Polymer Vol. 37 No. 10, pp. 1815–1823, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/\$15.00+0.00

Theoretical investigation of the origins of abrupt thermochromism in the polysilanes

Tamara Gahimer and William J. Welsh*
Department of Chemistry, University of Missouri–St Louis, St Louis, MO 63121, USA
(Received 5 June 1995; revised 17 July 1995)

Values of the conformation-dependent polymer-solvent interaction parameter V_D have been calculated for some simple polysilane model compounds using quantum-mechanically derived molecular polarizabilities coupled with London's dispersion formula. The value $V_D = 0.97\,\mathrm{kcal\,mol^{-1}}$ obtained in the present study for the σ-conjugated polysilanes nearly equals the $V_D \approx 1.1\,\mathrm{kcal\,mol^{-1}}$ estimated by Schweizer for the analogous π-conjugated carbon-backbone polymers, assuming similar physical conditions. The present results thus provide theoretical evidence in support of the pertinence of Schweizer's theory of abrupt thermochromism to the polysilanes. The conformational flexibility and versatility of the backbone is much greater for the polysilanes compared with most π-conjugated polymers, hence the conformational 'defect energy' ε of the former should be small or even negative. The combination of large V_D (favouring the 'ordered' backbone) and small ε (favouring the 'disordered' backbone) predicted for the polysilanes would place the critical V_D/ε parameter well in excess of the limiting value $V_D/\varepsilon \geq 0.37$ required for onset of abrupt thermochromism according the Schweizer. The (Austin Model 1) AM1-calculated change in polarizability $\Delta\alpha$ with respect to backbone rotation ϕ was 0.63 Å^3 for the model polysilane but only 0.08 Å^3 for the analogous non-conjugated carbon-backbone model polymer. This substantial difference substantiates the existence of strong coupling between the molecular polarizability and the backbone conformation in the polysilanes. Only the longitudinal polarizability α_{xx} contributes substantially to $\Delta\alpha$, while the transverse polarizabilities α_{yy} and α_{zz} essentially combine with no net effect on $\Delta\alpha$ (i.e. $\Delta\alpha_{yy} \cong -\Delta\alpha_{zz}$). The variation of the calculated band-gap energy E_g with α for corresponding values of ϕ fits a second-order regression curve (correlation coefficient $r = 0.98$). As the silicon backbone approaches an all-*trans* conformation, the highest occupied molecular orbital (HOMO) energy increases while the lowest unoccupied molecular orbital (LUMO) energy decreases to reduce E_g. This increase in the HOMO energy is balanced by a nearly equal decrease in the HOMO−1 energy; likewise, the decrease in the LUMO energy is balanced by an increase in the LUMO+1 energy. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polysilanes; abrupt thermochromism; interaction parameter)

INTRODUCTION

The polysilanes [–SiRR′–], where R and R′ can represent a variety of aliphatic and aromatic groups, possess highly interesting physical, chemical and electronic properties of potential use in advanced technologies. (For background and reviews, see refs 1–15.) Some polysilanes have shown promise as u.v. photoresists in microlithography, as radical photoinitiators, as impregnating agents for strengthening ceramics and as precursors of silicon carbide fibres for use in advanced composites. Owing to their σ-conjugated silicon backbone, polysilanes have attracted interest as dopable electrical conductors and semiconductors[16], as photoconductors[17–20], as charge-transport materials in electrophotography[21–23] and as non-linear optical materials[24–30].

An interesting feature of the polysilanes is their unusual electronic structure. All substituted silane high polymers absorb strongly in the u.v. at 300–400 nm. Their absorption characteristics depend on the molecular weight of the polymer and on the conformation of the silicon backbone; consequently, many polysilanes are thermochromic both in solution and in the solid state[1–15]. For example, the homologous series of symmetrically substituted poly(di-n-alkylsilane)s [–SiR$_2$–], from R = methyl to R = n-octyl, exhibit a wide range of structural and thermochromic properties (*Table 1*).

