

The first optically active polygermanes: preferential screw sense helicity of enantiopure chiral-substituted aryl polygermanes and comparison with analogous polysilanes

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Abstract

Circular dichroism and ultraviolet spectroscopic studies of *meta* and *para* poly[methyl{(S)-2-methylbutylphenyl}germane]s, the first enantiopure chiral substituted polygermanes, indicate that the polymer main chains are induced to adopt preferential screw sense helical conformations and the values of the Kuhn dissymmetry ratio ($g_{\text{abs}} = \Delta\epsilon/\epsilon$) at -70°C were evaluated as -0.34×10^{-4} and -0.38×10^{-4} , respectively for the polymers above. The analogous polysilanes have g_{abs} , values of -0.76×10^{-4} and -0.81×10^{-4} , which indicate a greater preferential screw sense selectivity. It is suggested that the origin of the lower screw sense selectivity in the polygermanes lies in the longer E–E bond in the backbone, leading to reduced steric interaction between the preferential screw sense-inducing enantiopure chiral side chain moieties.

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1. Introduction

The heavier Group 14 catenates, polygermanes and polystannanes, are analogous in many respects to their silicon analogues, the polysilanes, in particular with regard to the fact that they all possess σ -delocalised backbone structures [1], but are rather less well known, primarily due to the lower stability of the polymers, the greater cost of the precursor materials (especially in the case of germanium), and the more considerable synthetic challenges, although a number of polygermanes and some different synthetic approaches to them have been described [2], and some polystannanes have been synthesised [3]. In contrast to the polysilanes, however,

there are no experimental or theoretical literature reports describing the induced preferential screw sense helical conformational properties of the heavier catenates. The chemistry of, and synthetic routes to, polysilanes, σ -delocalised helical chains of silicon atoms, are well known [4], and their conformational characteristics have been the subject of intensive research [5]. The polymers typically exhibit an intense σ – σ^* backbone electronic transition with a UV–vis absorption between 320 and 400 nm, depending on side chain substituents. Whilst reasonably stable towards photolytic degradation in the solid state, the polymers tend to degrade in solution upon irradiation with ultraviolet light (the heavier Group 14 catenates degrade much more rapidly [6]). Despite the fact that the polymer main chains are observed [7] and calculated [8] to be helical and that a helix is a chiral motif, the polymers are not normally

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optically active. This is because both plus (*P*) and minus (*M*) counter-rotatory screw sense helical turns are of equal energy and thus coexist in equal proportions, resulting in an optically inactive *meso* form or internal racemate. If however, the energies of *P* and *M* screw senses are rendered unequal, then the lower energy screw sense is preferentially populated, which results in the adoption by the main chain of a preferential helical screw sense, and, as *P* and *M* counter-rotatory influences no longer cancel, optical activity [9]. For the electronically delocalised backbone polysilanes, such optical activity due to preferential screw sense (PSS) induction is evidenced by a Cotton effect in the circular dichroism (CD) spectrum coincident with the σ – σ^* backbone absorption in the ultraviolet (UV) spectrum. The helical conformational properties (screw sense and pitch) of these polysilanes may be controlled by a variety of different techniques, including incorporation of enantiopure chiral groups in homo- or copolymer side chains [9] or chain termini [10], by block copolymerisation with inherently single screw sense polymers [11] or by doping with enantiopure chiral additives [12]. In each case, PSS induction depends on strong steric interaction between neighbouring repeat units in the main chain to lock the conformation in a particular screw sense. It is the strength of this interaction which determines the relative proportions of *P* and *M* turns. For weak steric interaction, little or no conformational locking occurs and little or no optical activity is observed. For strong steric interactions, the conformational locking may be sufficient to induce an essentially single screw sense backbone helix [9,13]. If such chiral steric interactions are strong enough, a PSS may even be induced cooperatively in non-enantiopure chiral substituted (i.e. achiral) repeat units in chiral/achiral copolymers [9c,13] as has been observed in a number of different polymer systems. We have shown for the enantiopure chiral side chain polysilanes that the distance of the chiral centre from the main chain is critical in determining whether a PSS can be induced [9]. If the chiral branching point is too far from the main chain, then side chain rotational freedom is often sufficient to reduce the steric interaction to an ineffective minimum.

Since in the heavier Group 14 catenates, the interatomic distances between backbone atoms increase down the group, it is reasonable to consider that the increased bond lengths in the catenating main chain should result in greater separation between neighbouring repeat units and hence reduced chiral steric interactions, and concomitantly reduced optical activity. It is to this area which the present paper is addressed. We report the syntheses and conformational analysis using UV–vis and CD spectroscopies of the first enantiopure chiral-substituted polygermanes and structurally analogous polysilanes and the results of forcefield calculations on 10-mer model compounds.

