

Switching handedness in optically active polysilanes

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Abstract

Chain-like optically active polysilanes comprise a helical main chain of Si–Si single bonds and chiral and/or achiral side groups. They exhibit unique absorption, circular dichroism, and fluorescence spectra around 300–400 nm due to the σ -conjugation. Since the first brief report of optically active polysilane synthesis in 1992, this research field has now widened to include various homo- and copolymers of optically active poly(dialkylsilane)s, poly(dialkoxysilane)s, poly[alkyl(aryl)silane]s, and poly(diarylsilane)s. This account focuses on screw-sense switchable, optically active poly(dialkylsilane)s among the above optically active polysilanes, including (i) (chir)optical properties, (ii) quantitative population analysis of right- and left-handed helices based on Kuhn's dissymmetry ratio, (iii) capability of screw-sense inversion, and (iv) chiroptical switch and memory, as consequences of side group internal interactions, double-well potential energy, and external stimuli. Such knowledge and understanding might stimulate a further polysilane research, and also may advance these polymers to the realization of Si-based nanomaterials and Si-based nanodevices in the future.

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Keywords: Polysilanes; Fluorescence spectra; Copolymers; Optically active; Helix; Circular dichroism

1. Introduction

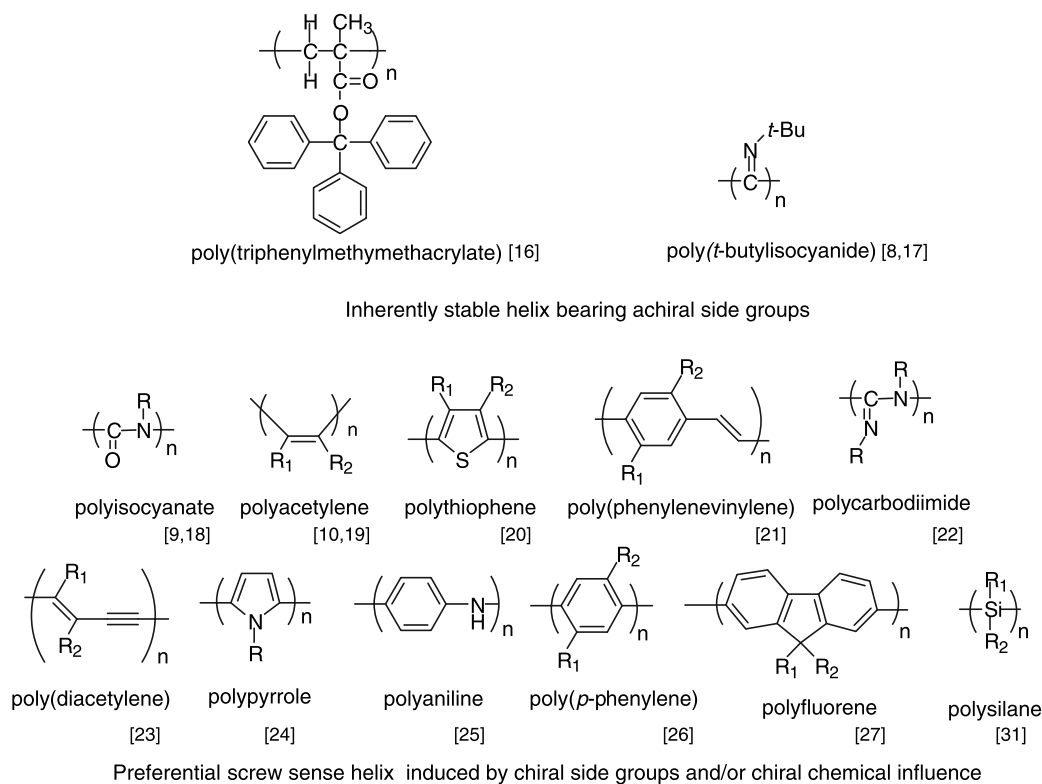
Amino acids and sugars, which are the most important molecular building blocks of our daily life, lead to left-handed and right-handed helical motifs of natural biopolymers, such as proteins, DNA, and polysaccharides. Presumably, since the beginning of life on the earth, living organisms might preferentially exploit L-form of amino acids and D-form of sugars. Optically active substances, hence, are ubiquitous on the earth and become the vital constituents of drug, vitamins, flavors, fragrances, herbicides, and pesticides. Although the origin and scenario of this biomolecular handedness may be a longstanding issue among chemists, physicists, biologists, and astronomers [1–5], our life is indeed the

consequence of chemistry and physics of the homochiral biomolecular substances.

By inspiration from the realm of these biopolymers, research and development on the synthesis, characterization, inherent chemical and physical properties, functionality, and application of optically active artificial polymers with a single screw-sense stiff helix [6–12] have long been of particular interest and subject in the areas of modern polymer science and engineering. This is because these synthetic helical polymers may be promising materials in such areas as enantioselective separation, molecular chirality recognition, chiral nematic liquid crystals, chiroptical switch and memory, nonlinear optics, circularly polarized photo- and electroluminescence. Knowledge and understanding of the structure–property–functionality relationship using chromophoric optically active, organic and inorganic polymers, thus, might be vital for further advancement in these and other new areas, as well as in organosilicon chemistry and in mainstream polymer science (see Scheme 1).

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Scheme 1. Chromophoric optically active organic polymers and polysilane with chromophoric main chain and side groups.

In the pioneering works of synthetic helical polymers two or three decades ago, a few polymers were known to predominantly adopt a single-screw-sense helical structure in solution at room temperature. For example, in 1970, Goodman and Chen [13] synthesized the first optically active polyisocyanate with chiral side chains. In 1974, Drenth and Nolte proved the 4_1 helical structure of poly(*t*-butyl isocyanide)s which was originally suggested by Millich in 1969 [14]. In 1960, Pino prepared an optically active, isotactic poly- α -olefin bearing a chiral side chain, poly(3-methylpentene), followed by optically active poly- α -olefin copolymers [15]. In 1979, Okamoto et al. [16] successfully obtained optically active, isotactic poly(trityl methacrylate) which was the first optically active vinyl polymer obtained from a prochiral monomer. In those cases, very special monomers and/or catalysts under carefully controlled polymerization conditions were required to form the stable helical structures. Since these pioneering works, many synthetic optically active polymers with π -conjugating chromophores, including polyisocyanides [8,17], polyisocyanates [9,18], polyacetylenes [10,19], polythiophenes [20], poly(*p*-phenylenevinylene)s [21], polycarbodiimides [22], polydiacetylenes [23], polypyrroles [24], polyanilines [25], poly(*p*-phenylene)s [26], polyfluorenes [27], and other π -conjugated polymers and oligomers [28] have reported so far. Historical topics of these synthetic helical polymers are reviewed recently [29].

On the other hand, polysilane chemistry has been attracting much attention due to its potential applications in the electronic and photonic fields. A modern polysilane chemistry was originally initiated by Kumada and Yamaguchi in 1954 [30]. Since this pioneering work on polysilane, a rich variety of polysilanes was prepared and studied from the viewpoint of chemistry, physics, and material sciences. However, optically active polysilanes bearing chiral and/or achiral side groups [31–36] may be classified to a new class of polysilanes, because intense and sharp UV absorption, circular dichroism (CD), and fluorescence (FL) spectra around 300–400 nm, due to the σ -conjugation in the helical main chain are uniquely demonstrated [36].

Since the first and early reports on the chiroptical properties of poly(dialkylsilane) copolymers with chiral (*S*)-2-methyl groups by Matyjaszewski et al. in 1992 and 1994 [31a,31b,31c], various optically active polysilane homo- and copolymers have been investigated [31–36]. It may be noted that optically active polysilanes may serve a unique nanostructural and multidisciplinary class of polymer, since rod-like helical polysilanes are regarded as ideal model polymers for one-dimensional silicon-based semiconductors or quantum wires with 0.2 nm width [31d,31f,37,38].

This account highlights several significant results characteristic of screw-sense switchable, optically active poly(dialkylsilane)s among a numbers of optically active polysilanes, describing (i) (chir)optical properties, (ii)

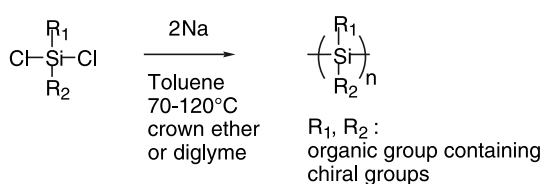
quantitative population analysis of right- and left-handed helices based on dimensionless dissymmetry ratio, (iii) capability and facile control of helix screw-sense inversion, (iv) molecular shape recognition ability, and (v) chiroptical switch and dynamic memory, as consequences of the side group interactions and other chemical and physical external stimuli.

2. Preparation of optically active polysilanes and characterization by circular dichroism–UV absorption–fluorescence spectroscopies

The synthesis of polysilanes with a high degree of stereogenic control is of particular interest [39,40] and of significant importance in a wide variety of high performance functions [41]. Although most optically active polysilanes including poly(dialkylsilane)s, poly(alkylaryl-silane)s, and poly(diarylsilane)s are generally prepared by the Wurtz-type condensation of the corresponding dichlorodiorganosilane with sodium in inert solvent [36,40], this reaction is essentially identical to the procedure of Kipping used in the 1920s, as shown in Scheme 2 [42]. An advanced modification for this reaction is to utilize a very small amount of crown ether or diglyme as an additive to activate sodium surface and promote polymerization. These additives effectively improve polymerization yields, shorten polymerization times, and modify molecular weight distributions [36,43].

However, even if an optically active polymer was prepared from an enantiopure monomer, it is difficult to identify whether the main chain in a given condition (solvent and temperature) has an enantiopure helical conformation with either P (plus, right-handed) or M (minus, left-handed) screw-sense, or is composed of a collection of diastereomerically and/or enantiomerically mixed P- and M-helical motifs.

Helical conformation of optically active polysilanes can be induced by chiral side chain interactions. Since they embody a chromophore and fluorophore in the same main chain, exhibiting intense UV, CD, and FL bands due to the $\text{Si}\sigma\text{--Si}\sigma^*$ transition around 300–400 nm, optically active polysilanes are particularly suitable chiroptical polymers for elucidating the intrinsic nature of a helical polymer itself.



Scheme 2. Synthesis of optically active polysilanes bearing chiral and/or achiral side groups by Wurtz-type reduction.

A combination of FL study with CD, UV, and/or NMR spectra of the main chain may be helpful in identifying screw-sense, uniformity, rigidity, and proportion of P- and M-screw-sense of optically active polysilanes. The utility of the electronic spectroscopies lies in the fact that the photoexcited energy above the optical bandgap migrates to the most energetically stable motif incorporated in a mobile main chain, from which emission then occur [31d,31e]. Furthermore, any desired molecular weight samples can be easily isolated by a simple fractional precipitation technique, since the molecular weights of the polysilanes are widely distributed between 10^3 and 10^7 . These unique features allow to investigate a more straightforward elucidation of the helix–property–functionality relationship [36].

In the case of chromophoric optically active polymers, the intuitive meaning of CD signal intensity is analogous to that of UV spectroscopy, with the additional dimension of the subtracted absorption between left- and right-circularly polarized light (L- and R-CPL) [36,44]. Absorption of light obeys the Beer–Lambert law and CD intensity is defined as $\Delta\varepsilon = \varepsilon_L - \varepsilon_R = (\text{Abs}_L - \text{Abs}_R)/cl$, where $\Delta\varepsilon$ is the molar circular dichroism intensity, ε_L and ε_R are the molar absorptivities for L- and R-CPL, respectively, Abs_L and Abs_R are the absorbances of L- and R-CPL, c is the molar concentration per repeat unit and l is the path length. CD bands are commonly referred to as either positive or negative Cotton effects, and the peaks and bottoms as extrema. It is very useful to express a ratio of the CD intensity to the UV absorption intensity. This is formalized in the dimensionless parameter, so-called Kuhn's dissymmetry ratio, $g_{\text{abs}} = 2\Delta\varepsilon/(\varepsilon_L + \varepsilon_R) = \Delta\varepsilon/\varepsilon$, where ε is the molar absorptivity per repeat unit. The dissymmetry ratio is functions of the magnetic dipole (m), electric dipole moments (μ), and the angle θ between them, such that $g_{\text{abs}} = 4R/D = 4|m||\mu|\cos\theta(m^2 + \mu^2)^{-1}$, where R and D are the rotational and dipole strengths, respectively. For optically active polysilanes, this g_{abs} ratio provides quantitative information on the helical characteristics such as screw pitch and sense, and diastereomeric and/or enantiomeric purities. Typical absolute magnitudes of g_{abs} values for optically active polysilanes in molecularly dispersed solution state are ranging from 2×10^{-4} and 1×10^{-5} . However, particular attention should be paid in the interpretation of g_{abs} due to the possible presence of segments of opposite screw-sense and helix reversals. This is because, if enantiomeric P- and M-motifs absorb at the same wavelength, the magnitude of g_{abs} would result in a smaller or zero value. In some case, apparent optical inactivity may arise from equal proportions of static and/or dynamic helical motifs under measurement conditions.

Apparent split-type Cotton CD signals may arise from two possibilities. In the case of a polymer containing both diastereomeric P- and M-screw-senses with

different absorption wavelengths, the positive and negative Cotton effects will be slightly offset with respect to each other [31d]. Absolute magnitudes of g_{abs} values for optically active polysilanes may range from 2×10^{-4} and 1×10^{-5} . In the case of two adjacent chromophores, coupling between the electronic dipole transition moments will give bisignate CD signals which is the so-called exciton couplet signal [31k,31n,45]. This couplet could be further classified as either an intramolecular interaction in the same molecule at a kink or upon chain folding, and/or an intermolecular interaction in aggregate phases. The sign of an exciton couplet signal affords a simple and convenient method for determining the chirality between the two interacting chromophores [31k,31n,45]. In the present case, absolute magnitudes of g_{abs} values for optically active polysilanes may be ranging from 10^{-3} and 10^{-1} .

3. Preferential screw-sense helical programming of polysilanes

Although the main chain local conformations of polysilanes may be classified as 7_3 - (deviant) or 15_7 - (*transoid*) helix, and all *anti* (achiral *trans*-planar or zigzag) structures on the basis of recent works [46], it is now generally accepted that most polysilanes tend to adopt helical main chain structures, regardless of side groups, temperature, and solvents. However, most polysilanes do not show any Cotton effects in their CD spectra, due to the existence of equal numbers of P- and M-helical segments, resulting in spatial and temporal averaged racemic helical conformation and apparent optical inactivity. If the helical main chain is induced by a chiral chemical influence to adopt a preferential screw-sense with an enantiomeric excess of either P- or M-screw-sense, Cotton effects will be seen in the CD spectrum. The interaction between side groups, solvents, temperature, and helical main chain structures of polysilanes in solution, thus, may be detectable by means of CD spectroscopy, combined with UV, FL, and ^{29}Si -/ ^{13}C -NMR spectroscopies and global conformational properties measurements.

