and f); however, the change of the λ_{max} ($\lambda_{\text{max}} = 261 \text{ nm}$ in acetonitrile, $\Delta\lambda_{\text{max}} = 101 \text{ nm}$) was smaller than that of **13a** ($\Delta\lambda_{\text{max}} = 123 \text{ nm}$).

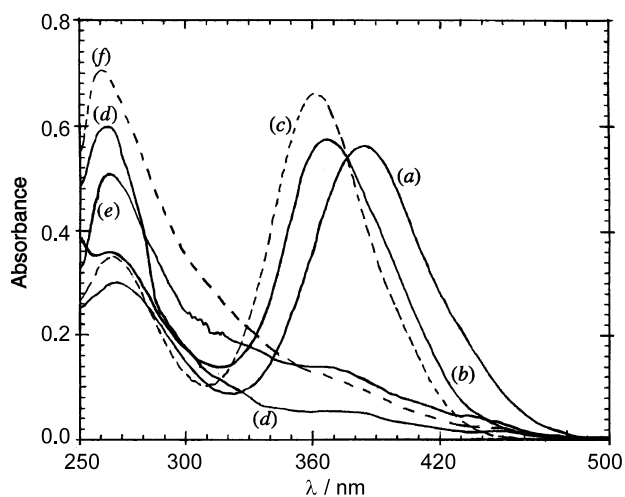


Fig. 9. UV–vis spectra of (a) **13a**, (b) **13b** and (c) complex **14** in cyclohexane. UV–vis spectra of (d) **13a**, (e) **13b** and (f) complex **14** in acetonitrile solution.

A reversible spectral change was also observed for **13b** (Fig. 9b and e), which showed an intense band at 367 nm in cyclohexane, but this band was completely replaced by a shorter wavelength band at 264 nm ($\epsilon = 8.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ per repeat unit) in acetonitrile.

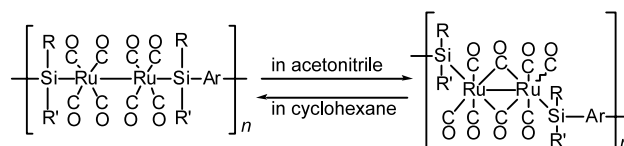
Unlike the solvatochromic shift of the λ_{max} observed for conjugated organic polymers such as polyacetylene [37] and polysilanes [38], where the spectral shift is in the range 20–70 nm, the spectral change exhibited by **13a** and **13b** are very large ($\Delta\lambda_{\text{max}} = 103\text{--}123 \text{ nm}$). These results revealed that the optical properties of the present polymers are extremely sensitive to a change of physical conditions, suggesting their potential applications as optoelectronic materials [39].

The solvatochromic behavior of these polymers is best explained by assuming a solvent-dependent equilibrium between bridged and non-bridged forms of the Si–Ru–Ru–Si units. These polymers prefer the non-bridged form in cyclohexane, but are exclusively bridged in acetonitrile as indicated by the absorptions in the range 250–270 nm, characteristic of dinuclear bridging carbonyl complexes [36,40]. The IR spectra of **13a** and **13b** in acetonitrile also support this assumption, showing CO stretching at 1865 cm^{-1} for **13a** and 1870 cm^{-1} for **13b**, which are assignable to bridging carbonyls [41]. In solid state, however, **13a** and **13b** seem to exist in the non-bridged form as proved by the X-ray structure of **14** Scheme 10.

Change of the optical properties of the polymers caused by skeletal rearrangement of metal moieties is a unique characteristic of transition metal-containing silicon polymers. Above results convincingly demonstrate that the properties of organometallic polymers can be modified dramatically by changes of chemical structure, that is, kind of metals, nature of ligands involved in metallic moieties, and structure of hydrocarbon units in the main chains. Thus, the possibility of using new organometallic moieties to prepare macromolecules with interesting and useful properties will open new territory of material science.

6. Conclusions

We have found that introduction of pentacoordinate silicon moieties into the oligosilane backbones effectively reduces the $\sigma_{\text{SiSi}} \rightarrow \sigma_{\text{SiSi}}^*$ transition energies by destabilizing the σ_{SiSi} . Furthermore, the backbone



Scheme 10. Solvent-dependent skeletal rearrangement of Si–Ru–Ru–Si unit in **13**.

conformation of oligosilanes which has the alternate arrangement of pentacoordinate and tetracoordinate silicon moieties is tightly locked into *all-transoid* form, promoting the σ -conjugation along the backbones. The polysilanes functionalized with (alkoxycarbonyl)methyl substituents exhibit the UV absorption at unusually long-wavelength extending to 480 nm, suggesting the effective promotion of σ -conjugation by polar substituents. Incorporation of ruthenium moieties into the polycarbosilane leads to an interesting photochemical properties such as solvent-dependent change of the UV–vis spectra and the significant decrease in $\sigma \rightarrow \sigma^*$ transition energy of the Ru–Ru bonds.

In this article, examples of our recent work illustrate the interesting potential of functionalized silicon polymers as novel materials which are characterized by highly delocalized electronic states. It should be also noted that these functionalized silicon compounds are highly crystalline materials and control of the solid structure would be easy. Thus, it is expected that the silicon polymers with polar functional groups will exhibit useful physical properties based on strong electronic interaction between the silicon chains in the solid state.

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