A most unusual phenomenon exhibited by some polysilanes is *abrupt thermochromism*, characterized by a dramatic (ca. 60 nm) and reversible bathocromic shift in the absorption maximum $\lambda_{\max}$ as the temperature falls below a critical transition temperature T_c. (The adjective 'abrupt' is meant to convey that this thermochromic transition is discontinuous with temperature and thus eludes interpretation by statistical-based treatments such as rotational isomeric state (RIS) theory[8,9].) A large body of experimental and theoretical evidence attributes these sharp red–blue thermochromic transitions to associated 'order–disorder' conformational transitions along the silicon backbone. Specifically, the low-temperature 'ordered' structure responsible for the red-shifted $\lambda_{\max}$ has been described in terms of long runs of the all-*trans* (or nearly all-*trans*) backbone

---

* To whom correspondence should be addressed

Table 1 Conformational and thermochromic behaviour of some poly(di-n-alkylsilanes) [–SiR$_2$–][a]

Polymer	R	Solid-state conformation[b]	Abrupt thermochromism? In solid state	In solution	Ref.
PDMS	n-methyl	*trans*	no	not sol.	31
PDES	n-ethyl	near *trans*	no	no	32
PDPrS	n-propyl	near *trans*	no	no	32
PDBS	n-butyl	7/3 helix	no	yes (−48°C)	33
PDPS	n-pentyl	7/3 helix	no	yes (−33°C)	33, 34
PDHS	n-hexyl	*trans*	yes (42°C)	yes (−28°C)	35
PDOS	n-octyl	*trans*	yes (−19°C)	yes (−35°C)	36
PDTDS	n-tetradecyl	*TGTG′*	yes (54°C)	–	37

[a] General information has been taken from refs 1–15 and 31–42. Particular references to individual polymers are also quoted
[b] Observed at ambient temperatures (below T_c) and pressures

conformation. These all-*trans* sequences extend the mean conjugation length of the σ-conjugated silicon backbone, thereby shifting absorption to the red. The 'disordered' structure is viewed as a conformationally extended but more disordered backbone containing kinks that disrupt the long runs of all-*trans* backbone and thus shift λ_{max} to the blue.

The molecular basis of these order–disorder transitions, particularly the solution phenomena, has been the subject of intense scrutiny[1–15]. A salient question concerns the precise mechanism by which the silicon backbone can suddenly and reversibly interconvert between the disordered and ordered forms over a span of typically only 1–2°C. Based on theoretical studies carried out in this laboratory[43–54] and by others[55–69], as well as on experimental data[1–15,31–37], ample evidence confirms that the silicon backbone is inherently flexible and capable of populating helical (i.e. non-*trans*) conformations. Some polysilanes are known to adopt such helical backbones in the solid state (*Table 1*). Hence, a unique driving force must be operative to stabilize the all-*trans* (or nearly all-*trans*) backbone conformation. In this regard, two opposing mechanisms have been suggested: (1) the 'single chain' model, which basically derives this driving force from the inherent σ-delocalized electronic structure of the polysilane chain[38]; and (2) the 'aggregation' model, whereby intermolecular (and perhaps intramolecular) side chain···side chain interactions promote alignment of the all-*trans* backbone[39–42].