It is established that the helicity of polypeptides is inherent, because the chiral stereogenic centers are incorporated into the main chain [29]. However, the helical structures of poly(triphenylmethyl methacrylate) [7,16,29] and polyisocyanide [8] produced by screw-sense selective polymerization are retained only through the stereochemical fixing effect of bulky achiral side groups, while poly(trityl methacrylate) contains stereogenic centers in the main chain and is needed to have a highly isotactic structure. In the case of optically active polysilanes, polyisocyanates, polyacetylenes, polythiophenes, polyphenylenevinylenes, and polycarbodiimides, their helical structures, however, are effectively

induced by chiral side chain interactions. The latter group of optically active helical polymers can be generally obtained by (a) polymerization of achiral and/or prochiral monomers with enantiopure chiral catalyst or initiator, (b) chiral doping of optically inactive polymers with enantiopure chiral moieties, (c) separation of a racemic mixture of enantiomeric helices using chiral stationary phase chromatography for non-dynamic helical systems, (d) complexation of optically inactive polymers with non-racemic chiral ligands, (e) post-polymerization functionalization with chiral moieties, (f) incorporation of enantiopure chiral end groups, (g) polymerization of non-racemic chiral monomers, (h) copolymerization of non-racemic chiral monomers with achiral monomers or with non-racemic monomers, and (i) circularly polarized irradiation of polymers bearing racemic sensitizers. Techniques from (d) to (h) have been applied to obtain optically active polysilanes [31–35].

4. A correlation between global conformation and optical characteristics

The main chain mobility of σ - and π -conjugating polymers is often connected to their electronic structures. Therefore, changes in the UV–Vis absorption and chiroptical spectra are spectroscopically discernible as thermo-, solvato-, piezo-, or and electrochromisms. Although several polysilanes remarkably exhibit these phenomena [40], their structural origins were controversial until recently, due to the limited information available on the correlation between the conformational structures of the main chain, electronic state, and (chir)optical characteristics. In 1996, the author reported that in various polysilanes in THF at 30 °C, the main chain peak intensity per silicon repeat unit, ε (Si repeat unit) $^{-1} \text{ dm}^3 \text{ cm}^{-1}$, is closely connected to the viscosity index, α [47,48].

Fig. 1 shows the UV absorption spectra of four typical optically active poly(dialkylsilane)s featuring different chiral side groups in THF at 30 °C [31k,36a]. Evidently, as the value of α increases from 0.59 to 1.25 in THF at 30 °C, the UV absorption intensity increases and the full-width at half-maximum (FWHM) decreases. Thus, the degree of σ -conjugation, global conformational structure, and UV absorption characteristics in optically active polysilanes are controllable by the choice of side groups.

Indeed, poly(*n*-hexyl-(*S*)-4-methylpentylsilane) (**2**) with $\alpha = 0.75$ is nearly randomly coiled, while poly(*n*-hexyl-(*S*)-2-methylbutylsilane) (**4**) with $\alpha = 1.25$ adopts almost a rod-like conformation; poly(*n*-hexyl-(*S*)-3-methylpentylsilane) **3** with $\alpha = 0.92$ shows an intermediate behavior between **2** and **4**. Recently, quantitative estimates of the persistence length (q) have been given: 85 nm for **4** in isooctane at 20 °C, but 6.2 nm for **3** in

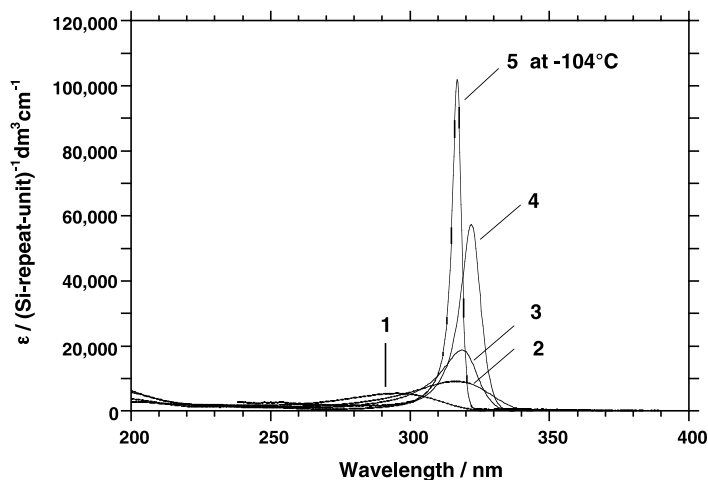
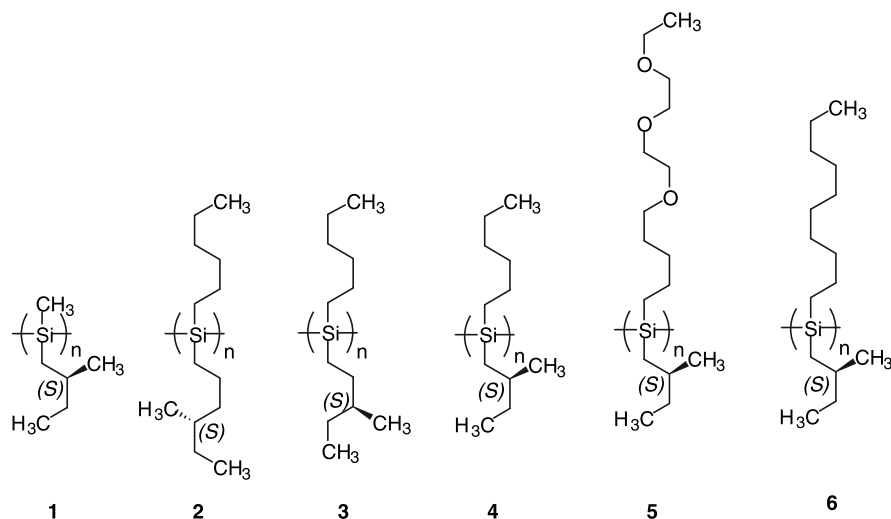


Fig. 1. UV absorption spectra of various optically active polysilanes in THF at 30 °C: Poly[methyl-(*S*)-2-methylbutylsilane] (**1**, $\alpha = 0.59$), poly[*n*-hexyl-(*S*)-4-methylpentylsilane] (**2**, $\alpha = 0.75$), poly[*n*-hexyl-(*S*)-3-methylpentylsilane] (**3**, $\alpha = 0.92$), poly[*n*-hexyl-(*S*)-2-methylbutylsilane] (**4**, $\alpha = 1.25$). For comparison, UV absorption spectrum of poly[6,9,12-trioxatetradecyl-(*S*)-2-methylbutylsilane] (**5**) in ethanol at -104 °C is also displayed. For clarity, spectroscopic features of poly[*n*-decyl-(*S*)-2-methylbutylsilane] (**6**) are almost identical to those of **4** because of the similar rigidity (see Fig. 3).

isooctane at 25 °C [31m]. The high q value of **4** is comparable to that in stiff polyisocyanate with (*R*)-2,6-dimethylheptyl groups ($q = 76$ nm). Comparative q values are reported for other polymers: poly(*n*-hexyl isocyanate) (20–43 nm), aromatic polyamides (20–50 nm), and the double helix DNA (~ 60 nm) [12b,12e]. It is noted that poly(methyl-(*S*)-2-methylbutylsilane) (**1**) has a shrunken shape, indicating a very short q value.

Thus, it is established that global structures of optically active polysilanes are significantly influenced by the position of the branching methyl group (β - or γ -) at the chiral center in the side chain, and also solution temperature. These results led to a semi-empirical relationship between the main chain absorption characteristics and the global conformation of various polysilanes in solution.

Fig. 2 shows a correlation between the values of ϵ , FWHM, and α of various poly(dialkylsilane)s and poly(alkylarylsilane)s in THF at 30 °C [46]. The polymers include seven optically active poly(dialkylsilane)s with four different types of chiral β -, γ -, or δ -branched alkyl substituents, 12 optically inactive poly(dialkylsilane)s with six different types of linear, β -, γ -, or δ -branched substituents, and two optically inactive poly(alkylphenylsilane)s. For the polysilanes exhibiting λ_{\max} ranging from 290 to 352 nm, it is evident that with increasing α , ϵ increases exponentially, but FWHM decreases exponentially. From this semi-empirical ϵ - α -FWHM relationship, either value of ϵ or FWHM renders information on the degree of chain coiling in solution at a given condition. This may be very useful for discussing the global shape of a polysilane in

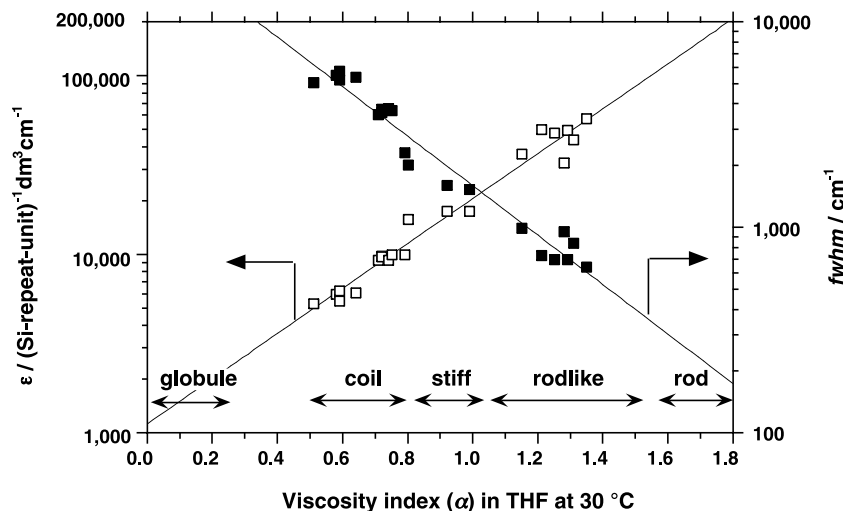


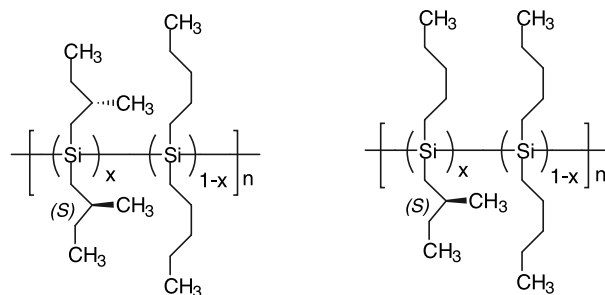
Fig. 2. Correlation between UV peak intensity (ϵ), full-width at half-maximum (FWHM), and the viscosity index (α) of various poly(dialkylsilane) and poly[alkyl(aryl)silane]s in THF at 30 °C.

solution at any temperature [31k]. A value of 150,000 (Si repeat unit) $^{-1}$ dm 3 cm $^{-1}$ for ϵ of an ideal rod polysilane is obtained by extrapolating ϵ using the above ϵ - α relationship to the limiting α for an ideal rigid rod polymer of 1.7–1.8 [47,48]. As demonstrated in Fig. 1, the ϵ value for rod-like optically active poly(6,9,12-trioxatetradecyl-(*S*)-2-methylpropyl)silane (**5**) in ethanol progressively increases from 42,000 with an FWHM of 800 cm $^{-1}$ (8 nm) at 323 nm to 102,000 with an FWHM of 400 cm $^{-1}$ (\sim 4 nm) at 318 nm when the temperature is cooled from 25 to -104 °C [31k]. This is the highest ϵ value corresponding to an almost perfect rod structure of **5** at such low temperatures.

5. Rigid rod-like helical polysilanes with a fixed preferential screw-sense

5.1. (*Chir*)optical properties of (*S*)-2-methylbutyl and *n*-alkyl side chain systems

The first CD spectrum and optical rotation of optically active poly(dialkylsilane) copolymer consisting of di-(*S*)-2-methylbutylsilane and di-*n*-pentylsilane repeat units in the solid film and in solution were briefly reported by Matyjaszewski in 1992 [31a]. This was followed by more detailed reports on the synthesis and chiroptical properties of the copolymers in solution and as solid films by Möller [31b] and Matyjaszewski and coworkers [31c] in 1994 and 1995. In 1994, it was clarified that the most fundamental chiroptical features and conformational properties in a series of optically active poly(dialkylsilane) homopolymers comprising alkyl-(*S*)-2-methylbutylsilane repeat units in solution [31d,31e,31f] (see Scheme 3).



Scheme 3. The first optically active polysilane copolymers featuring (*S*)-2-methylbutyl and *n*-pentyl groups.

Poly(*n*-decyl-(*S*)-2-methylbutylsilane) (**6**), among those polysilanes, showed ideal UV, CD, and FL spectral characteristics of a rod-like helical chromophore and fluorophore due to the preferential single-screw-sense structure induced by side group interactions in isoctane at 20 °C. As evident in Fig. 3(a) and (b), (i) **6** exhibits a very intense, narrow UV absorption with no discernible phonon side bands at 323 nm, with $\epsilon = 55,000$ (Si repeat unit) $^{-1}$ dm 3 cm $^{-1}$ and an FWHM value of 8 nm (ϵ is about six times greater and the FWHM narrower by one-sixth than typical random coil poly(dialkylsilane)s), (ii) the FL spectral profile at 328 nm is the mirror image of the UV and CD band profiles, (iii) the CD band profile fits fully within the UV spectrum, and (iv) the FL anisotropy (FLA) around the 323-nm UV-CD bands approaches the theoretical limit of 0.4 expected for the random distribution of a rod chromophore being collinear with the fluorophore in a rigid medium. It should be noted that these helical exciton transitions (due to a photoexcited electron-hole pair) with negligibly weak electron-phonon coupling are unique, since these features are not seen in π -conjugating polymers or small molecules. These novel

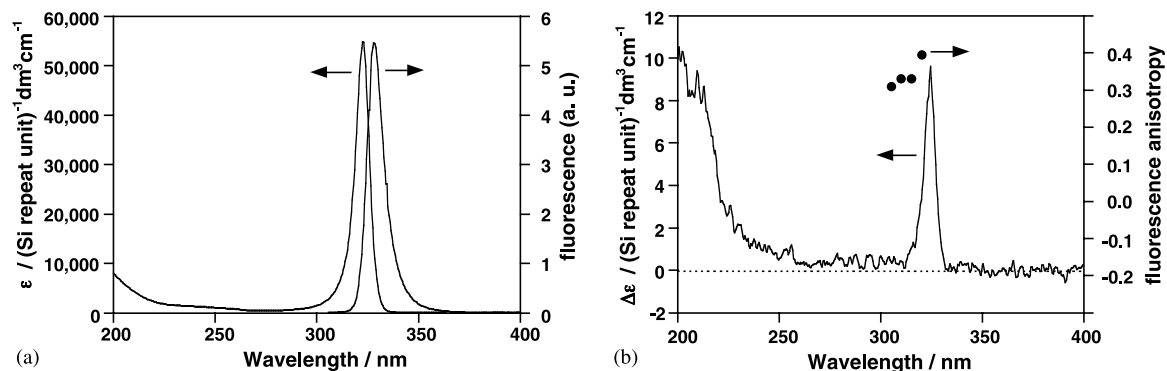


Fig. 3. (a) UV and CD spectra and (b) FL spectrum and FL anisotropy (FLA) of poly(*n*-decyl-(*S*)-2-methylbutylsilane) (**6**, $M_w = 5.3 \times 10^6$, $M_n = 4.1 \times 10^6$, $\alpha = 1.35$ in THF at 30 °C) in isoctane at 20 °C.

UV-CD-FL-FLA characteristics of **6** could be the first demonstration of uniqueness among other optically active polysilanes and optically active organic polymers.