2. Experimental

2.1. General

All manipulations were carried out in dried glassware under a nitrogen atmosphere in a dry box or using standard Schlenk and high vacuum line techniques. Solvents were dried over sodium benzophenone ketal and then refluxed and distilled under nitrogen prior to use. Molecular weights were determined by size exclusion chromatography (SEC) on a Shodex column (eluant THF) in a Shimadzu liquid chromatograph machine equipped with a diode array detector and calibrated with polystyrene standards or were calculated by light scattering. Polymer chain scission was effected by controlled photodegradation by ultraviolet irradiation of a 2×10^{-4} mol dm⁻³ solution sample stirred at 20 °C using a 6 W UV source (Hunakoshi UVGL-58) at 365 nm for ca. 90 s. UV–vis spectra (room temperature (r.t.); 21 °C) were recorded on a JASCO V-570 spectrometer at 1×10^{-4} mol dm⁻³ concentration. Variable temperature CD and simultaneous UV–vis spectra were recorded using a JASCO J-720 spectropolarimeter and Peltier control for temperatures from 80 to –10 °C (1 cm path length cell; sample concentration 1×10^{-4} mol dm⁻³), and with a liquid nitrogen-cooled cryostat for temperatures down to –70 °C (0.5 cm path length cell; sample concentration 2×10^{-4} mol dm⁻³). Fluorescence spectra were recorded on a Hitachi F-850 spectrofluorimeter at r.t. NMR spectra of the silanes were recorded on a Varian Unity 300 spectrometer for silicon at 59.591 MHz, for carbon at 75.431 MHz and for proton at 299.954 MHz and also on a Varian Unity 500 spectrometer at 99.303, 125.695 and 499.836 MHz, respectively. ¹H-NMR spectra of the germanes were obtained on a Bruker AC-200 spectrometer at r.t. using benzene-*d*₆ (dried over Na/K alloy) as a solvent. Chemical shifts were referenced to internal or external Me₄Si.

2.2. Germanes

2.2.1. Materials and procedures

p-Bromo-*N,N*-dimethylaniline was purified by sublimation before use. Dimethylchlorogermane was prepared by the r.t. reaction of dimethylgermane and mercuric chloride 14a. Tetrakis(trimethylphosphine)dimethylruthenium was synthesized as described previously 14b. *p*-Bromodiphenylamine was prepared by bromination of triphenylamine with NBS 14c.

2.2.2. Monomer synthesis

The *meta* and *para* (*S*)-2-methylbutylphenyldimethylgermanes (**1** and **2**, respectively) were synthesised by reaction of the appropriate aryl lithium compound

with chlorodimethylgermane. The synthesis of the *meta* derivative, **1**, is representative.

2.2.3. *m*-(*S*)-2-Methylbutylphenyldimethylgermane (**1**)

m-(*S*)-2-Methylbutylphenyl bromide (1.010 g, 4.45 mmol) was dissolved in 20 ml THF and 6 ml *n*-pentane in a 2-neck flask equipped with nitrogen inlet and pressure-equalised addition funnel. After cooling the solution to $-100\text{ }^{\circ}\text{C}$ (diethyl ether/liquid N_2 bath), 2.8 ml *n*-BuLi (1.6 M in hexanes, 4.48 mmol) was added rapidly. While the solution was stirred for 25 min, the temperature was monitored carefully so that it never exceeded $-95\text{ }^{\circ}\text{C}$. A solution of Me_2GeHCl (0.73 g, 5.25 mmol) in 5 ml THF was added dropwise to the reaction mixture at about $-110\text{ }^{\circ}\text{C}$ over a period of 15 min. The resulting colorless solution was allowed to gradually warm to r.t. and stirred overnight. After removal of the solvent in vacuo, the product was extracted into ether and washed three times with aqueous 10% ammonium chloride solution. The organic layer was dried over magnesium sulphate and the solvent removed in vacuo leaving a clear, colorless liquid; yield 96%. $^1\text{H-NMR}$ data (C_6D_6) for **1**: δ/ppm 7.38–7.03 (m, 4H, aryl); 4.67–4.64 (m, 1H, GeH); 2.61–2.51, 2.33–2.22 (d of q, 2H, Ar- CH_2); 1.63–1.54 (m, 1H, Ar- CH_2 -CH); 1.41–1.25, 1.15–0.98 (m, m, each 1H, Ar- CH_2 -CH- CH_2); 0.86–0.79 (m, 6H, $2 \times \text{CH}_3$); 0.38–0.36 (d, 6H, Ge- CH_3). Data for **2**: 7.44–7.40 (d, 2H, aryl); 7.10–7.06 (d, 2H, aryl); 4.66–4.63 (m, 1H, Ge-H); 2.58–2.49, 2.31–2.21 (d of q, 2H, Ar- CH_2); 1.62–1.52 (m, 1H, Ar- CH_2 -CH); 1.40–0.98 (2m, each 1H, Ar- CH_2 -CH- CH_2); 0.87–0.79 (m, 6H, $2 \times \text{CH}_3$); 0.37–0.35 (d, 6H, Ge- CH_3).