In recent years, Schweizer has proposed an interesting theory in support of the 'single chain' model[70–72]. According to his theory, abrupt thermochromism can be induced by a unique conformation-dependent polymer–solvent interaction associated with conjugated polymers. In the polysilanes, this interaction arises from the dispersion-like attractions between the σ-delocalized electrons of the silicon backbone and the polarizable local medium—which can be solvent molecules, neighbouring chains, or even the polymer's own side chains. Schweizer formulated his theory in terms of the ratio V_D/ϵ where V_D is the conformation-dependent dispersion energy per backbone bond or atom and ϵ is the 'defect energy' representing the free-energy cost to rotate the bond in question from *trans* to the 'defect' conformation. The parameter V_D/ϵ is conveniently employed as a guide for predicting whether the thermochromic transition will be continuous or abrupt. Specifically, abrupt thermochromism increases in likelihood with increasing V_D/ϵ and, at least for the π-conjugated polymers, appears to satisfy the limiting condition $V_D/\epsilon \geq 0.37$. For the polysilanes and most other conjugated polymers, the electron delocalization and, in turn, longitudinal polarizability α_{xx} are highly dependent on the backbone conformation and will approach a maximum at all-*trans*. Since dispersion forces depend in general on the polarizability α of the interacting atoms or groups, the contribution of this special conformation-dependent dispersion energy will stabilize the all-*trans* backbone conformation.

The polysilanes represent excellent candidates to explore the relationship between Schweizer's theory and abrupt thermochromism. Their σ-delocalized electronic structure should translate to large values of V_D, and the inherent conformational flexibility of the Si–Si bond implies small values of ϵ. This combination suggests that the limiting condition $V_D/\epsilon \geq 0.37$ for onset of abrupt thermochromism should be easily satisfied by the polysilanes. Most π-conjugated polymers (e.g. polyacetylene) are conformationally inflexible and strongly prefer the all-*trans* backbone or nearly so. The polysilanes, by contrast, are conformationally more versatile and capable for populating the same non-*trans* helical backbone conformations (*Table 1*) that are associated with the conformational 'defect' parameter ϵ. As a consequence, the conformational defect energy ϵ is likely to be small or even negative for many polysilanes. This combination of large V_D and small (or negative) ϵ fulfils the conditions of Schweizer's theory, according to which a pseudo-first-order phase transition between the ordered and disordered phase requires a bimodal conformational free-energy surface afforded by a large V_D (favourable to *trans*) and a small or negative ϵ (unfavourable to *trans*).

The merit of Schweizer's theory in explaining the observed order–disorder transitions in the polysilanes and other conjugated polymers depends in part on the magnitude of V_D. Combining theoretical and experimental data with a general dispersion expression, Schweizer obtained $V_D \approx 1.1\ \mathrm{kcal\,mol^{-1}}$ as a reasonable estimate for the π-conjugated polyenes. Taking $\epsilon \approx 1\ \mathrm{kcal\,mol^{-1}}$ from the literature, he concluded that

$V_D/\epsilon \approx 1.1$ exceeds the threshold value of 0.37 required for onset of the abrupt order–disorder transition[70–72].

In the present study, the relevance of Schweizer's theory to the polarizability α were derived quantum-mechanically for model compounds of the simple polysilanes [$-SiH_2-$] (polysilane, PS) and [$-Si(CH)_3)_2-$] (polydimethylsilane, PDMS) as a function of rotation ϕ about an internal Si–Si bond. The variation in α (and α_{xx} in particular) with ϕ is substantially larger for the polysilanes than for the analogous non-conjugated carbon-backbone polymer. Specifically, the present results reveal that $\Delta\alpha$, defined as the maximum change in α with ϕ, is 0.6 Å^3 for H–[SiH_2]$_{10}$–H but only 0.08 Å^3 for H–[CH_2]$_{10}$–H. This difference is consistent with the notion that conjugated polymers uniquely exhibit strong coupling between the backbone conformation and the extent of electron delocalization. The quantity $\Delta\alpha$, which can be ascribed to a single atom in the rotated bond, represents the maximum enhancement in the polarizability of the atom resulting from electron delocalization.

V_D was calculated for the polysilanes from $\Delta\alpha_{Si}$ and the polarizability α_s of the solvent particles using the Slater–Kirkwood formula[73–75] in conjunction with the classical London dispersion expression[76,77]. A crude estimate of $V_D = 0.97\,\mathrm{kcal\,mol^{-1}}$ was obtained based on a simple representation of the 'solvent' in the vicinity of the subject Si atom. This value is nearly identical to the $V_D \cong 1.1\,\mathrm{kcal\,mol^{-1}}$ obtained by Schweizer for polyenes under similar physical conditions[70–72]. Therefore, the present work supports the applicability of Schweizer's 'single chain' theory to the polysilanes in that V_D is sufficiently large to stabilize the all-*trans* backbone conformation and thereby promote abrupt thermochromism. At the same time, the role of side chain···side chain aggregation and precipitation in this phenomenon cannot be ruled out and many indeed function independently of 'single chain' effects.