Furthermore, the UV, CD, FL, and FL excitation (FLE) spectral characteristics of a series of poly(*n*-alkyl-(*S*)-2-methylbutylsilane) in isoctane at 20 °C were measured to elucidate the effects of the *n*-alkyl side group and main chain length [31f]. It was concluded that the rod-like helical structure was retained, even when the *n*-alkyl side group length is increased from *n*-propyl to *n*-dodecyl and the main chain length is increased from 20 to 3000 silicon units. This was supported by the unique UV-CD-FL-FLE spectroscopic features of **6** and the fact that the g_{abs} value of $\sim 2.0 \times 10^{-4}$ was almost independent of both *n*-alkyl side group length and silicon main chain repeat length, as is evident in Fig. 4(a). On the other hand, the peak intensities of UV and CD bands at 323 nm increase nonlinearly as the main chain repeat number increases and tend to reach constant values, as shown in Fig. 4(b), while the respective values of the UV peak wavelength and FWHM of the band converged to limiting values of 322 and 8 nm in isoctane at 20 °C.

It is noted that the dipole strength of UV absorption band is independent of the *n*-alkyl side group length and main chain repeat numbers. Actually, integration of the 323 nm UV absorption band of the poly(*n*-alkyl-(*S*)-2-methylbutylsilane) derivatives depends very weakly on the repeat numbers. These results led to the important idea that, in the case of optically active polysilanes, the value of g_{abs} ($= \int \Delta\epsilon \, d\lambda / \int \epsilon \, d\lambda$) should be used to characterize helical structures such as the proportion of P- and M-motifs and their regularity, rather than the values of $\Delta\epsilon$ or optical rotation.

5.2. AFM single molecular imaging of rod-like structure for nanoscience and nanotechnology

Chain dimensional parameters of polymers such as the value of persistent length, q , in dilute solution can be determined by well-established light scattering, sedimentation equilibrium, and viscometric techniques [12]. Concerning solid-state analysis, imaging of the detailed molecular structure of individual polymer chains on a solid surface is of growing interest in the design and control of the optoelectronic properties of functional polymers and nanomaterials. Recent advances in atomic

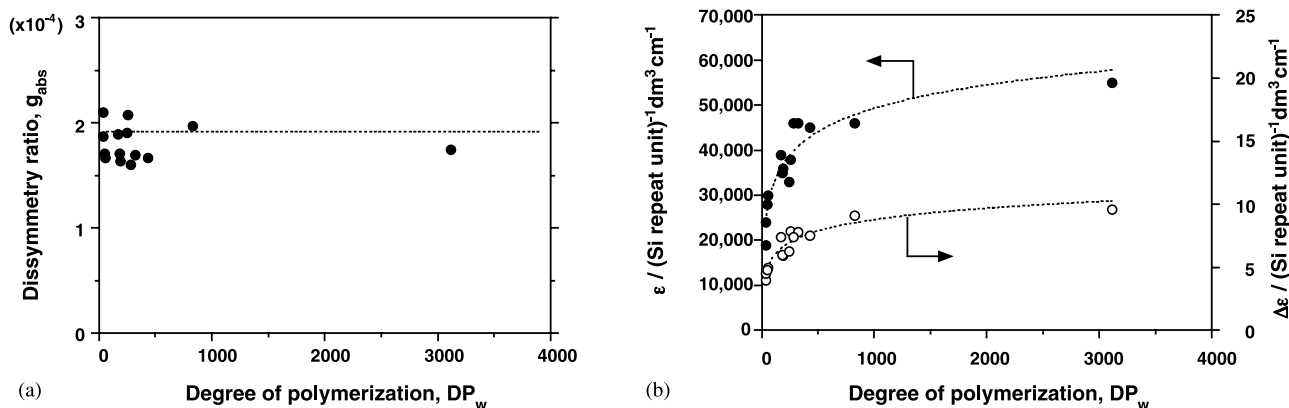


Fig. 4. UV and CD bands characteristics at around 323 nm of 14 samples isolated from nine poly(*n*-alkyl-(*S*)-2-methylbutylsilane) derivatives as a function of the degree of polymerization (DP_w) in isoctane at 20 °C: (a) the dissymmetry ratio (g_{abs}) and (b) ϵ and $\Delta\epsilon$.

force microscopy (AFM) and scanning tunneling microscopy (STM) have now enabled direct imaging of polymer molecules. For example, AFM images of a few insulating polymers such as cyclic DNA and random coiled polystyrene-block-poly(methyl methacrylate) on mica, poly(*para*-phenylene) on a gold surface, and twinned chiral polyacetylene on a highly oriented pyrolytic graphite substrate have been reported [49].

In 1997, the first molecular AFM images of rod-like **6** with a high molecular weight ($M_w = 5.3 \times 10^6$, $M_n = 4.1 \times 10^6$; total molecular contour length ~ 2000 nm) on sapphire was reported by Ebihara et al. [50a]. The individual molecular image appears to essentially adopt rod-like structures accompanied by slight structural fluctuations. The rod-like objects consisted of several segments separated by kinks, in which the segment lengths are ranged from 150 and 800 nm. These long segments may be responsible for the unique UV-CD-FL spectroscopic features of **6** and its derivatives. AFM/STM studies of various polymers might be the challenging issue in the forthcoming organosilicon chemistry, polymer science, and nanomaterial science [50b,50c]. Recently, Furukawa et al. [50c] successfully obtained a similar AFM molecular image of **6**, one end terminus of which had been chemically immobilized anchored on a silicon substrate, as well as of other flexible polysilanes bonded on solid substrates.

It is possible that polysilanes with different stiffnesses and degree of wire structure fluctuation serve as polymer models of quantum-wire semiconductors with a 0.2 nm silicon atomic size width in areas of nanoscience and nanotechnology [31f,37,38]. The advanced one-dimensional exciton theory for a semiconducting polymer infinite chain with different degrees of disorder in the electronic state demonstrated that the exciton absorption significantly weakens and broadens as the degree of structural disorder increases [38f]. The disorders should involve structural deviations in Si–Si bond length, and Si–Si–Si bond and Si–Si–Si–Si dihedral angles. Such deviations are considered to determine the persistence length, mean free path, the effective σ -conjugation length, and degree of delocalization of hole and electron carriers in the main chain [31i]. As exemplified in Figs. 2–4, individual rod-like polysilanes in dilute solution indeed afford ultimately intense, narrow exciton absorption and emission, which nicely fit to the theoretical simulation for a one-dimensional exciton in idealized semiconducting polymers, while coiled flexible polysilanes with an inhomogeneous electronic state afford a weak, broad exciton absorption along with sharp emission [38].

Further developments of AFM/STM instruments and measurement techniques would permit the direct characterization of the helical pitch, screw-sense, helix reversal, and supramolecular structures of individual polysilane molecules in the near future.

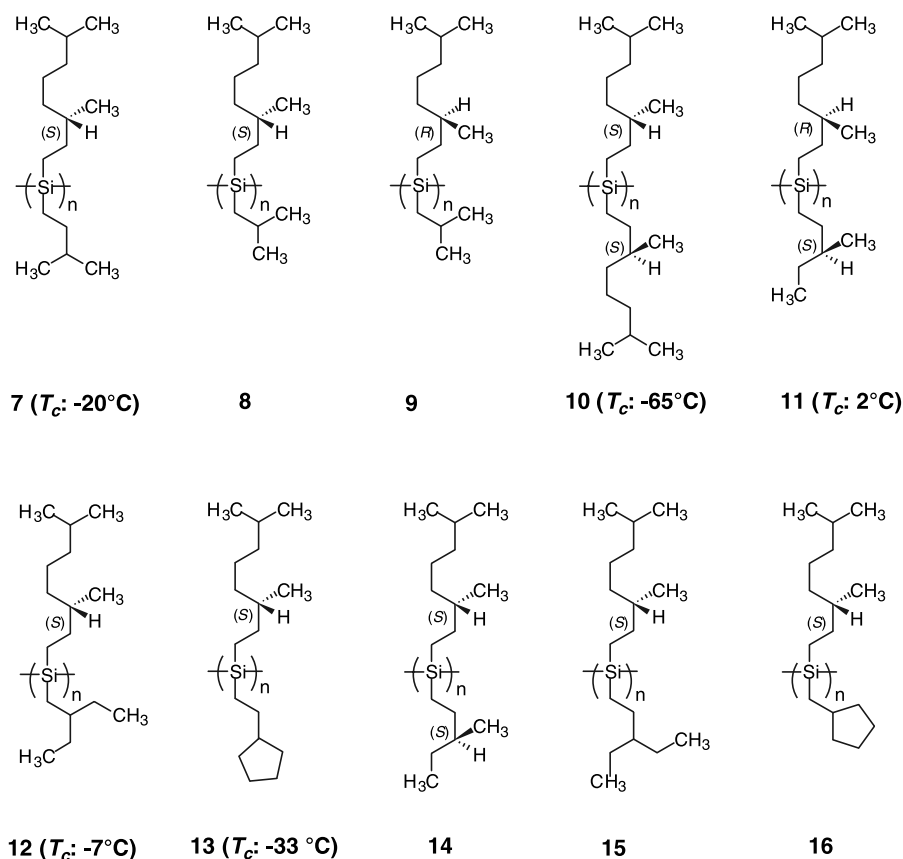
6. Flexible rod-like helical polysilanes with inversion of preferential screw-sense

6.1. (*Chir*)optical properties of (*S*)- or (*R*)-3,7-dimethyloctyl and β - or γ -branched side chain systems

A current challenging issue in the area of helical polymer and oligomer research is to design and realize dynamic chiroptical properties in response to external chemical and physical biases [8–10,12,28,35]. The most striking dynamic property for a helical polymer may be its chiroptical inversion associated with a helix–helix (PM) transition in response to external physical and/or chemical stimuli. Although biochemists originally discovered this phenomenon three decades ago in synthetic oligo-DNA (driven by a change in NaCl concentration) [51] and poly(L-aspartic acid ester)s (driven by changes in temperature and organic acid) [52], a few synthetic organic polymers are known to undergo a PM transition in solution, or as the solid film state. For example, polyisocyanates [18e,18f,18m,18o,18s], polyacetylenes [19g,19k,19l,19m,19p], polypeptides [53], polythiophenes [20c,20d,20h], poly(triarylmethyl methacrylate) [54], and calf thymus DNA [55] underwent PM transition by chemical and/or physical biases. Recently, the author and coworkers found that certain poly(dialkylsilane) homopolymers and copolymers [32], poly(alkyl(alkoxyphenyl)silane) homopolymer [33e], and a poly(diarylsilane) copolymer [34b,34c] undergo a thermo-driven PM transition in solution by controlling side chains and composition of co-monomers in copolymers (see Scheme 4).

Poly[(*S*)-3,7-dimethyloctyl-3-methylbutylsilane] (**7**) may be classified to a family of rod-like helical homopolymers bearing enantiopure alkyl side groups, since **7** affords an intense, narrow UV absorption band, completely matching the corresponding CD and FL band mirror image profiles, similar to the rigid rod-like helical polysilane homo- and copolymers described above. However, **7** undergoes a thermo-driven PM transition in isooctane at -20 °C, which is spectroscopically detectable as an inversion of the Cotton CD band.

Fig. 5(a) and (b) compares the CD and UV absorption spectra of **7** at -40 and -5 °C and of poly[(*S*)-3,7-dimethyloctyl-2-methylpropylsilane] (**8**) at -82 and $+80$ °C in isooctane. The positive-signed CD spectrum of **7** with λ_{ext} of 320 nm at -40 °C is almost the inverse of the negative-signed CD spectrum with λ_{ext} of 322 nm at -5 °C. It is evident that **7** undergoes a PM transition between the two temperatures, though the helical motifs at -40 and -5 °C are energetically and spectroscopically non-equivalent. On the other hand, neither **8** nor its mirror image poly[(*R*)-3,7-dimethyloctyl-2-methylpropylsilane] (**9**) undergo any such inversion of the CD spectra in isooctane between -90 and $+80$ °C.



Scheme 4. Helix–helix transition (whose temperature is indicated in parentheses) and non-helix–helix transition poly(dialkylsilane) homopolymers (7–14) featuring an enantiopure (*S*-) or (*R*-)3,7-dimethyloctyl group.

Polymers 6–9 are thought to adopt rod-like 7_3 -helical conformations (dihedral angle of about 150° or 210°) in solution [31d,31m,31n,31o,31p,31q,31r,31s,31t], since these λ_{max} near 323 nm are almost identical to that of poly(di-*n*-pentylsilane) and poly(di-*n*-butylsilane) adopting a 7_3 -helical form in the solid state [40b]. Indeed, it was concluded that 6 adopts 7_3 -helix in the solid state from X-ray analysis [31n]. Although rod-like behavior of these polymers is expected by the high values of α , the α values for 7 and 8 in CHCl_3 at 30°C are 1.11 and 1.29, respectively (for 6 in THF at 30°C ,

$\alpha = 1.35$) [32a], polymer 7 is more flexible than 6, 8, and 9, according to the following ^{29}Si -NMR results.

Fig. 6 displays the ^{29}Si -NMR spectra of 6–8 in CDCl_3 at 30°C . Since these polysilanes have two different types of side groups attached to the main chain, they may essentially comprise isotactic (*it*-), syndiotactic (*st*-), and heterotactic (*ht*-) sequences. Indeed, 6 exhibits a major signal at -22.2 ppm along with a weak signal at -23.1 ppm, suggesting an almost single configurational sequence with a minor fraction of another sequence in the same main chain. Although 7 and 8 exhibit single ^{29}Si -

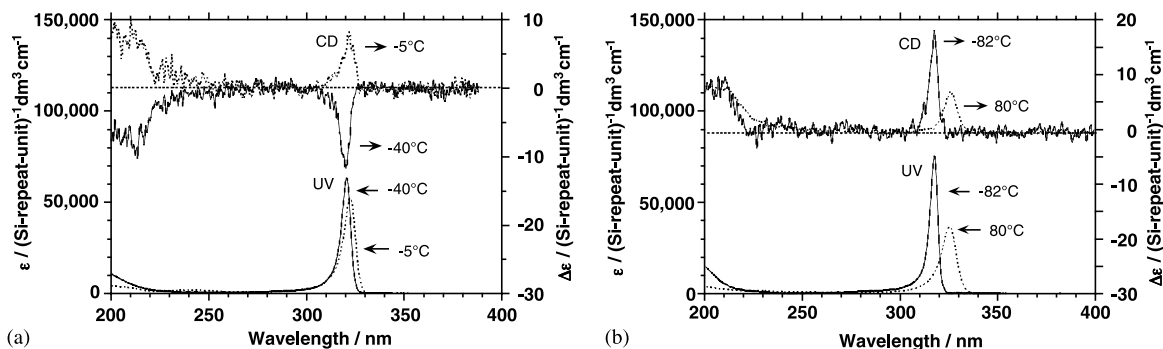


Fig. 5. (a) CD and UV absorption spectra of poly[(*S*)-3,7-dimethyloctyl-3-methylbutylsilane] (7, $M_w = 1.6 \times 10^6$ and $M_w/M_n = 1.53$) at -40°C (solid line) and -5°C (dotted line) in isoctane, (b) CD and UV absorption spectra of poly[(*S*)-3,7-dimethyloctyl-2-methylpropylsilane] (8, $M_w = 4.2 \times 10^4$ and $M_w/M_n = 1.51$) at -82°C (solid line) and $+80^\circ\text{C}$ (dotted line) in isoctane.