2.2.4. Polymerisation

The synthesis of *meta* and *para* poly[methyl{(*S*)-2-methylbutylphenyl}germane]s (**3** and **4**, respectively) were carried out by demethanative coupling of the respective monomers mediated by a ruthenium catalyst, tetrakis(trimethylphosphine)dimethylruthenium. The synthesis of **3** is representative: {(*S*)-2-methylbutylphenyl}dimethylgermane (0.151 g, 0.641 mmol) was added to a Wheaton vial containing $[(\text{PMe}_3)_4\text{RuMe}_2]$ (0.019 g, 0.044 mmol, 7 mol%). The colorless solution turned orange with vigorous bubbling within 30 min, and was solid within 4 h. After 2 days, 100 μl of THF was added to the reaction mixture. After an additional 4 days the polymer was dissolved in THF (ca. 2 ml) and placed under nitrogen. Methanol (100 ml) was added to precipitate out the polymer. Filtration through a 0.2 μm nylon filter and drying under vacuum afforded **3** as a beige solid in 63% yield. GPC: (light scattering) $M_w = 18,500$; $M_n = 11,000$; (polystyrene) $M_w = 10,000$; PDI (polydispersity index = M_w/M_n) = 1.6. FL λ_{max} (excitation at 340 nm; $20\text{ }^{\circ}\text{C}$): 371 nm. $^1\text{H-NMR}$ (toluene- d_8) for **3**: δ/ppm 7.2–6.6 (4H, Ar); 2.5, 2.2 (2H, Ar- CH_2);

1.5 (1H, Ar- CH_2 -CH); 1.4, 1.1 ($2 \times 1\text{H}$, Ar- CH_2 -CH- CH_2); 0.9, 0.8 (6H, $2 \times \text{CH}_3$); 0.4–0.2 (3H, Ge- CH_3) [Ar = aryl]. $^{13}\text{C-NMR}$ (toluene- d_8): δ/ppm 142–130 (Ar); 43.6, 37.0, 29.6, 19.2, 11.6 (alkyl carbons); -4.3 (Ge- CH_3). Data for **4**: GPC: (polystyrene) $M_w = 8,000$; PDI = 1.5. $^1\text{H-NMR}$ (toluene- d_8) δ/ppm 7.3–6.6 (4H, Ar); 2.5, 2.1 (2H, Ar- CH_2); 1.5 (1H, Ar- CH_2 -CH); 1.4, 1.1 ($2 \times 1\text{H}$, Ar- CH_2 -CH- CH_2); 1.0, 0.8 (6H, $2 \times \text{CH}_3$); 0.4–0.2 (3H, Ge- CH_3) [Ar = aryl]. $^{13}\text{C-NMR}$ (toluene- d_8): δ/ppm 143–130 (Ar); 43.5, 37.0, 29.6, 19.3, 11.5 (alkyl carbons); -4.6 (Ge- CH_3).

2.3. Silanes

2.3.1. Materials and procedures

Enantiopure chiral *para*- and *meta*-substituted (*S*)-2-methylbutylphenyl bromides were custom synthesized by Chemical Soft Co., Kyoto, Japan, and purified prior to use by distillation using a Perkin–Elmer autoannular still.

2.3.2. Monomer synthesis

The *meta* and *para*-substituted methyl{(*S*)-2-methylbutylphenyl}dichlorosilanes (**5** and **6**, respectively) were prepared similarly. The synthesis of **6** is representative. To a cold ($-5\text{ }^{\circ}\text{C}$) solution of *para*-(*S*)-2-methylbutylphenyl bromide (10.00 g, 44.03 mmol) in diethyl ether (40 ml) was added dropwise with mechanical stirring a solution of *n*-butyl lithium (1.54 M in hexane, 28.6 ml, 44.03 mmol). After addition was complete, the mixture was stirred for a further hour. The solution was then transferred by cannula to a dropping funnel and added dropwise to a cold ($-5\text{ }^{\circ}\text{C}$) solution of methyltrichlorosilane (6.58 g, 44.03 mmol) in hexane (50 ml). The solution was allowed to warm to r.t. with stirring. Filtration of the solution and distillation under reduced pressure afforded $>98\%$ pure (by GC) monomer in ca. 60% yield. $^1\text{H-NMR}$ (toluene- d_8) for **6**: δ/ppm 7.4–6.8 (4H, Ar); 2.65, 2.4 (2H, Ar- CH_2); 1.6 (1H, Ar- CH_2 -CH); 1.4, 1.2 ($2 \times 1\text{H}$, Ar- CH_2 -CH- CH_2); 0.9, 0.8 (6H, $2 \times \text{CH}_3$); 0.61 (3H, Si- CH_3) [Ar = aryl]. $^{13}\text{C-NMR}$ (CDCl_3): δ/ppm 145–129 (Ar); 43.5, 36.6, 29.3, 19.0, 11.5 (alkyl carbons); 5.0 (Si- CH_3). $^{29}\text{Si-NMR}$ (toluene- d_8): δ/ppm 18.2.