COMPUTATIONAL METHODOLOGY

The two simple polysilanes [$-SiH_2-$] (PS) and [$-Si(CH_3)_2-$] (PDMS), represented respectively by the oligomeric model compounds H–[SiH_2]$_n$–H (where $n = 5$, 10) and CH_3–[$Si(CH_3)_2$]$_5$–CH_3, were chosen for the present calculations. The choice of these simple structures, devoid of long side chains, afforded computational efficiency while at the same time focused attention on the inherent properties of the silicon backbone.

Construction, visualization and manipulation of all molecular structures were carried out using Biosym's molecular modelling program *Insight*. (*Insight*, a molecular modelling program, and *DMol*, a quantum-mechanical program based on density functional theory, are products of Biosym Technologies, San Diego, CA.) For the two PS model compounds, PS-5 and PS-10, full geometry optimization via energy minimization was performed on all conformations using Biosym's *DMol* module. *DMol* utilizes numerical atomic-orbital basis sets to calculate the variational self-consistent solutions to the density function theory (DFT) equations. The most rigorous (*DNP*) basis set and mesh parameters and the maximum number of mesh points available in *DMol* were utilized for this study. The *DNP* basis set employs double numeric basis functions and polarization functions to define the atomic orbitals.

For the PDMS model compound PDMS-5, the all-*trans* form was full geometry-optimized using *DMol* in order to obtain reasonable geometric parameters, viz. Si–Si = 2.33 Å, Si–C = 1.83 Å, C–H = 1.09 Å and Si–Si–Si = 111°. The computational demands of the DFT calculations precluded full geometry optimization for the other conformers. Instead, the geometric parameters were fixed to those calculated for the all-*trans* form while the torsion angle ϕ was incremented.

At the time of the present study, calculations of molecular polarizability were not feasible using *DMol*. Therefore, the molecular polarizabilities for each of the previously *DMol*-optimized geometries were computed using the Austin Model 1 (AM1)[78] Hamiltonian coupled with the finite-field methodology accessed through *Insight*'s *Mopac* module. Values of the average molecular polarizability α and its components α_{xx}, α_{yy} and α_{zz} (where $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$) were generated *versus* rotation ϕ about an internal Si–Si bond (*Figure 1*) varied from *trans* ($\phi = 180°$) to *cis* ($= 0°$) in increments of 15°. The energies of the electronic band gap $E_g = E_{LUMO} - E_{HOMO}$ and of the six frontier molecular orbitals HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1, and LUMO+2 were also extracted from the *Mopac* AM1 output for use in interpreting the polarizability data. The finite-field methodology[79] employed in *Mopac* solves the molecular wave function ψ as a function of an external electric field F. From the wave function $\psi(F)$, both the field-dependent molecular energy $E(F)$ and dipole moment $\mu(F)$ can then be used to calculate α.

To calculate values of α for these systems with absolute accuracy would surely require application of rigorous *ab initio* theory with large basis sets inclusive of correlation[80]. Such calculations would have overwhelmed the available computational resources and, in fact, would have exceeded the primary objectives of the present study, which was to evaluate Schweizer's theory qualitatively and to identify general trends in α with respect to ϕ. The semiempirical AM1 method offers a feasible alternative to *ab initio* approaches for the present purposes owing to its computational efficiency and its demonstrated ability to capture many of the essential electronic features of molecules and polymers[81,82]. The ability of AM1 (coupled with the finite-field methodology) to discern the sharp differences between PS-10 and PC-10 with regard to their α *versus* ϕ profiles builds confidence in the validity of the present approach.