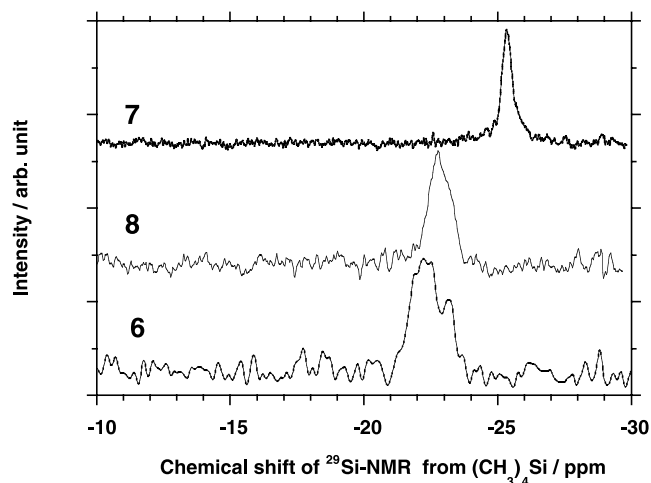


Fig. 6. ^{29}Si -NMR spectra between (top) poly[(*S*)-3,7-dimethyloctyl-3-methylbutylsilane] (**7**), (middle) poly[(*S*)-3,7-dimethyloctyl-2-methylpropylsilane] (**8**), and (bottom) poly[*n*-decyl-(*S*)-2-methyl-butylsilane] (**6**) in CDCl_3 at 30°C .

NMR signals near -23 to -25 ppm, respectively, implying mainly *it*- or *st*-sequences, a remarkable difference in ^{29}Si -NMR linewidth ($\Delta\nu_{1/2}$) between **6**, **7**, and **8** can be seen. The greater flexibility of **7** compared to **6** and **8** is suggested by the narrower $\Delta\nu_{1/2}$: for **7**, $\Delta\nu_{1/2} = 29$ Hz at -25.3 ppm, while for **6**, $\Delta\nu_{1/2} = 90$ Hz at -22.3 ppm and for **8**, $\Delta\nu_{1/2} = 65$ Hz at -22.7 ppm.

Recently, we reported four more examples of PM transition rod-like polysilanes in isooctane upon application of a thermal energy bias: poly[bis[(*S*)-3,7-dimethyloctyl]silane] (**10**) [32b], poly[(*R*)-3,7-dimethyloctyl-(*S*)-3-methylpentyl]silane] (**11**) [32c,32d], poly[(*S*)-3,7-dimethyloctyl-(2-ethylbutyl)silane] (**12**) [32e], and poly[(*S*)-3,7-dimethyloctyl-(2-cyclopentylethyl)silane] (**13**) [32f] have T_c of 2, -65 , -7 , and -33°C , respectively. However, poly[(*S*)-3,7-dimethyloctyl-(*S*)-3-methylpentyl]silane] (**14**) [32c], poly[(*S*)-3,7-dimethyloctyl-(3-ethylpentyl)silane] (**15**) [32e], and poly[(*S*)-3,7-dimethyloctyl-(1-cyclopentylmethyl)silane] (**16**) [32f] did not undergo a PM transition. Recently, it was reported that the value of q for **11** is as large as 103 nm in isooctane at 25°C .

Although homopolymers bearing two γ -branched side groups per repeat unit may have a great possibility of undergoing a PM transition, polymers with a combination of β - and non-branched side groups or β - and γ -branched groups are unlikely to undergo a PM transition. However, exceptionally **12** featuring β - and γ -branched groups *does* undergo a PM transition [31e], while **15** featuring two γ -branched groups *does not* [57]. Additionally, although **10** and **14** have similar γ -chiral side groups, only **10** undergoes a PM transition. In this case, the choice of handedness in the two γ -chiral side groups definitively determines the capability of a PM transition. Thus, very minute modification and the choice of handedness in the side groups of polysilanes

definitively determines the capability of the PM transition and the value of T_c . Beyond the factors discussed above, it is still difficult to find general guidelines for designing polysilanes with a PM transition capability.

6.2. Origin of helix–helix transition

Considering the variable temperature dependence of λ_{ext} , λ_{max} , and intensities of $\Delta\varepsilon$ and ε of **7** and **8** in isooctane, the λ_{ext} and λ_{max} values of **7** and **8** linearly blue-shift from 325 to 318 nm as the temperature decreases from 80 to -82°C . The ε values of **7** and **8** increase monotonically from 40,000 to 80,000 over the same range. The former may be ascribed to a slight decrease in screw-pitch, deviating from an ideal 7_3 -helical structure, and the latter arises from a progressive increase in dimension of the main chain. However, the $\Delta\varepsilon$ value of **7** monotonically increases from ca. 3 at $+80^\circ\text{C}$ to ca. 8 at -5°C , goes to zero abruptly at -20°C , and then decreases to -15°C monotonically at -82°C , while that of **8** monotonically increases from 7 to 18. Mutual cancellation of positive and negative Cotton signals is indeed occurring at T_c , resulting from an equal population of pseudo-enantiomeric P- and M-motifs with the same λ_{ext} and λ_{max} values.

To quantitatively characterize the PM-populations using chiroptical characteristics, it is appropriate to use the g_{abs} values of **7** at each temperature with reference to the regression curve of these g_{abs} values in **8** which is assumed to adopt a purely P- 7_3 helical structure, instead of the $\Delta\varepsilon$ value. The population analysis is based on the assumption that the weak temperature dependence of the g_{max} for **8** is due to a minute modification in the screw-pitch of the P-helix, rather than any formation of the M-helical motif.

Fig. 7 plots the temperature dependence of the dissymmetry ratios and the PM-populations in three different M_w samples of **7** in isooctane based on the above analysis. It is evident that although the PM-populations in the three samples depend slightly on M_w , a steep PM transition clearly occurs at -20°C . The highest M_w polymer (closed circles) contains 12% P- and 88% M-motifs at -90°C , while at 25°C these values invert to 84% P- and 16% M-motifs. The medium and lower M_w samples contain 15% P- and 85% M-motifs at -90°C , while at 25°C these values are 76% P- and 24% M-motifs. However, the transition temperature width (ΔT_c) tends to slightly broaden as M_w decreases. It is concluded that the PM transition characteristics including T_c , ΔT_c , and PM-populations weakly depend on the molecular weight, and the PM-transition characteristics may vary with segment length, for segments shorter than 50 silicon repeat units and/or the nature of two chain termini.

Although the origin of the PM transition remains obscure, the marked differences in potential energy

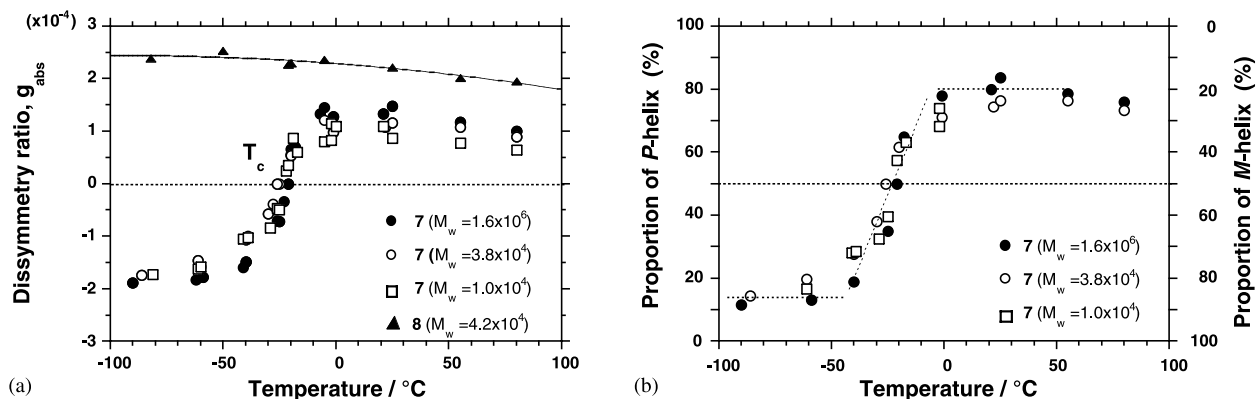


Fig. 7. (a) Temperature dependence of the dissymmetry ratios of poly[(*S*)-3,7-dimethyloctyl-3-methylbutylsilane] (**7**) with three different M_w samples and poly[(*S*)-3,7-dimethyloctyl-2-methylpropylsilane] (**8**) which is assumed to be a purely P-helix in isoctane. The values of M_w were (i) 1.6×10^6 (closed circles), (ii) 3.8×10^4 (open circles), and (iii) 1.0×10^4 (open squares) for **7**, and 4.2×10^4 (filled triangles and solid curve) for **8**. (b) Temperature dependence of P- and M-populations of **7** in isoctane by reference to the regression curve of g_{abs} values in **8**.

curves and main chain stiffness between **7** and **8** may be critical. Fig. 8 shows the dihedral angle dependence on the potential energy of (*S*)-3,7-dimethyloctyl-3-methylbutylsilane (31 repeat units with hydrogen termini) (oligo-**7**) and (*S*)-3,7-dimethyloctyl-(2-methylpropyl)silane (31 repeat units with hydrogen termini) (oligo-**8**) for their *it*- and *st*-sequences, respectively. An *it*-oligo-**7** clearly shows a double-well potential curve, i.e. two local energy minima with almost enantiomeric helices at dihedral angles of P-157° and M-210°. The global minimum M is slightly more stable than that of P by about 0.67 kcal per repeat unit and the barrier heights of the M- and P-screw-senses are 2.3 and 1.7 kcal per repeat unit, respectively. Also, *st*-oligo-**7** has a similar double-well potential curve at about P-160° and M-200° and the global minimum M is slightly more stable than the corresponding P by about 1.3 kcal per repeat unit. The barrier heights for the respective M- and P-screw-senses are about 4.6 and 3.4 kcal per repeat unit. Thus, the calculation of oligo-**7** suggests that both pseudo-enantiomeric P- and M-motifs are likely to coexist in the

same main chain at any temperature, regardless of microtacticity.

On the other hand, *it*-oligo-**8** shows an unclear double-well potential at dihedral angles of P-160° and M-200°. The P-helix is much more stable compared to the corresponding M by about 2.3 kcal per repeat unit. The barrier heights of the respective M and P are about 3.9 and 1.4 kcal per repeat unit, leading to the idea that P-helix might be more stable. An *st*-oligo-**8** has an almost single-well potential with dihedral angles of P-160°. These calculations assume that the P-motifs of **7** and **8** are more stable at all temperatures, regardless of tacticity.

To discuss the origin of the PM transition, some simple energy parameters of the P- and M-states for oligo-**7** and oligo-**8** may be useful. Here, ΔG is the difference in free energy between the P- and M-states, whereas ΔH and ΔS are the differences in enthalpy and entropy between the P- and M-states, respectively.

$$\begin{aligned} \Delta G &= G_P - G_M = \Delta H - T \Delta S \\ &= H_P - H_M - T(S_P - S_M) \end{aligned} \quad (1)$$

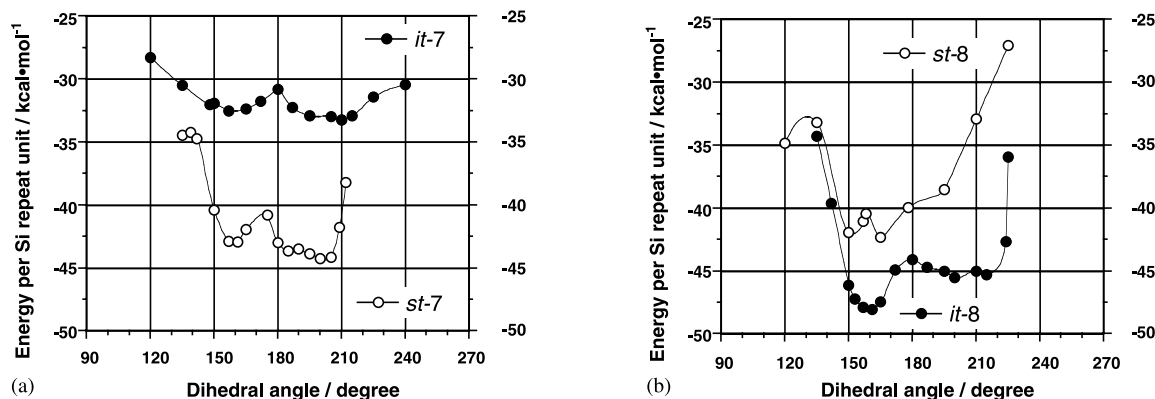


Fig. 8. Molecular mechanics calculation. Main chain dihedral angle dependence on the potential energy (per repeat unit) of (a) *it*- and *st*-(*S*)-3,7-dimethyloctyl-3-methylbutylsilane 31 repeat units with hydrogen termini (oligo-**7**), and (b) *it*- and *st*-(*S*)-3,7-dimethyloctyl-2-methylpropylsilane 31 repeat units with hydrogen termini (oligo-**8**). Discover 3 (ver. 4.00, simple minimization, MSI) was used for this calculation.

where

$$\Delta H = H_P - H_M, \quad \Delta S = S_P - S_M \quad (2)$$

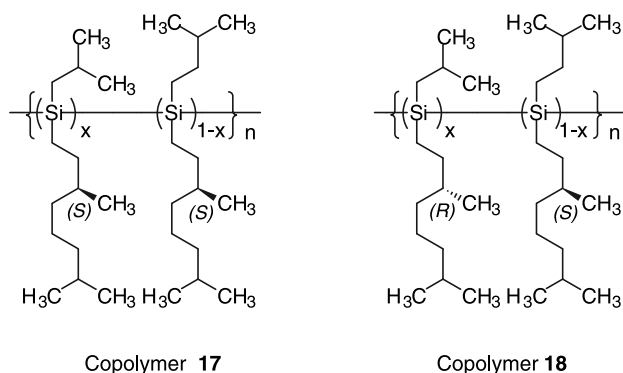
$$\text{at } T_c, \Delta G = 0, \quad \text{then } T_c = \frac{\Delta H}{\Delta S} \quad (3)$$

Using the values of $T_c = 253 \text{ K}$ of **7** and $\Delta H = -0.67 \text{ kcal}$ per repeat unit for oligo-**7**, one can obtain that $\Delta S = -2.6 \text{ cal K}^{-1}$ at T_c . Since the sign of the ΔG term below T_c is negative, P is more stable than M, and vice versa. To design a thermo-driven PM transition polysilane for switching at a desired temperature, it appears essential that the polysilane has a double-well potential curve, small ΔH , and small potential barrier height. If the ΔS term contributes to the inversion capability of preferential screw-sense, P-polysilane in a low entropy state below T_c may take an ordered packing of side groups, whereas M-polysilane in the higher entropy state above T_c may have a disordered arrangement of side groups.

6.3. Control of helix–helix transition temperature by copolymerization

Qualitative understanding of PM-transition characteristics and main chain stiffness of rod-like polysilanes, thus, led to the new idea that subtle structural modification of the achiral and chiral alkyl side groups controls critically the transition characteristics. Indeed, in a series of **7**-based copolymers, poly[*((S)*-3,7-dimethyloctyl-3-methylbutylsilane)-*co*-*((S)*-3,7-dimethyloctyl-2-methylpropylsilane)] (**17**) and poly[*((S)*-3,7-dimethyloctyl-3-methylbutylsilane)-*co*-*((R)*-3,7-dimethyloctyl-2-methylpropylsilane)] (**18**) (see Scheme 5), PM-transition characteristics are controllable by the choice of side groups.