2.3.3. Polymerisation

Poly[methyl{*m*-(*S*)-2-methylbutylphenyl}silane] (**7**), and poly[methyl{*p*-(*S*)-2-methylbutylphenyl}silane] (**8**), were prepared according to the sodium-mediated Wurtz-type method in toluene. The synthesis of **8** is representative: methyl{*p*-(*S*)-2-methylbutylphenyl}dichlorosilane (3.00 g, 11.483 mmol) was added in toluene (3 ml) to 2.5 equivalents sodium (0.66 g, 28.71 mmol) dispersed in toluene (11 ml) and surface-activated by diglyme (13 μl). The mixture was stirred slowly at $70\text{ }^{\circ}\text{C}$, shielding the vessel from light and monitoring the

molecular weight periodically by SEC. After 3 h, 0.1 equivalent trimethylchlorosilane (0.125 g, 1.148 mmol) was added as terminator and stirring continued for a further 30 min, after which the mixture was pressure filtered through two Teflon membranes (pore size 40 and 10 μm). The high molecular weight (M_w) fraction was isolated as a white powder or fibrous material by fractional precipitation from a mixed isopropanol–toluene solution, followed by centrifugation, and vacuum dried in an oven at 80 °C overnight. Yield: 0.14 g, (6.4%); M_w : 643,000. UV λ_{max} (20 °C): 342 nm. FL λ_{max} (excitation at 329.5 nm; 20 °C): 357 nm. $^1\text{H-NMR}$ (toluene- d_8) for **8**: δ/ppm 7.2–6.4 (4H, Ar); 2.4, 2.2 (2H, Ar- CH_2); 1.5 (1H, Ar- CH_2 -CH); 1.4, 1.1 ($2 \times$ 1H, Ar- CH_2 -CH- CH_2); 0.9, 0.8 (6H, $2 \times$ CH_3); 0.4–0.4 (3H, Si- CH_3) [Ar = aryl]. $^{13}\text{C-NMR}$ (toluene- d_8): δ/ppm 142–130 (Ar); 43.8, 36.8, 29.7, 19.6, 11.8 (alkyl carbons); –6 (Si- CH_3). $^{29}\text{Si-NMR}$ (toluene- d_8): δ/ppm –38.8, –40.0, –40.7.

Data for **7**: M_w : 570,000. UV λ_{max} (20 °C): 341 nm. FL λ_{max} (excitation at 329.5 nm; 20 °C): 355 nm. 7.1–6.4 (4H, Ar); 2.5, 2.2 (2H, Ar- CH_2); 1.6 (1H, Ar- CH_2 -CH); 1.4, 1.2 ($2 \times$ 1H, Ar- CH_2 -CH- CH_2); 0.85, 0.8 (6H, $2 \times$ CH_3); 0.2–0.4 (3H, Si- CH_3). $^{13}\text{C-NMR}$ (toluene- d_8): δ/ppm 140–130 (Ar); 43.9, 36.8, 29.7, 19.5, 11.9 (alkyl carbons); –5 (Si- CH_3). $^{29}\text{Si-NMR}$ (toluene- d_8): δ/ppm –38.8, –39.8, –41.3.

2.3.4. Polymer chain scission

The molecular weights (M_w) and polydispersities ($\text{PDI} = M_w/M_n$) of the as-obtained polysilanes (**7**: $M_w = 570,000$, $\text{PDI} = 4.28$; **8**: $M_w = 643,000$, $\text{PDI} = 3.52$) and polygermanes (**3**: $M_w = 10,000$, $\text{PDI} = 1.6$; **4**: $M_w = 8000$, $\text{PDI} = 1.5$) differed considerably. Since the polysilane UV absorption intensity (dipole transition moment) is known to depend on molecular weight [4b,5a], and the CD intensity also has a similar dependence, a comparison of polysilane and polygermane CD and UV intensities is only valid if the molecular weights are approximately the same. This requirement can be circumvented by comparing not the UV or CD intensities themselves, but the ratios of CD/UV intensity, $\Delta\epsilon/\epsilon$ (the Kuhn dissymmetry ratio, also known as g_{abs}). However, since the helical characteristics themselves may depend on molecular weight, we considered it more appropriate to use similar molecular weight samples in the spectroscopic measurements. It was thus necessary to produce polysilane with a molecular weight of ca. 10,000. This was accomplished by controlled photodegradation of a 2×10^{-4} mol dm^{-3} solution sample stirred at 20 °C using a 6 W UV source at 365 nm for ca. 90 s. The final molecular weights and PDI for the polysilanes were **7**: $M_w = 13,600$, $\text{PDI} = 1.59$; **8**: $M_w = 8500$, $\text{PDI} = 1.38$.

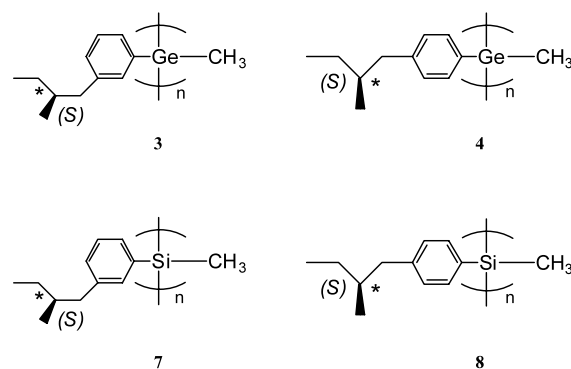
2.4. Forcefield calculations

All forcefield calculations were carried out using the CAChe WorkSystem programs [*] on a Windows PC. The minimum energy conformations (simple energy minimization) of the polymers were optimized by using CAChe Augmented MM3 [CAChe WorkSystem Pro Ver. 5.01, Fujitsu Ltd. (2001)]. Initially polymer models with ten repeat units were constructed with a main chain dihedral angle of 180°, coplanar phenyl rings orthogonal to the main chain and butyl substituents orthogonal to the phenyl rings. Isotactic configurations were constructed. The main chain dihedral angles were then assigned different values and the side chains were allowed to reach minimum energies. The overall minimum energies were then plotted as a function of the dihedral angle.

3. Results and discussion

Representative repeat unit structures for the *meta* and *para*-substituted polygermanes (**3** and **4**, respectively) and polysilanes (**7** and **8**, respectively) are shown in Scheme 1.

The polygermanes were prepared by the demethanative coupling of the aryldimethylgermane monomers catalysed by a ruthenium catalyst [2c,2d] since the yields in this method are high and the syntheses can be carried out on a small scale (expedient, financially) and poly[methyl(phenyl)]germane synthesised by this method have been shown to be analogous to poly[methyl(phenyl)]germane synthesised by the Wurtz coupling technique [2d]. The demethanative coupling method is not applicable in the case of the analogous polysilanes, so these were synthesised according to the classical Wurtz-type sodium-mediated coupling of dichlorosilane monomers.



Scheme 1. Polygermanes and silicon analogues.

3.1. Spectroscopic analysis

The UV and CD spectra for the *meta* and *para*-substituted polygermanes, **3** and **4**, and similar molecular weight polysilane derivatives, **7'** and **8'**, are shown in Fig. 1(a–d), respectively.

In all plots, the lower trace corresponds to the UV spectrum while the upper trace corresponds to the CD spectrum. The UV absorption maxima (λ_{max}) for the polygermanes **3** and **4** are at 331 and 329 nm, and for the analogous polysilanes, **7'** and **8'**, at 333 and 332 nm, respectively at 20 °C. For the non-photodegraded polysilanes, **7** and **8**, the λ_{max} values are 341 and 342 nm.

The shift of λ_{max} to shorter wavelength for lower molecular weight (i.e. shorter chain length) polysilanes is well documented and arises due to the decrease in number of conjugating backbone atoms and concomitant increase in the HOMO–LUMO gap [4b]. Thus in a comparison of spectroscopic properties, it is more appropriate to compare polygermanes with similar molecular weight (or actually slightly greater molecular weight, due to the greater formula weight) polysilanes. It has been theoretically [15] and experimentally [16] shown that polygermanes have a smaller HOMO–LUMO gap (longer λ_{max}) than analogous polysilanes. In the present comparison, however, the polygermane absorption maxima are at slightly shorter wavelengths than the analogous polysilanes. One possible origin for this is that the polygermanes, synthesised by ruthenium-catalysed demethanative coupling, may contain slightly more defects (branching points) than the polysilanes

(also suggested from the slightly broader absorption of, for example, polygermane **3** compared with polysilane **7'**), which are synthesised by the Wurtz coupling technique, although a previous report on the polymerization of aryl dimethylgermanes indicates that, at least in comparison with the alkylgermane analogues, the degree of branching is low [2d]. Another possible reason (which we suggest below is less likely) is that the polygermane backbone conformations are less extended than the polysilanes, resulting in reduced σ conjugation [5a].

The observation of a Cotton effect in each case indicates the induction of a preferential screw sense in the main chain [9] arising from adoption of a stereochemically preferred E–E–E–E (E = Si or Ge) polymer backbone dihedral angle, and since both Cotton effects are of the same sign (negative), the main chain screw senses are the same. In order to make a comparison of the helical properties of the polysilanes and polygermanes, it is necessary to exclude possible effects from different dipole transition moments and molecular weights (i.e. it is not appropriate to directly compare the UV or CD molar absorptivities, ϵ and $\Delta\epsilon$, respectively). Instead, the dimensionless Kuhn dissymmetry ratio, g_{abs} , defined as $\Delta\epsilon/\epsilon$ is used, which, for polygermanes **3** and **4**, respectively at –70 °C, has values of -0.34×10^{-4} and -0.38×10^{-4} and for photolysed polysilanes **7'** and **8'**, respectively at –70 °C, has values of -0.76×10^{-4} and -0.81×10^{-4} (interestingly the Kuhn dissymmetry ratio appeared to slightly increase for the polysilanes on photolysis: for **7** and **8**, respec-