Fig. 9 shows the temperature dependence of the g_{abs} values and PM populations in **17** (80 mol% of **7** and 20 mol% of **8**), **7**, and **18** (80 mol% of **7** and 20% of **9**) in isooctane between -82 and $+80 \text{ }^\circ\text{C}$. It is evident that, compared to the T_c of **7**, that of **17** containing two identical (*S*)-chiral side groups decreases by $16 \text{ }^\circ\text{C}$,



Scheme 5. Two series of screw-sense switchable poly(dialkylsilane) copolymers (**17** and **18**), featuring (*S*)- and (*R*)-3,7-dimethyloctyl, 2-methylpropyl, and 3-methylbutyl side chains.

whereas that of **18** containing the opposite (*S*)- and (*R*)-chiral side groups increases by $16 \text{ }^\circ\text{C}$. The CD spectral profile for the respective copolymers still matches the corresponding UV absorption spectrum at temperatures. However, as introduction of **8** or **9** to pure **7** causes an increase of the transition breadth ΔT_c (defined as a difference between T_c^{up} and T_c^{down}), due to the randomness of the two different silane repeat units incorporated in the same main chain.

The variation of the values of T_c is plotted in Fig. 10, as a function of the mole fraction of **8** in **17**, and **9** in **18**. As the mole fraction of **8** in **17** and **9** in **18** increases, the value of T_c changes nonlinearly from -64 to $+79 \text{ }^\circ\text{C}$ and the value of ΔT_c is nonlinearly broadened. As demonstrated in certain poly(alkylisocyanate) copolymer undergoing a PM transition [18s], although a further mechanistic study is needed to clarify the realistic origin of the transition, presumably the two local free energy minimum potentials and entropy term in the free energy stability may be tunable by the choice of side chain chirality and the branch position in the side chain. Even in this case, the coexistence of P- and M-motifs in the same main chain at any temperature may be essential for the capability of the PM-transition.

This knowledge and understanding might be helpful in designing PM-transition capability and characteristics in diverse screw-sense inversion-related applications, such as a chiroptical switch and memory, a preference molecule switchable chiral separation column, molecular recognition ability, and molecular machinery in the future.

6.4. Quantized and superposed right- and left-handed helicities

Designing and realizing miniature-scale computing devices are now the most challenging issues in nanoscience and nanotechnology [56]. Optically active molecules with bi- and multi-stable switch and memory functions associated with molecular motions such as twist, rotate, fold, shrink, stack, and shuttle may be a candidate as basic elements in these devices [57]. Generally, great problems remain in the design and manufacture of such molecular elements, due to difficulties in the wiring of these elements with functions of “memory and storage”, defined threshold, processing, and error correction. Understanding and measuring the superposition of quantum states in nano-systems based on semiconductors and superconductors directed towards the realization of quantum computing have been achieved theoretically and experimentally so far [58]. If the essence of “quantum computing” is regarded as the controlled mixing of two quantum states by physical and/or chemical biases, this may also be in the realm of molecular and polymer sciences [59,60]. It may be noted that before these boom studies, several quantum che-

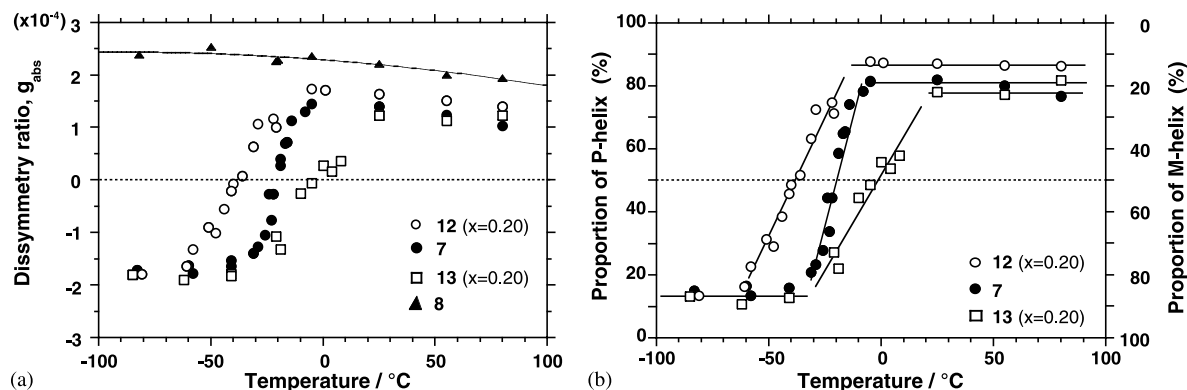


Fig. 9. (a) Temperature dependence of the g_{abs} values of **17** (80% of **7**, 20% of **8**, $M_w = 5.0 \times 10^4$, open circles), **7** ($M_w = 3.8 \times 10^4$, filled circles), **18** (80% of **7**, 20% of **9**, $M_w = 4.8 \times 10^4$, open squares), and **8** ($M_w = 4.2 \times 10^4$, filled triangles with a solid curve) in isooctane. (b) Temperature dependence of the PM-populations of **7**, **17**, and **18** in isooctane by reference to the regression curve of g_{abs} values in **8**.

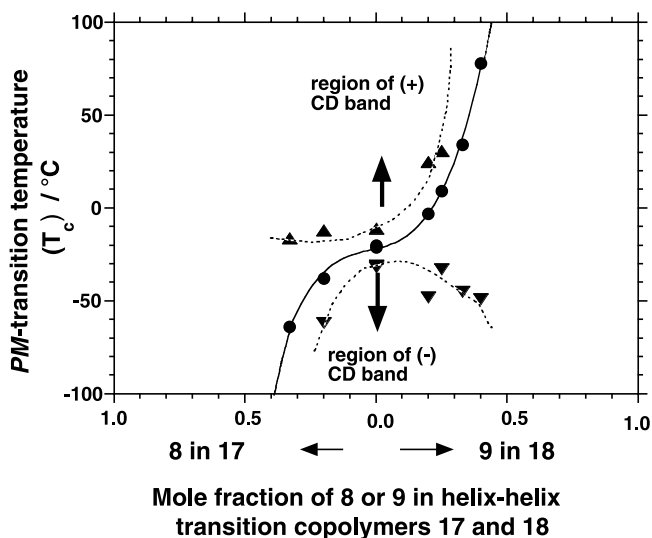


Fig. 10. Values of T_c as a function of mole fraction of **8** in **17** and **9** in **18** along with **7** in isooctane. The M_w values in all the homopolymer and copolymers and ranged from 3.5×10^4 to 8.5×10^4 .

mists had already discussed quantum tunneling and oscillation, and the preparation and detection of superposed optical activity for a hypothetical chiral molecule with a double-well potential using an ultra-short-light pulse, although they did not extend their ideas to the possibility of chiral molecule-based quantum computing [59,60].

As noted earlier, it is reasonable to use the dimensionless parameter to quantitatively evaluate the PM-population of **11** and **14** in solution by reference to the regression curve of the g_{abs} values for **8**, which is assumed to be in a purely P-motif over the temperature range, although the temperature dependence of the g_{abs} values in **8** shows a slight change of screw-pitch. Variable temperature g_{abs} values and the proportion of P- and M-motifs of **8**, **11**, and **14** in isooctane between -80 and 80 °C are plotted in Fig. 11(a) and (b). It is evident that **11** features three distinct switching regions,

1 (-80 to -10 °C), 2 (-10 to $+10$ °C), and 3 ($+10$ to $+80$ °C). Polymer **11** in region 1 contains a constant 80% P and 20% M (60% P excess over M), but contrarily in region 3, it has 80% M and 20% P (60% M excess over P). However, **14** invariably contains 80% P and 20% M (60% P excess) over the entire temperature range. This behavior may be related to greater differences in the potential energy curve between **11** and **14**.

Similarly, variable temperature g_{abs} values and the proportion of P- and M-motifs of **12** in isooctane between -80 and 80 °C are plotted in Fig. 12(a) and (b). It is also evident that **12** features three thermally accessible regions, 1 (-80 to -30 °C), 2 (-30 to 25 °C), and 3 (25 to 80 °C), as already demonstrated in **11**. In region 1, **11** contains a constant 15% P and 85% M (70% M excess), but on the other hand, in region 3, it has an 82% P and 18% M (64% P-excess). The switching features in region 2 are thus ascribed to be the consequence of the quantized and superposed helicities between the 70% M- and 64% P-excess states, although the superpositions of chirality and optical activity were classically discussed by Hund [60] and several quantum physicists [4e,59].

Also, the variable temperature g_{abs} values and PM-populations of **13** and **16** in isooctane are displayed in Fig. 13. Polymer **13** undergoes a helix-helix transition at the T_c , accompanied by a temperature-dependent mixing state between the pure P- and M-helicities. For example, the PM-population of **13** continuously changes from 70% P and 30% M (40% P excess) at 80 °C to 82% P and 18% M (64% P excess) at -10 °C, but goes to 50% P and 50% M (zero% P or M excess) at -33 °C, and then inverts to 12% P and 88% M (76% M excess) at -80 °C. On the other hand, the PM-population of **16** is almost a constant 99% P and 1% M (98% P excess) between -61 and 80 °C, except for a slight change to 93% P and 7% M (86% P excess) at around -20 °C. The switching properties of the optical activity and the features of the screw-sense inversion are thus ascribed

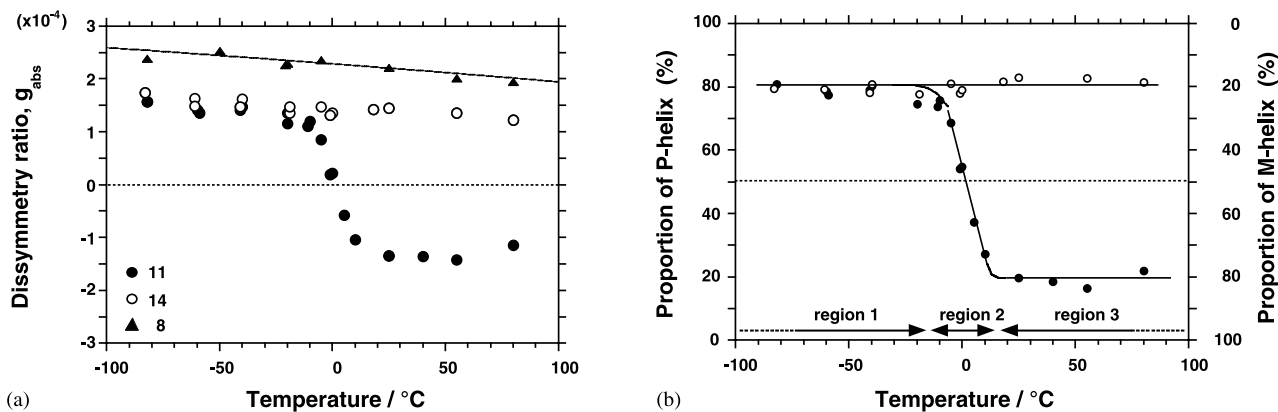


Fig. 11. (a) Variable temperature g_{abs} values of **11** ($M_w = 5.8 \times 10^6$, $M_n = 3.4 \times 10^6$, filled circles), **14** ($M_w = 4.7 \times 10^6$, $M_n = 2.1 \times 10^6$, open circles), and **8** (filled triangles) in isooctane in the range -80 and $+80$ $^{\circ}\text{C}$. (b) Proportion of P- and M-motifs of **11** (filled circles) and **14** (open circles) as a function of temperature.

as the consequence of the superposition of the P- and M-helicities.

The temperature dependence of the λ_{max} values of **12** and **13** in isooctane are shown in Fig. 14(a) and (b). Although a progressive blue shift of λ_{max} for **12** is seen with decreasing temperature, two discontinuous changes around -10 $^{\circ}\text{C}$ are recognized. Similarly, for **13**, although a progressive blue shift in λ_{max} is seen with decreased temperature, a very weak discontinuous change around the T_c of around -33 $^{\circ}\text{C}$ is evident. By extrapolating the two straight lines A and B, the energy gap is estimated to be ~ 0.01 eV, implicating the occurrence of slight conformational changes in the Si–Si main chain structure to relax the overcrowded steric environment (corresponding to barrier height for tunneling process) of the chiral and achiral side chains.

6.5. Control of helix–helix transition temperature by solvent molecular shape

The most important feature of **11** exists in region 2, because the superposed state almost linearly varies with

thermal energy bias, ranging from 60% M- to 60% P-excess. It is noted that **11** sensitively recognizes the topology of small molecules due to the two branched side chain structures. This superposed helical states linked by dynamic twisting motions is thought to have a “dynamic memory” function, since, if the solvent molecules (external chemical bias) are taken away, the superposed state may modify the PM population. This led to a change in T_c value with a range of non-polar hydrocarbon solvent molecules with different degrees of branching. This “solvent effect” of optically active polymers able to alter a preferential screw-sense was demonstrated in the optical activity of poly(*n*-hexyl isocyanate) induced by enantiopure chiral, racemic, and achiral solvents [18k].

Fig. 15(a) compares the variable temperature P–M population of **11** ($M_w = 7.4 \times 10^4$, $M_n = 2.5 \times 10^4$) in three solvents with different degree of branching, including *n*-heptane (linear hydrocarbon), methylcyclohexane (cyclic hydrocarbon), and 2,2,4,4,6,8,8-heptamethylnonane (highly branched hydrocarbon). The quantized helicity below and above T_c , and the super-

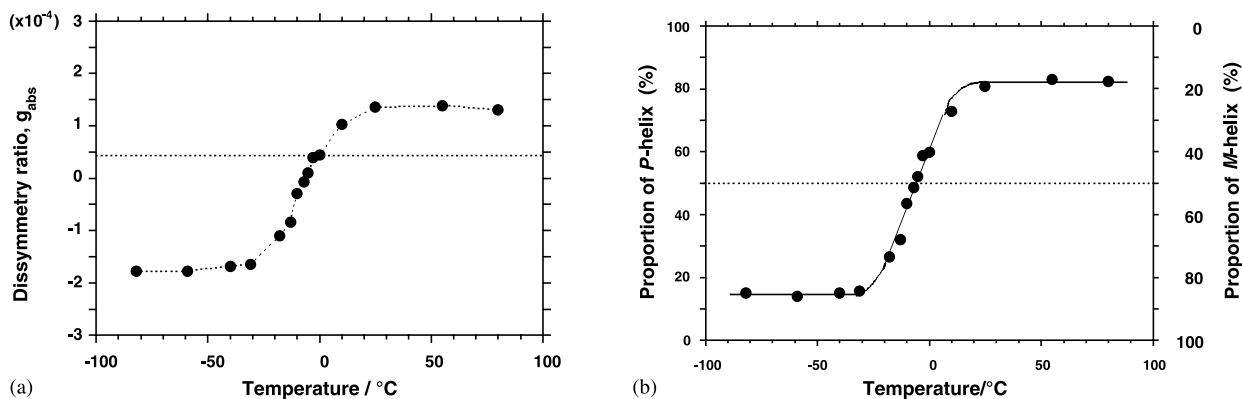


Fig. 12. (a) CD ($\Delta\epsilon$, open circles) and UV (ϵ , filled circles) band intensities of **12** around 320 nm in isooctane in the range 80 to -82 $^{\circ}\text{C}$. (b) Population of P- and M-motifs in **12** in isooctane as a function of temperature, evaluated using the g_{abs} values for **12** by reference to the regression curve of the g_{abs} values for **8**.