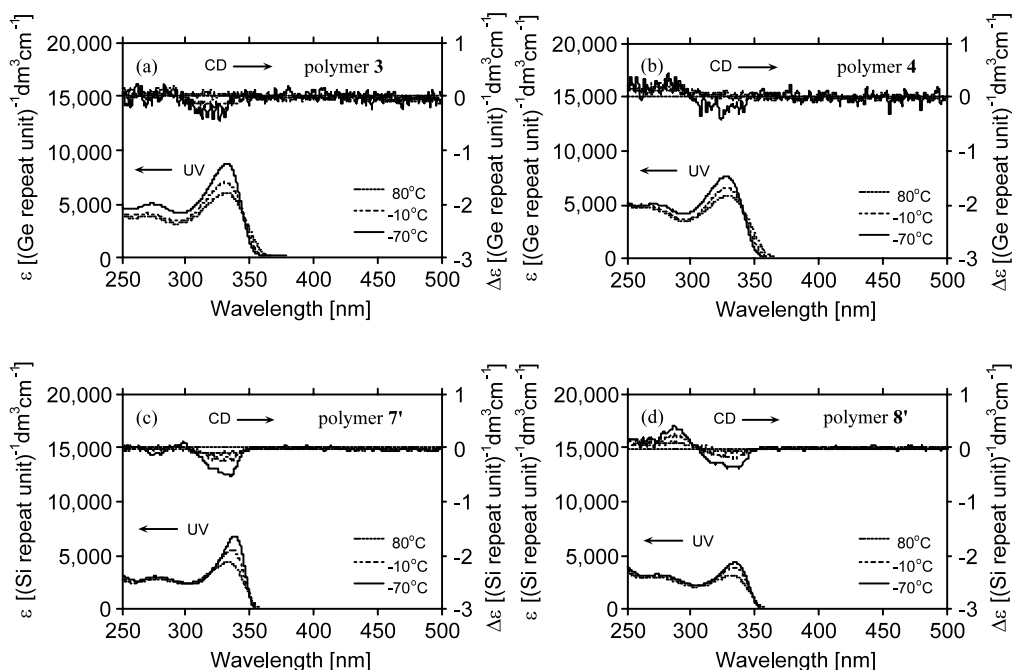


Fig. 1. UV (lower trace) and CD spectra for: (a) *meta*-substituted polygermane, **3**; (b) *para*-substituted polygermane, **4**; (c) *meta*-substituted polysilane, **7'**; and (d) *para*-substituted polysilane, **8'**.

Table 1
Thermal dependence of Kuhn dissymmetry ratio (g_{abs}) for all polymers

Temperature (°C)	$g_{\text{abs}} \times 10^4$					
	3	4	7'	8'	7	8
-70	-0.342	-0.377	-0.760	-0.814	-0.588	-0.656
-10	-0.255	-0.130	-0.391	-0.475	-0.212	-0.251
20	-0.209	0	-0.306	-0.203	-0.177	-0.188
80	0	0	-0.273	-0.225	-0.149	-0.085

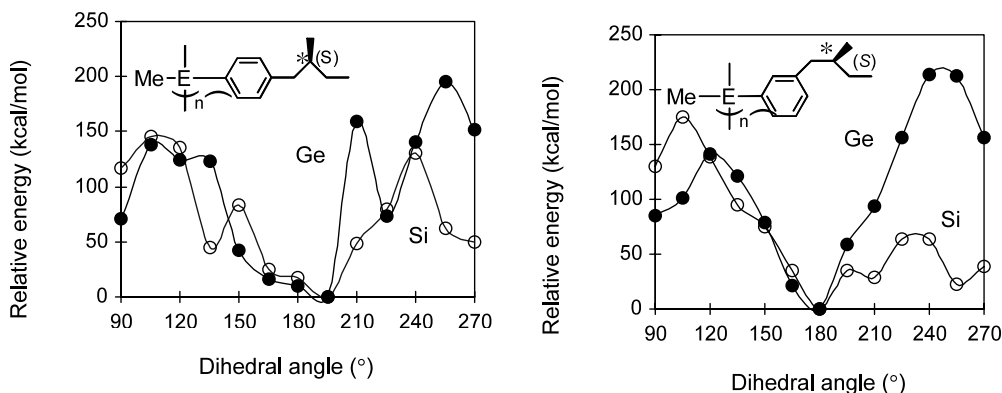


Fig. 2. Forcefield calculated plots of relative energy vs. E–E–E–E dihedral angle.

tively at $-70\text{ }^{\circ}\text{C}$ $g_{\text{abs}} = -0.59 \times 10^{-4}$ and -0.66×10^{-4}). The Kuhn dissymmetry ratio is smaller in the case of the polygermanes, **3** and **4**, which could indicate either or both of the following: firstly that the helical purity is less, i.e. the preference for one helical screw sense over the other is reduced, or secondly that the helical pitch is less, i.e. the main chain adopts a looser helical conformation. Given that theoretically, polygermanes should have UV absorptions which are red-shifted compared to their polysilane analogues [15], and that among structurally similar polysilanes a blue shift generally indicates a *tighter* helical conformation, the fact that the polygermane UV λ_{max} for **3** and **4** are at a shorter wavelength (331 and 329 nm, respectively at $20\text{ }^{\circ}\text{C}$) than those for the analogous polysilanes, **7'** and **8'** (333 and 332 nm, respectively at $20\text{ }^{\circ}\text{C}$), makes the second possibility for the reduced g_{abs} value less likely. The CD and UV spectra of all polymers exhibit temperature dependence of their intensities, as is evident in Fig. 1, though the λ_{max} value hardly changes, indicating little net thermal effect on σ conjugation. The reduction in CD intensity as the temperature increases, however, is greater than the decrease of UV intensity, and in most cases to near zero above $80\text{ }^{\circ}\text{C}$, i.e. the Kuhn dissymmetry ratio (g_{abs}) decreases with increase in temperature, as is evident in Table 1. This is consistent with the loss of helical screw sense preference due to the thermal energy exceeding that of the conformational fixing effect and consequent partial

cancellation of oppositely signed CD bands [9]. This effect is greater for the polygermanes, and again can be understood as a decrease in screw sense selectivity compared with the polysilanes.

It thus appears that the polygermanes exhibit less preference in screw sense selection than structurally analogous polysilanes. This is consistent with the greater interatomic distance of the Ge–Ge bond (ca. 2.4 \AA) as compared with the Si–Si bond (ca. 2.2 \AA), since the increase in E–E bond length of about 10% should result also in an increase in the distances between side chains on neighbouring repeat units, which would in turn result in a reduction in the steric interaction between chiral groups in neighbouring repeat units.

3.2. Forcefield calculations

To corroborate the experimental observations described above, forcefield (MM3) calculations were performed on 10-mer models of both *meta* and *para*-chiral-substituted polygermanes and polysilanes to determine the energies of the molecules as a function of E–E–E–E dihedral angle. The results are shown in Fig. 2.

At this level of calculation, only a few comments can be made. Firstly, the plots for the chiral-substituted oligogermanes and oligosilanes are different and asymmetric, suggesting that some experimental difference between the Ge- and Si-based polymers may also be observed, and that. Secondly, from the local minima

near to 180°, transoid conformations are suggested. Thirdly, from the asymmetry of the plots, it is suggested that the polymers may exhibit some helical screw sense selectivity, in particular for the *para*-substituted case, for which a preferential screw sense helix is suggested from the minimum at around 195°. The presence of the minimum much closer to 180° in the case of the *meta*-substituted models is presumably due to the greater ability of the *meta*-substituted phenyl ring to rotate around the Si–C axis to reduce chiral side chain interactions to a minimum.

In conclusion, we have described the first enantiopure chiral-substituted preferential screw sense polygermanes and their Kuhn dissymmetry ratios are reported. The silicon analogues are shown to have greater Kuhn dissymmetry ratios, indicative of greater screw sense selectivity. These observations are consistent with the increased E–E bond length in the polygermanes, due to the concomitantly reduced interaction between chiral side chain substituents.