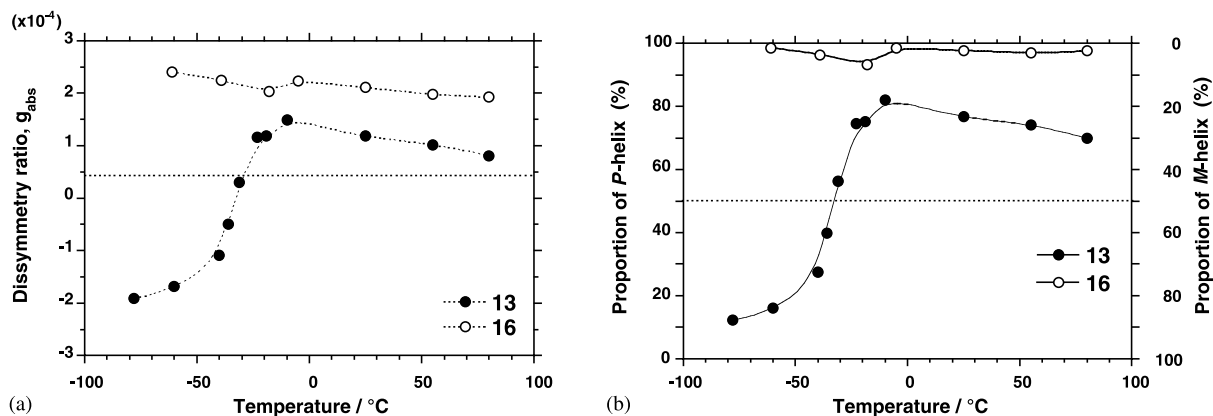


Fig. 13. (a) Kuhn's dissymmetry ratios for **13** in isooctane between -82 and 80 °C and **16** in isooctane between -61 to 80 °C. (b) Populations of P- and M-motifs in **13** and **16** in isooctane as a function of temperature, evaluated using the g_{abs} values of **13** and **16** by reference to the regression curve of the g_{abs} values for **8**.

posed helicity around T_c are conserved in these solvents. Although the value of T_c greatly varies with the degree of branching of the solvent, the P–M population below T_c is insensitive to the degree of branching, but, above T_c , however, it is sensitive to this.

Fig. 15(b) plots the effects of solvent topology on T_c for various solvents as a function of the Balaban index number which is a gauge of degree of branching [61]. Quantitatively, although T_c increases nonlinearly with increasing the index number, straight chain alkyl molecules affords a lower T_c , whereas branched chain alkyl molecules tend to give a higher T_c and branched cyclic solvents lie at intermediate values.

Molecular mechanics calculations were also made on 31-mers of *it-11* and *it-14*, with the results shown in Fig. 16(a). Both 31-mers are characterized by double-well potentials. The P minimum for *it-11* is slightly deeper than the M minimum, indicating that both M- and P-conformers may coexist. On the other hand, the P minimum for *it-14* is significantly deeper than the M minimum, suggesting that the chain conformation is predominantly P-helical. If the double-well potential of *it-11* is assumed to change with temperature as shown in Fig. 16(b), the three temperature regions noted for **11**

are qualitatively explained. However, it was recently found that the P–M population f_P for **11** depends significantly on chain length as well as temperature [32d]. A similar molecular weight dependence was also found with **3** [31q].

To explain these quantized and superposed helicities, cooperativity in coupled electronic and conformational transitions is assumed to be the origin of the step-like switching response to the thermal energy bias. In an electronically conjugating stiff helical polysilane with discrete energy levels in a double-well potential, it is possible that the wavefunction of the lowest ground-state of an M-state electronically communicates with that of a P-state through quantum mechanical tunneling between the P- and M-electronic states. The superposition of chirality and optical activity for hypothetical chiral molecules were discussed theoretically by Hund in 1927 [4e,5b,60] and by several quantum physicists [59]. It is necessary to invoke the presence of helix reversals in the case of helical polymers. The helix reversal, presumably consisting of several silicon–silicon single bonds (corresponding to a sub-nanometer barrier thickness), is the section in which the screw-sense changes direction, and might act as a small tunneling barrier

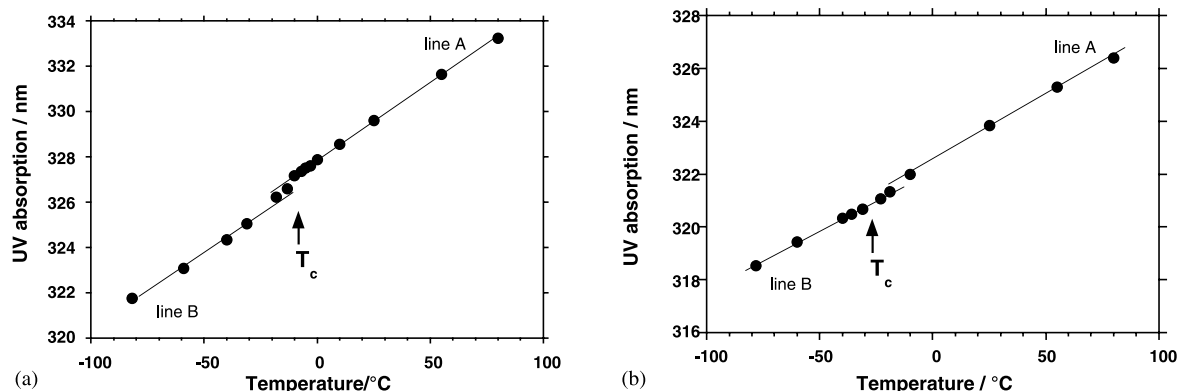


Fig. 14. Temperature-dependent λ_{max} values of **12** and **13** in isooctane.

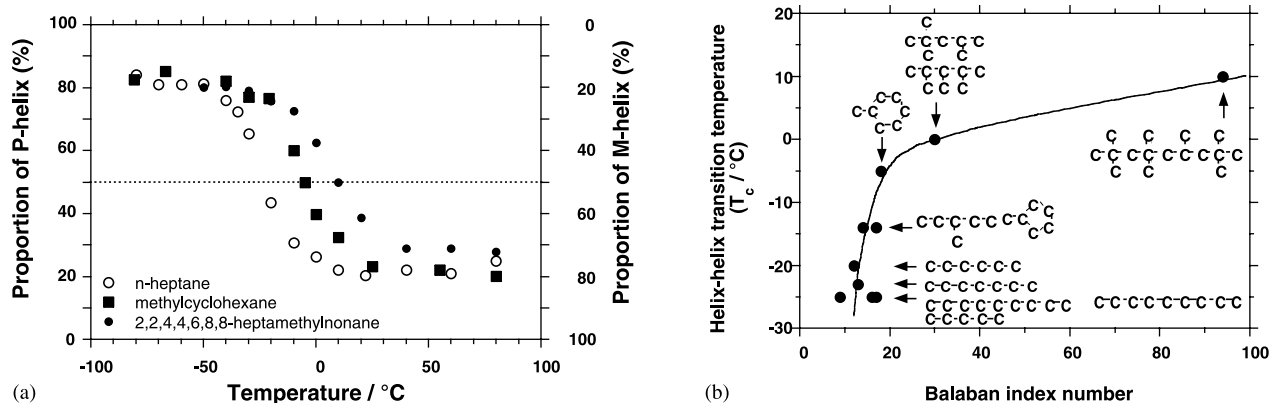


Fig. 15. (a) Variable temperature P–M proportion of **11** ($M_w = 7.4 \times 10^4$, $M_n = 2.5 \times 10^4$) in 2,2,4,4,6,8,8-heptamethylnonane (filled circles), methylcyclohexane (filled squares), and *n*-heptane (open circles) in the range -80 and $+80$ °C. (b) Change in the T_c value of **11** ($M_w = 7.4 \times 10^4$, $M_n = 2.5 \times 10^4$) as a function of degree of branching in a range of hydrocarbon solvent molecules in which the degree of branching is evaluated by the Balaban index number.

[4e,32c,60b]. The reversal may play a crucial role in correcting errors from thermal noise through dynamic twisting motions from one screw-sense to the other. The helix reversal could exist as a very short all-*anti*, or *transoid* sequence. Apparent time-averaged optical inactivity at T_c should result from a rapid interconversion between P- and M-motifs, which may be considered as oscillating helicity or dynamic pseudo-racemization. In this quasi-stationary state, the wavefunctions of the superposed P- and M-states (Ψ_s - and Ψ_{Ms} -states) may produce two splitting sub-levels, $\Psi = 1/\sqrt{2} [\Psi_{Ps} \pm i\Psi_{Ms}]$, as illustrated in Fig. 16(b). This is a result of electronic coupling between the lowest energy levels of almost degenerate P- and M-states in the same helical main chain.

7. Concluding remarks

Amongst numbers of optically active synthetic polymers, optically active polysilanes exhibit unique absorption, circular dichroism, and fluorescence spectra around 300–400 nm due to σ -conjugation. Since the first brief report concerning optically active polysilanes in 1992, the field of optically active polysilane homo- and copolymers has grown and evolved to the present. This account focuses on screw-sense switchable, optically active poly(dialkylsilane) homo- and copolymers among optically active polysilane, including (i) (chir)optical properties, (ii) quantitative population analysis of right- and left-handed helices based on Kuhn's dissymmetry ratio, (iii) inversion of screw-sense, (iv) solvent

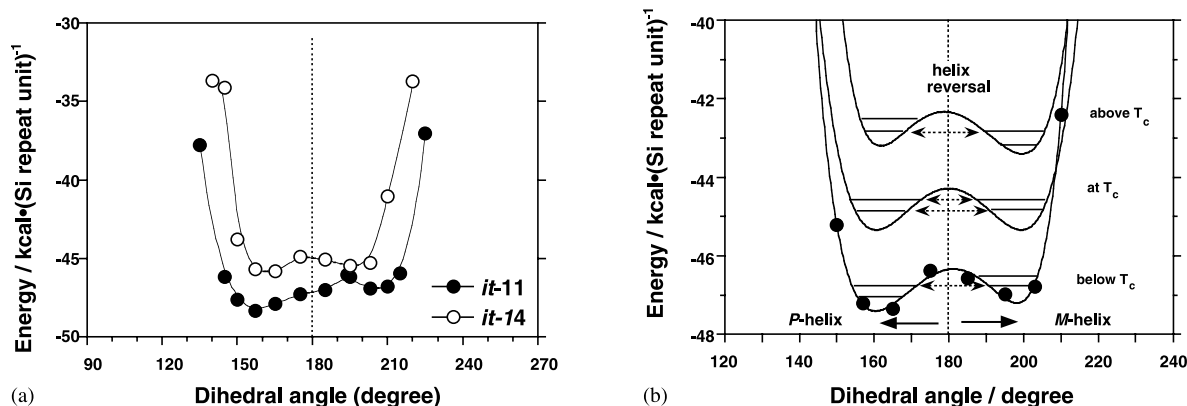


Fig. 16. (a) Dihedral angle dependence of the potential energy for *it*-11 and *it*-14 model molecules with 31 repeating units and hydrogen termini (oligo-11 or *it*-14). (b) Potential energy as a function of main chain dihedral angles of *it*-oligo-11 with three switching regions. Below T_c (bottom trace with filled circles), at T_c (middle trace, hypothetical curve), and above T_c (upper trace, hypothetical curve). Dotted arrows indicate tunneling processes between wavefunctions of P- and M-motifs existing in the same main chain. Discover 3, ver. 4.00, simple minimization was used for this calculation.

molecular shape recognition ability, and (v) chiroptical switch and dynamic memory, as consequences of side group internal interactions and other external stimuli. These advances should contribute to organosilicon chemistry and optically active polymer chemistry, and also in the applied areas of nanomaterial science and nanotechnology in the future.

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References

- [1] S.F. Mason, *Nature* 311 (1984) 19.
- [2] W.A. Bonner, P.R. Kavasmaneck, F.S. Martin, J.J. Flores, *Science* 186 (1974) 143.
- [3] M. Avalos, R. Babiano, P. Cintas, J.L. Jiménez, J.C. Palacios, L.D. Barron, *Chem. Rev.* 98 (1998) 2391.
- [4] (a) A. Yamagata, *J. Theoret. Biol.* 11 (1966) 495;
(b) R.A. Harris, L. Stodolsky, *Phys. Lett. B* 78 (1978) 313;
(c) D.K. Kondepudi, G.W. Nelson, *Nature* 314 (1985) 438;
(d) R.A. Hegstrom, *Nature* 315 (1985) 749;
- (e) M. Quack, *Chem. Phys. Lett.* 132 (1986) 1471;
- (f) L. Wiesenfeld, *Mol. Phys.* 64 (1988) 739;
- (g) A. Salam, *J. Mol. Evol.* 33 (1991) 105.
- [5] (a) M. Gardner, *The New Ambidextrous Universe—Symmetry and Asymmetry from Mirror Reflections to Superstrings*, 3rd ed., Freeman, New York, 1990;
(b) H. Latel, in: R. Janoschek (Ed.), *Chirality—From Weak Bosons to the α -Helix* (Chapter 1), Springer, Berlin, 1992 (Chapter 1).
- [6] (a) M. Farina, *Top. Stereochem.* 17 (1987) 1;
(b) K.P. Meurer, F. Vögtle, *Top. Curr. Chem.* 127 (1985) 1;

For reviews on vinyl polymers and molecular helicity, see:

- [7] T. Nakano, Y. Okamoto, *Macromol. Rapid. Commun.* 21 (2000) 603
For a recent review on poly(triphenylmethyl methacrylate), see:
- [8] R.J.M. Nolte, *Chem. Soc. Rev.* 23 (1994) 11
For a review of helical polyisocyanide, see:
- [9] M.M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R.L.B. Selinger, J.V. Selinger, *Angew. Chem. Int. Ed.* 38 (1999) 3138
For a review of optically activity induction in polyisocyanates, see:
- [10] E. Yashima, Y. Okamoto, in: N. Berova, K. Nakanishi, R.W. Woody (Eds.), *Circular Dichroism: Principles and Applications*, 2nd ed. (Chapter 18), Wiley-VCH, New York, 2000 (Chapter 18)
For a book of induced optical activity in polyacetylenes, see:
- [11] L. Pu, *Acta. Polym.* 48 (1997) 116
For a review of optically active chromophoric polymers, see:
- [12] (a) O. Kratky, G. Porod, *Recl. Trav. Chim.* 68 (1949) 1106;
(b) T. Norisuye, T. Yanaki, H. Fujita, *J. Polym. Sci. Phys. Ed.* 18 (1980) 547;
(c) H. Murakami, T. Norisuye, H. Fujita, *Macromolecules* 13 (1980) 345;
(d) T. Norisuye, *Prog. Polym. Sci.* 18 (1993) 543;
(e) H. Yamakawa, *Helical Worm-like Chains in Polymer Solutions*, Springer, Berlin, 1997;
(f) A. Teramoto, *Prog. Polym. Sci.* 26 (2001) 667;

For reviews of helical polymer characterization, see:

- [13] (a) M. Goodman, S.-C. Chen, *Macromolecules* 3 (1970) 398;
(b) M. Goodman, S.-C. Chen, *Macromolecules* 4 (1971) 625.
- [14] (a) F. Millich, G.K. Baker, *Macromolecules* 2 (1969) 122;
(b) R.J.M. Nolte, A.J.M. van Beijnen, W. Drenth, *J. Am. Chem. Soc.* 96 (1974) 5932;
(c) A.J.M. van Beijnen, R.J.M. Nolte, W. Drenth, A.M.F. Hezemans, *Tetrahedron* 32 (1976) 2017.
- [15] (a) P. Pino, G.P. Lorenzi, *J. Am. Chem. Soc.* 82 (1960) 4745;
(b) P. Pino, F. Ciardelli, G. Montagnoli, O. Pieroni, *J. Polym. Sci. Polym. Lett. Ed.* 5 (1967) 307;
(c) C. Carlini, P. Pino, F. Ciardelli, *Makromol. Chem.* 119 (1968) 244.
- [16] Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, H. Yuki, *J. Am. Chem. Soc.* 101 (1979) 4768.
- [17] (a) P.C.J. Kamer, M.C. Cleij, R.J.M. Nolte, T. Harada, A.M.F. Hezemans, W. Drenth, *J. Am. Chem. Soc.* 110 (1988) 1581;
(b) M.M. Green, R.A. Gross, F.C. Schilling, K. Zero, C.C. Crosby, III, *Macromolecules* 21 (1988) 1839;
(c) T.J. Deming, B.M. Novak, *J. Am. Chem. Soc.* 114 (1992) 7926;
(d) Y. Ito, E. Ihara, M. Murakami, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1509;
(e) M. Kauranen, T. Verbiest, C. Boutton, M.N. Teerenstra, K. Clays, A.J. Schouten, R.J.M. Nolte, A. Persoons, *Science* 270 (1995) 966;
(f) F. Takei, K. Yanai, K. Onitsuka, S. Takahashi, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1554;
(g) Y. Itoh, T. Ohara, R. Shima, M. Sugimoto, *J. Am. Chem. Soc.* 118 (1996) 9188;

- (h) E. Ramos, J. Bosch, J.-L. Serrano, T. Sierra, J. Veciana, J. Am. Chem. Soc. 118 (1996) 4703;
- (i) D.B. Amabilino, E. Ramos, J.-L. Serrano, T. Sierra, J. Veciana, J. Am. Chem. Soc. 120 (1998) 9126;
- (j) Y. Ito, T. Miyake, S. Hatano, R. Shima, T. Ohara, M. Suginome, J. Am. Chem. Soc. 120 (1998) 11880;
- (k) F. Takei, H. Hayashi, K. Onitsuka, N. Kobayashi, S. Takahashi, Angew. Chem. Int. Ed. Engl. 41 (2001) 4092;
- (l) F. Takei, H. Hayashi, K. Onitsuka, S. Takahashi, Polym. J. 33 (2001) 310;
- (m) F. Feng, T. Miyashita, F. Takei, K. Onitsuka, S. Takahashi, Chem. Lett. (2001) 764.;
- (n) J.J.L.M. Cornelissen, J.J.J.M. Donners, R. de Gelder, W.S. Graswinckel, G.A. Metselaar, A.E. Rowan, N.A.J.M. Sommerdijk, R.J.M. Nolte, Science 293 (2001) 676;
- (o) J.J.L.M. Cornelissen, W.S. Graswinckel, P.J.H.M. Adams, G.H. Nachttegaal, A.P.M. Kentgens, N.A.J.M. Sommerdijk, R.J.M. Nolte, J. Polym. Sci. A 39 (2001) 4255;
- (p) Y. Yamada, T. Kawai, J. Abe, T. Iyoda, J. Polym. Sci. A 40 (2002) 399.
- [18] (a) M.M. Green, C. Andreola, B. Muñoz, M.P. Reidy, K. Zero, J. Am. Chem. Soc. 110 (1988) 4043;
- (b) M.M. Green, M.P. Reidy, R.J. Johnson, G. Darling, D.J. O'Leary, G. Willson, J. Am. Chem. Soc. 111 (1989) 6452;
- (c) Y. Okamoto, M. Matsuda, T. Nakano, E. Yashima, Polym. J. 25 (1993) 391;
- (d) M.M. Green, C. Khatri, N.C. Peterson, J. Am. Chem. Soc. 115 (1993) 4941;
- (e) M. Müller, R. Zentel, Macromolecules 27 (1994) 4404;
- (f) G. Maxein, R. Zentel, Macromolecules 28 (1995) 8438;
- (g) K. Maeda, M. Matsuda, T. Nakano, Y. Okamoto, Polym. J. 27 (1995) 141;
- (h) M.M. Green, B.A. Garetz, B. Munoz, H.-P. Chang, J. Am. Chem. Soc. 117 (1995) 4181;
- (i) M. Müller, R. Zentel, Macromolecules 29 (1996) 1609;
- (j) J.M. Guenet, H.S.J. Jeon, C. Khatri, S.K. Jha, N.P. Balsara, M.M. Green, A. Brulet, A. Thierry, Macromolecules 30 (1997) 4590;
- (k) C.A. Khatri, Y. Pavlova, M.M. Green, H. Morawetz, J. Am. Chem. Soc. 119 (1997) 6991;
- (l) S. Mayer, G. Maxein, R. Zentel, Macromolecules 31 (1998) 8522;
- (m) K. Maeda, Y. Okamoto, Macromolecules 31 (1998) 5164;
- (n) K. Maeda, Y. Okamoto, Macromolecules 31 (1998) 1046;
- (o) K. Maeda, Y. Okamoto, Macromolecules 32 (1999) 974;
- (p) S.K. Jha, K.-S. Cheon, M.M. Green, J.V. Selinger, J. Am. Chem. Soc. 121 (1999) 1665;
- (q) K. Ute, Y. Fukunishi, S.K. Jha, K.-S. Cheon, B. Munoz, K. Hatada, M.M. Green, Macromolecules 32 (1999) 1304;
- (r) H. Gu, Y. Nakamura, T. Sato, A. Teramoto, M.M. Green, C. Andreola, Polymer 40 (1999) 849;
- (s) K.S. Cheon, J.V. Selinger, M.M. Green, Angew. Chem. Int. Ed. 39 (2000) 1482;
- (t) J. Li, G.B. Schuster, K.-S. Cheon, M.M. Green, J.V. Selinger, J. Am. Chem. Soc. 122 (2000) 2603.
- [19] (a) O. Pieroni, F. Matera, F. Ciardelli, Tetrahedron Lett. 7 (1972) 597;
- (b) F. Ciardelli, S. Lanzillo, O. Pieroni, Macromolecules 7 (1974) 174;
- (c) J.S. Moore, C.B. Gorman, R.H. Grubbs, J. Am. Chem. Soc. 113 (1991) 1704;
- (d) E. Yashima, T. Matsushima, Y. Okamoto, J. Am. Chem. Soc. 117 (1995) 11596;
- (e) E. Yashima, T. Nimura, T. Matsushima, Y. Okamoto, J. Am. Chem. Soc. 118 (1996) 9800;
- (f) E. Yashima, T. Matsushima, Y. Okamoto, J. Am. Chem. Soc. 119 (1997) 6345;
- (g) E. Yashima, K. Maeda, Y. Okamoto, J. Am. Chem. Soc. 120 (1998) 8895;
- (h) E. Yashima, K. Maeda, Y. Okamoto, Nature 399 (1999) 449;
- (i) H. Nakako, R. Nomura, M. Tabata, T. Masuda, Macromolecules 32 (1999) 2861;
- (j) T. Aoki, Y. Kobayashi, T. Kaneko, E. Oikawa, Y. Yamamura, Y. Fujita, M. Teraguchi, R. Nomura, T. Masuda, Macromolecules 32 (1999) 79;
- (k) R. Nomura, Y. Fukushima, H. Nakako, T. Masuda, J. Am. Chem. Soc. 122 (2000) 8830;
- (l) H. Nakako, Y. Mayahara, R. Nomura, M. Tabata, T. Masuda, Macromolecules 33 (2000) 3978;
- (m) H. Nakako, R. Nomura, T. Masuda, Macromolecules 34 (2001) 1496;
- (n) R. Nomura, J. Tabei, T. Masuda, J. Am. Chem. Soc. 123 (2001) 8430;
- (o) H. Onouchi, K. Maeda, E. Yashima, J. Am. Chem. Soc. 123 (2001) 7441;
- (p) E. Yashima, K. Maeda, O. Sato, J. Am. Chem. Soc. 123 (2001) 8159;
- (q) A.P.H.J. Schenning, M. Fransen, E.W. Meijer, Macromol. Rapid. Commun. 23 (2002) 265.
- [20] (a) M. Lemaire, D. Delabouglise, R. Garreau, A. Guy, J. Roncali, J. Chem. Soc. Chem. Commun. (1988) 658.;
- (b) M. Andersson, P.O. Ekeblad, T. Hjertberg, O. Wennerström, O. Inganäs, Polym. Commun. 32 (1991) 546;
- (c) M.M. Bouman, E.W. Meijer, Adv. Mater. 7 (1995) 385;
- (d) G. Bidan, S. Guillerez, V. Sorokin, Adv. Mater. 8 (1996) 157;
- (e) F. Andreani, L. Angiolini, D. Caretta, E. Salatelli, J. Mater. Chem. 8 (1998) 1109;
- (f) E.R. Lermo, B.M.W. Langeveld-Voss, R.A.J. Janssen, E.W. Meijer, Chem. Commun. (1999) 791.;
- (g) E. Yashima, H. Goto, Y. Okamoto, Macromolecules 32 (1999) 7942;
- (h) Z.-B. Zhang, M. Fujiki, M. Motonaga, H. Nakashima, K. Torimitsu, H.-Z. Tang, Macromolecules 35 (2002) 941.
- [21] E. Peeters, M.P.T. Christiaans, R.A.J. Janssen, H.F.M. Schoo, H.P.J.M. Dekkers, E.W. Meijer, J. Am. Chem. Soc. 119 (1997) 9909.
- [22] (a) A. Goodwin, B.M. Novak, Macromolecules 27 (1994) 5520;
- (b) M.-P. Nieh, A.A. Goodwin, J.R. Stewart, B.M. Novak, D.A. Hoagland, Macromolecules 31 (1998) 3151;
- (c) D.S. Schiltzer, B.M. Novak, J. Am. Chem. Soc. 120 (1998) 2196.
- [23] (a) J.-H. Fuhrhop, P. Blumtritt, C. Lehmann, P. Luger, J. Am. Chem. Soc. 113 (1991) 7437;
- (b) D.A. Frankel, D.F. O'Brien, J. Am. Chem. Soc. 116 (1994) 10057;
- (c) J.M. Schnur, B.R. Ratna, J.V. Selinger, A. Singh, G. Jyothi, K.R.K. Easwaran, Science 264 (1994) 945;
- (d) A.F. Drake, P. Udvarhelyi, D.J. Ando, D. Bloor, J.S. Obhi, S. Mann, Polymer 30 (1989) 1043.
- [24] (a) M. Salmon, G. Bidan, J. Electrochem. Soc. 132 (1985) 1897;
- (b) D. Delabouglise, F. Garnier, Synth. Met. 39 (1990) 117.
- [25] (a) M.R. Majidi, L.A.P. Kane-Maguire, G.G. Wallace, Polymer 35 (1994) 3113;
- (b) P.C. Innis, I.D. Norris, L.A.P. Kane-Maguire, G.G. Wallace, Macromolecules 31 (1995) 6521;
- (c) S.-J. Su, N. Kuramoto, Chem. Lett. (2001) 504.;
- (d) S.-J. Su, N. Kuramoto, Macromolecules 34 (2001) 7249.
- [26] R. Fiesel, U. Scherf, Acta Polym. 49 (1998) 445.
- [27] (a) M. Oda, H.-G. Nothofer, G. Lieser, U. Scherf, S.C. Meskers, D. Neher, Adv. Mater. 12 (2000) 362;
- (b) M. Oda, S.C.J. Meskers, H.G. Nothofer, U. Scherf, D. Neher, Synth. Met. 111–112 (2000) 575;
- (c) M. Leclerc, J. Polym. Sci. A 39 (2001) 2867;
- (d) D. Neher, Macromol. Rapid. Commun. 22 (2001) 1365;