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References

- [1] I. Manners, Ann. Rep. Prog. Chem. Sect. A: Inorg. Chem. 93 (1997) 129.
- [2] (a) R.D. Miller, R. Sooriyakumaran, J. Polym. Sci. Part A: Polym. Chem. 25 (1987) 111;
(b) K. Mochida, H. Chiba, J. Organomet. Chem. 473 (1994) 45;
(c) J.A. Reichl, C.M. Popoff, L.A. Gallagher, E.E. Remsen, D.H. Berry, J. Am. Chem. Soc. 118 (1996) 9430;
(d) S.M. Katz, J.A. Reichl, D.H. Berry, J. Am. Chem. Soc. 120 (1998) 9844.
- [3] (a) K. Takeda, K. Shiraishi, Chem. Phys. Lett. 195 (1992) 121;
(b) T. Imori, T.D. Tilley, Chem. Commun. (1993) 1607;
(c) T. Imori, V. Lu, H. Cai, T.D. Tilley, J. Am. Chem. Soc. 117 (1995) 9931;
(d) L.R. Sita, Adv. Organomet. Chem. 38 (1995) 189.
- [4] (a) R. West, J. Organomet. Chem. 300 (1986) 327;
(b) R.D. Miller, J. Michl, Chem. Rev. 89 (1989) 1359.
- [5] (a) M. Fujiki, J. Am. Chem. Soc. 118 (1996) 7424;
(b) R. West, in: Z. Rappoport, Y. Apeloig (Eds.), Chemistry of Organic Silicon Compounds (and references therein), John Wiley & Sons Ltd, Chichester, 2001, p. 541 (and references therein).
- [6] (a) K. Mochida, S. Nagano, H. Kawata, M. Wakasa, H. Hayashi, J. Organomet. Chem. 542 (1997) 75;
(b) W.K. Zou, N.L. Yang, Polym. Prepr. 33 (1992) 188.
- [7] J. Michl, R. West, in: R.G. Jones, W. Ando, J. Chojnowski (Eds.), Silicon-Containing Polymers: The Science and Technology of their Synthesis and Applications, Kluwer, Dordrecht, 2000, p. 499.
- [8] (a) H. Teramae, K. Takeda, J. Am. Chem. Soc. 111 (1989) 1281;
(b) K. Takeda, J. Phys. Soc. Jpn. 63 (1994) (Suppl. B) 1.;
(c) H. Sun, Macromolecules 28 (1995) 701;
(d) C.H. Ottosson, J. Michl, J. Phys. Chem. Sect. A 104 (2000) 3367.
- [9] (a) M. Fujiki, J. Am. Chem. Soc. 116 (1994) 6017;
(b) M. Fujiki, J. Am. Chem. Soc. 116 (1994) 11976;
(c) M. Fujiki, Polym. Prepr. 37 (1996) 454;
(d) M. Fujiki, S. Toyoda, C.-H. Yuan, H. Takigawa, Chirality 10 (1998) 667;
(e) S. Toyoda, M. Fujiki, Chem. Lett. (1999) 699;
(f) J.R. Koe, M. Fujiki, H. Nakashima, J. Am. Chem. Soc. 121 (1999) 7934;
(g) J.R. Koe, M. Fujiki, M. Motonaga, H. Nakashima, Chem. Commun. (2000) 389;
(h) J.R. Koe, M. Fujiki, M. Motonaga, H. Nakashima, Macromolecules 34 (2001) 1082.
- [10] (a) K. Obata, C. Kabuto, M. Kira, J. Am. Chem. Soc. 119 (1997) 11345;
(b) K. Obata, M. Kira, Macromolecules 31 (1998) 4666.
- [11] T. Sanji, K. Takase, H. Sakurai, J. Am. Chem. Soc. 123 (2001) 12690.
- [12] (a) M.R. Majidi, L.A.P. Kane-Maguire, G.G. Wallace, Polymer 35 (1994) 3113;
(b) M.R. Majidi, L.A.P. Kane-Maguire, G.G. Wallace, Polymer 36 (1995) 3597;
(c) M.R. Majidi, L.A.P. Kane-Maguire, G.G. Wallace, Polymer 37 (1996) 359;
(d) E.E. Havinga, M.M. Bouman, E.W. Meijer, A. Pomp, M.M. Simenon, Synth. Met. 66 (1994) 93;
(e) E. Yashima, T. Matsushima, Y. Okamoto, J. Am. Chem. Soc. 117 (1995) 11597;
(f) E. Yashima, S. Huang, T. Matsushima, Y. Okamoto, Macromolecules 28 (1995) 4184;
(g) E. Yashima, Y. Maeda, Y. Okamoto, J. Am. Chem. Soc. 120 (1998) 8895;
(h) E. Yashima, Y. Maeda, Y. Okamoto, Nature 399 (1999) 449;
(i) P. Dellaportas, R.G. Jones, S.J. Holder, Macromol. Rap. Commun. 23 (2002) 99;
(j) H. Nakashima, J.R. Koe, K. Torimitsu, M. Fujiki, J. Am. Chem. Soc. 123 (2001) 4847.
- [13] (a) 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) 3139;
(b) B.M.W. Langeveld-Voss, R.J.M. Waterval, R.A.J. Janssen, E.W. Meijer, Macromolecules 32 (1999) 227;
(c) J.V. Selinger, R.L.B. Selinger, Macromolecules 31 (1998) 2488.
- [14] (a) H. Anderson, J. Am. Chem. Soc. 82 (1960) 3016;
(b) P.S. Hallman, T.A. Stephenson, G. Wilkinson, Inorg. Synth. 12 (1970) 237;
(c) M.F. Abd El-Wahab, M.Z. Barakat, Monatsh. Chem. 88 (1957) 692.
- [15] N. Matsumoto, in: J.F. Harrod, R.M. Laine (Eds.), Inorganic and Organometallic Oligomers and Polymers, Kluwer, Dordrecht, 1991, p. 97.
- [16] (a) R. West, P. Trefonas, J. Polym. Sci. Polym. Chem. Ed. 23 (1985) 2099;
(b) R.D. Miller, R. Sooriyakumaran, J. Polym. Sci. Polym. Chem. Ed. 28 (1987) 111.