- (e) H.-Z. Tang, M. Fujiki, T. Sato, *Macromolecules* 35 (2002) 6439;
- (f) H.-Z. Tang, M. Fujiki, M. Motonaga, *Polymer* 43 (2002) 6213.
- [28] (a) J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* 84 (1987) 2565;
- (b) U. Koert, M.M. Harding, J.-M. Lehn, *Nature* 346 (1990) 339;
- (c) E.C. Constable, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1450;
- (d) Y. Dai, T.J. Katz, D.A. Nichols, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2109;
- (e) T. Takata, Y. Furusho, K.-i. Murakawa, T. Endo, H. Matsuoka, T. Hirasa, J. Matsuo, M. Sisido, *J. Am. Chem. Soc.* 120 (1998) 4530;
- (f) A. Williams, *Chem. Eur. J.* 3 (1997) 15;
- (g) T. Yokozawa, R.B. Prince, J.S. Moore, *J. Am. Chem. Soc.* 121 (1999) 2643;
- (h) R. Fiesel, C.E. Halkyard, M.E. Rampey, L. Kloppenburg, S.L. Studer-Martinez, U. Scherf, U.H.F. Bunz, *Macromol. Rapid. Commun.* 20 (1999) 107;
- (i) E. Yashima, K. Maeda, T. Yamanaka, *J. Am. Chem. Soc.* 122 (2000) 7813;
- (j) R.B. Prince, L. Brunsveld, E.W. Meijer, J.S. Moore, *Angew. Chem. Int. Ed.* 39 (2000) 228.
- [29] (a) P. Urnes, P. Doty, *Adv. Protein Chem.* 16 (1961) 401;
- (b) G.D. Fasman (Ed.), *Poly- α -Amino Acids*, Dekker, New York, 1967.;
- (c) A. Teramoto, H. Fujita, *Adv. Polym. Sci.* 18 (1975) 65;
- (d) A. Teramoto, H. Fujita, *J. Macromol. Sci.-Rev. Macromol. Chem.* C15 (1976) 165;
- (e) A. Chakrabartty, R.L. Baldwin, *Adv. Protein Chem.* 46 (1995) 141;
- (f) T. Nakano, Y. Okamoto, *Chem. Rev.* 101 (2001) 4013;
- (g) E. Lacroix, A.R. Viguera, L. Serrano, *J. Mol. Biol.* 284 (1998) 173;
- (h) J.J.L.M. Cornelissen, A.E. Rowan, R.J.M. Nolte, N.A.J.M. Sommerdijk, *Chem. Rev.* 101 (2001) 4039;
- For reviews on chiral polymers including polypeptides, see:
- [30] M. Kumada, S. Yamaguchi, *J. Chem. Soc. Jpn. Ind. Chem. Sect.* 57 (1954) 175 (In Japanese).
- [31] (a) K. Matyjaszewski, *J. Inorg. Organomet. Polym.* 2 (1992) 5;
- (b) H. Frey, M. Möller, K. Matyjaszewski, *Macromolecules* 27 (1994) 1814;
- (c) H. Frey, M. Möller, A. Turetskii, B. Lots, K. Matyjaszewski, *Macromolecules* 28 (1995) 5498;
- (d) M. Fujiki, *J. Am. Chem. Soc.* 116 (1994) 6017;
- (e) M. Fujiki, *J. Am. Chem. Soc.* 116 (1994) 11976;
- (f) M. Fujiki, *Appl. Phys. Lett.* 65 (1994) 3251;
- (g) M. Fujiki, *Polym. Prepr. (Am. Chem. Soc. Polym. Sci. Div.)* 37 (1996) 454;
- (h) K. Obata, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* 119 (1997) 11345;
- (i) K. Shinohara, T. Aoki, T. Kaneko, E. Oikawa, *Chem. Lett.* (1997) 361.;
- (j) K. Obata, M. Kira, *Macromolecules* 31 (1998) 4666;
- (k) M. Fujiki, S. Toyoda, C.-H. Yuan, H. Takigawa, *Chirality* 10 (1998) 667;
- (l) T. Ichikawa, Y. Yamada, J. Kumagai, M. Fujiki, *Chem. Phys. Lett.* 306 (1999) 275;
- (m) K. Terao, T. Terao, A. Teramoto, N. Nakamura, I. Terakawa, T. Sato, M. Fujiki, *Macromolecules* 34 (2001) 2682;
- (n) J. Watanabe, H. Kamee, M. Fujiki, *Polym. J.* 33 (2001) 495;
- (o) K. Terao, Y. Terao, A. Teramoto, N. Nakamura, M. Fujiki, T. Sato, *Macromolecules* 34 (2001) 4519;
- (p) K. Terao, Y.-I. Terao, A. Teramoto, N. Nakamura, M. Fujiki, T. Sato, *Macromolecules* 34 (2001) 6519;
- (q) T. Natsume, L. Wu, T. Sato, K. Terao, A. Teramoto, M. Fujiki, *Macromolecules* 34 (2001) 7899;
- (r) T. Sanji, T. Takase, H. Sakurai, *J. Am. Chem. Soc.* 123 (2001) 12690;
- (s) T. Sato, K. Terao, A. Teramoto, M. Fujiki, *Macromolecules* 35 (2002) 2141;
- (t) K. Okoshi, H. Kamee, G. Suzaki, M. Tokita, M. Fujiki, J. Watanabe, *Macromolecules* 35 (2002) 4556;
- For optically active poly(dialkylsilane)s, see:
- [32] (a) M. Fujiki, *J. Am. Chem. Soc.* 122 (2000) 3336;
- (b) M. Fujiki, *Macromol. Rapid. Commun.* 22 (2001) 669;
- (c) M. Fujiki, J.R. Koe, H. Nakashima, M. Motonaga, K. Terao, A. Teramoto, *J. Am. Chem. Soc.* 123 (2001) 6253;
- (d) A. Teramoto, K. Terao, Y. Terao, N. Nakamura, T. Sato, M. Fujiki, *J. Am. Chem. Soc.* 123 (2001) 12303;
- (e) M. Fujiki, M. Motonaga, H.-Z. Tang, K. Torimitsu, Z.-B. Zhang, J.R. Koe, J. Watanabe, K. Terao, T. Sato, A. Teramoto, *Chem. Lett.* (2001) 1218.;
- (f) M. Fujiki, H.-Z. Tang, M. Motonaga, K. Torimitsu, J.R. Koe, J. Watanabe, T. Sato, A. Teramoto, *Silicon Chem.* 1 (2002) 67;
- For helix–helix transition poly(dialkylsilane)s, see:
- [33] (a) D. Terunuma, K. Nagumo, N. Kamata, K. Matsuoka, H. Kuzuhara, *Chem. Lett.* (1998) 681.;
- (b) S. Toyoda, M. Fujiki, *Chem. Lett.* (1999) 699.;
- (c) H. Nakashima, M. Fujiki, J.R. Koe, *Macromolecules* 32 (1999) 7707;
- (d) D. Terunuma, K. Nagumo, N. Kamata, K. Matsuoka, H. Kuzuhara, *Polym. J.* 32 (2000) 113;
- (e) H. Nakashima, M. Fujiki, J.R. Koe, M. Motonaga, *J. Am. Chem. Soc.* 123 (2001) 1963;
- (f) S. Toyoda, M. Fujiki, *Macromolecules* 34 (2001) 640;
- (g) H. Nakashima, J.R. Koe, K. Torimitsu, M. Fujiki, *J. Am. Chem. Soc.* 123 (2001) 4877;
- (h) P. Dellaportas, R.G. Jones, S.J. Holder, *Macromol. Rapid. Commun.* 23 (2002) 99;
- For optically active poly(alkylarylsilane)s, see:
- [34] (a) J.R. Koe, M. Fujiki, H. Nakashima, *J. Am. Chem. Soc.* 121 (1999) 9734;
- (b) J.R. Koe, M. Fujiki, M. Motonaga, H. Nakashima, *Chem. Commun.* (2000) 389.;
- (c) J.R. Koe, M. Fujiki, M. Motonaga, H. Nakashima, *Macromolecules* 34 (2001) 1082;
- For optically active poly(diarylsilane)s, see:
- [35] J.R. Koe, M. Motonaga, M. Fujiki, R. West, *Macromolecules* 34 (2001) 706
- For optically active poly(dialkoxysilane)s, see:
- [36] (a) M. Fujiki, *Macromol. Rapid. Commun.* 22 (2001) 539For a review and books of optically active polysilanes, see.;
- (b) M. Fujiki, J.R. Koe, *Silicon-containing Polymers: The Science and Technology of Their Synthesis and Applications* (Chapter 24), Kluwer Academic Publishers, Dordrecht, 2000 (Chapter 24);
- (c) J.R. Koe, M. Fujiki, H. Nakashima, M. Motonaga, in: I. Khan (Ed.), *Synthetic Macromolecules with Higher Structural Order*, ACS Advance in Chemistry Series No. 812, 2002, Oxford.
- [37] (a) K. Takeda, *J. Phys. Soc. Jpn. Suppl. B* 1 (1994) 1;
- (b) K. Takeda, K. Shiraishi, *Comments Cond. Mat. Phys.* 18 (1997) 91;
- (c) N. Matsumoto, *Jpn. J. Appl. Phys.* 37 (1998) 5425;
- For reviews of electronic structure of Si-based material, see:
- [38] (a) S. Abe, *J. Phys. Soc. Jpn.* 58 (1989) 62;
- (b) H. Tachibana, Y. Kawabata, S. Koshihara, T. Arima, Y. Moritomo, Y. Tokura, *Phys. Rev. B* 44 (1991) 5487;
- (c) S. Abe, M. Schreiber, W.P. Su, J. Yu, *Phys. Rev. B* 45 (1992) 9432;

- (d) R. Nötzel, K.H. Ploog, *Int. J. Mod. Phys. B* 7 (1993) 2743;
 (e) S. Glutsch, F. Bechstedt, *Phys. Rev. B* 47 (1993) 4315;
 (f) M. Schreiber, S. Abe, *Synth. Met.* 55–57 (1993) 50;
 (g) X.-F. He, *Phys. Rev. B* 43 (1991) 2063.
- [39] (a) K. Sakamoto, K. Obata, H. Hirata, M. Nakajima, H. Sakurai, *J. Am. Chem. Soc.* 111 (1989) 7461;
 (b) K. Sakamoto, M. Yoshida, H. Sakurai, *Macromolecules* 23 (1990) 4494;
 (c) H. Sakurai, M. Yoshida, *Silicon-containing Polymers: The Science and Technology of Their Synthesis and Applications* (Chapter 13), Kluwer Academic Publishers, Dordrecht, 2000 (Chapter 13).
- [40] (a) R. West, *J. Organomet. Chem.* 300 (1986) 327;
 (b) R.D. Miller, J. Michl, *Chem. Rev.* 89 (1989) 1359;
 (c) J.M. Ziegler, F.W.G. Fearson (Eds.), *Silicon-based Polymer Science, Advances in Chemistry Series, Vol. 224*, American Chemical Society, Washington, DC, 1990;
 (d) R. West, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, A.G. Davies, Chapter Ed, Pergamon Press, Oxford, 1995, pp. 77–110;
 (e) R.G. Jones, S.J. Holder, *Silicon-containing Polymers: The Science and Technology of Their Synthesis and Applications* (Chapter 12), Kluwer Academic Publishers, Dordrecht, 2000 (Chapter 12);
 (f) J. Michl, R. West, *Silicon-containing Polymers: The Science and Technology of Their Synthesis and Applications* (Chapter 18), Kluwer Academic Publishers, Dordrecht, 2000 (Chapter 18);
- For reviews and books of polysilanes, see:
- [41] (a) S. Yamaguchi, K. Tamao, *Silicon-containing Polymers: The Science and Technology of Their Synthesis and Applications* (Chapter 17), Kluwer Academic Publishers, Dordrecht, 2000 (Chapter 17);
 (b) H. Suzuki, S. Hoshino, K. Furukawa, K. Ebata, C.-H. Yuan, I. Bleyl, *Polym. Adv. Technol.* 11 (2000) 460.
- [42] (a) F.S. Kipping, *J. Chem. Soc.* 119 (1921) 830;
 (b) F.S. Kipping, *J. Chem. Soc.* 125 (1924) 2291.
- [43] M. Fujino, H. Isaka, *J. Chem. Soc. Chem. Commun.* (1989) 466.
- [44] (a) M. Sisido, S. Egusa, A. Okamoto, Y. Imanishi, *J. Am. Chem. Soc.* 105 (1983) 3351;
 (b) J.P. Riehl, F.S. Richardson, *Chem. Rev.* 86 (1986) 1;
 (c) S.H. Chen, D. Katsis, A.W. Schmid, J.C. Mastrangelo, T. Tsutsui, T.N. Blanton, *Nature* 397 (1999) 506;
 (d) H.P.J.M. Dekkers, in: N. Berova, K. Nakanishi, R.W. Woody (Eds.), *Circular Dichroism: Principles and Applications*, 2nd ed. (Chapter 7), Wiley-VCH, New York, 2000 (Chapter 7).
- [45] (a) N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Chemistry*, University Science Books, Oxford, 1983;
 (b) N. Berova, K. Nakanishi, in: N. Berova, K. Nakanishi, R.W. Woody (Eds.), *Circular Dichroism: Principles and Applications*, 2nd ed. (Chapter 12), Wiley-VCH, New York, 2000 (Chapter 12).
- [46] (a) R. Zink, T.F. Magnera, J. Michl, *J. Phys. Chem. A* 104 (2000) 3829;
 (b) C.-H. Otsson, J. Michl, *J. Phys. Chem. A* 104 (2000) 3367;
 (c) J. Michl, R. West, *Acc. Chem. Res.* 33 (2000) 821.
- [47] M. Fujiki, *J. Am. Chem. Soc.* 118 (1996) 7424.
- [48] P.A. Lovell, in: C. Booth, C. Price (Eds.), *Comprehensive Polymer Science*, vol. 1 (Chapter 9), Pergamon Press, Oxford, 1989 (Chapter 9).
- [49] (a) H.G. Hansma, J. Vesenka, C. Siegerist, G. Kelderman, H. Morrett, R.L. Sinsheimer, V. Elings, C. Bustamante, P.K. Hansma, *Science* 256 (1992) 1180;
 (b) B. Samori, C. Nigro, A. Gordano, I. Muzzalupo, C. Quagliariello, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 529;
 (c) J. Kumaki, Y. Nishikawa, T. Hashimoto, *J. Am. Chem. Soc.* 118 (1996) 33213;
 (d) U.B. Steiner, M. Rehahn, W.R. Caseri, U.W. Suter, *Macromolecules* 27 (1994) 1983;
 (e) K. Shinohara, S. Yasuda, G. Kato, M. Fujita, H. Shigekawa, *J. Am. Chem. Soc.* 123 (2001) 3619.
- [50] (a) K. Ebihara, S. Koshihara, M. Yoshimoto, T. Maeda, T. Ohnishi, H. Koinuma, M. Fujiki, *Jpn. J. Appl. Phys.* 36 (1997) L1211;
 (b) K. Ebata, K. Furukawa, N. Matsumoto, *J. Am. Chem. Soc.* 120 (1998) 7367;
 (c) K. Furukawa, K. Ebata, M. Fujiki, *Adv. Mater.* 12 (2000) 1033.
- [51] (a) F.M. Pohl, T.M. Jovin, *J. Mol. Biol.* 67 (1972) 375;
 (b) F.M. Pohl, *Nature* 260 (1976) 365.
- [52] E.M. Bradbury, B.G. Carpenter, H. Goldman, *Biopolymers* 6 (1968) 837.
- [53] (a) H. Toriumi, N. Saso, Y. Yasumoto, S. Sasaki, I. Uematsu, *Polym. J.* 11 (1979) 977;
 (b) J. Watanabe, S. Okamoto, A. Abe, *Liq. Cryst.* 15 (1993) 259;
 (c) J. Watanabe, S. Okamoto, K. Satoh, K. Sakajiri, H. Furuya, A. Abe, *Macromolecules* 29 (1996) 7084;
 (d) A. Abe, H. Furuya, S. Okamoto, *Biopolymers* 43 (1997) 405;
 (e) K. Sakajiri, K. Satoh, S. Kawauchi, J. Watanabe, *J. Mol. Struct.* 476 (1999) 1.
- [54] Y. Okamoto, T. Nakano, E. Ono, K. Hatada, *Chem. Lett.* (1991) 525.
- [55] S. Mahadevan, M. Palaniandavar, *Chem. Commun.* (1996) 2547.
- [56] (a) E.K. Wilson, *Chem. Eng. News* (Nov. 6) 35 (2000).;
 (b) R. Feynman, *Science* 254 (1991) 1300;
 (c) K.E. Drexler, *Nanosystems: Molecular Machinery, Manufacturing and Computing*, Wiley, New York, 1992.
- [57] (a) B.L. Feringa, W.F. Jager, B. de Lange, E.W. Meijer, *J. Am. Chem. Soc.* 113 (1991) 5468;
 (b) H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, N. Nakashima, *J. Am. Chem. Soc.* 119 (1997) 7605;
 (c) T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.* 119 (1997) 6066;
 (d) S. Zahn, J.W. Canary, *Angew. Chem. Int. Ed.* 37 (1998) 305;
 (e) K.S. Burnham, G.B. Schuster, *J. Am. Chem. Soc.* 121 (1999) 10245;
 (f) C. Mao, W. Sun, Z. Shen, N.D. Seeman, *Nature* 397 (1999) 144;
 (g) N. Koumura, R.W. Zijlstra, R.A. van Delden, N. Harada, B.L. Feringa, *Nature* 401 (1999) 152;
 (h) T.R. Kelly, H. De Silva, R.A. Silva, *Nature* 397 (1999) 150;
 (i) R. Schmieder, G. Hübner, C. Seel, F. Vögtle, *Angew. Chem. Int. Ed.* 38 (1999) 3528;
 (j) H. Engelkamp, R. Middelbeek, R.J.M. Nolte, *Science* 284 (1999) 785;
- For examples:
- [58] (a) S. Lloyd, *Sci. Am.* 273 (1995) 140;
 (b) N. Gershenfeld, I.L. Chuang, *Sci. Am.* 278 (1998) 66;
 (c) T.H. Oosterkamp, T. Fujisawa, W.G. van der Wiel, K. Ishibashi, R.V. Hijman, S. Tarucha, L.P. Kouwenhoven, *Nature* 395 (1999) 873;
 (d) Y. Nakamura, Y.-A. Pashkin, J.S. Tsai, *Nature* 398 (1999) 786.
- [59] (a) J.A. Cina, R.A. Harris, *J. Chem. Phys.* 100 (1994) 2531;
 (b) R.A. Harris, *Chem. Phys. Lett.* 223 (1994) 250;
 (c) J.A. Cina, R.A. Harris, *Science* 267 (1995) 832.
- [60] (a) F. Hund, *Z. Physik.* 43 (1927) 805;
 (b) R. Janoschek, in: R. Janoschek (Ed.), *Chirality—From Weak Bosons to the α -Helix* (Chapter 2), Springer, Berlin, 1992 (Chapter 2).
- [61] D.H. Rouvray, *Sci. Am.* 255 (1986) 36.