A complete set of α *versus* ϕ values was calculated for three specific polysilane oligomers: H-[SiH_2]$_5$–H (PS-5), H–[SiH_2]$_{10}$–H (PS-10) and CH_3–[$Si(CH_3)_2$]$_5$–CH3 (PDMS-5). PS-5 and PDMS-5 each contained four Si–Si bonds and two Si–Si–Si–Si torsion angles, of which one torsion angle was taken as ϕ while the other was

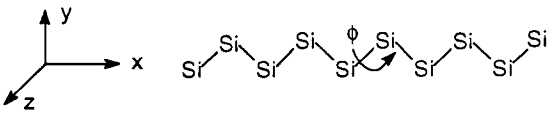

Figure 1 Silicon backbone of the H–[SiH_2]$_{10}$–H (PS-10) model compound, indicating rotation ϕ about the central Si–Si bond

held at *trans*. PS-10 contains nine Si–Si bonds and seven Si–Si–Si–Si torsion angles, of which the central torsion angle (i.e. the fifth Si–Si bond) was taken as ϕ while the remaining six torison angles were held in the *trans* conformation (*Figure 1*). The conformational defect in PS-10 is straddled by pentameric silicon sequences, which are sufficiently long to mimic the chain-like features of the polysilanes.

RESULTS AND DISCUSSION

Polarizabilities versus ϕ

The calculated values of α *versus* ϕ have been tabulated for the polysilane model compounds PS-5, PS-10 and PDMS-5 (*Table 2*). For comparison, *Table 2* also includes corresponding values for the non-conjugated carbon-backbone model compound H–$(CH_2)_{10}$–H (PC-10) analogous to PS-10. The results show that $\Delta\alpha = \alpha_{180^\circ} - \alpha_{0^\circ}$ is substantially larger for the three polysilane model compounds than for PC-10. Specifically, $\Delta\alpha$ is 0.63 Å^3 for PS-10 but only 0.08 Å^3 for PC-10. This result substantiates the existence of strong coupling between the molecular polarizability and backbone conformation in the polysilanes.

It is convenient to normalize α by defining the quantity $\alpha' = \alpha - \alpha_0$, where α is the AM1-calculated molecular polarizability and α_0 is the polarizability of the $\phi = 0^\circ$ (*cis*) conformation for a given polymer. Plotting α' *versus* ϕ for PS-5, PS-10 and PDMS-5 (*Figure 2*), the curves reveal that α' (and, hence, α) diminishes gradually, at first sharply, as ϕ deviated from $\phi = 180^\circ$ (*trans*). For PS-10, for example, α' decreases from its maximum value of 0.63 Å^3 at $\phi = 180^\circ$ by approximately 1.3% at 165°, 17% at 150° and 81% at 90°. Similar trends were obtained for PS-5 and PDMS-5.

It is apparent from *Table 2* and *Figure 2* that $\Delta\alpha$ is roughly twice as large for PS-10 as for PS-5 and PDMS-5, a result that is consistent with the relative lengths of their respective silicon backbones. As expected, the magnitude of $\Delta\alpha$ correlates with the length of the all-*trans* backbone that is being disrupted by the conformational defect. Since V_D is a function of $\Delta\alpha$ through the Slater–Kirkwood formula (*vide infra*), the magnitude of V_D will likewise depend on the lengths of all-*trans* backbone that straddle the conformational defect. The present calculation of V_D pertains to PS-10, in which case the decameric all-*trans* silicon backbone is essentially being divided by the conformational defect into two pentameric all-*trans* subunits. This scenario might represent a typical case occurring in the polymer.

Table 2 Calculated values of α *versus* ϕ for PS-5, PS-10 PDMS-5 and PC-10

	Average polarizabilities (Å^3)			
ϕ (deg)	PS-5	PS-10	PDMS-5	PC-10
180	16.8580	36.2646	24.4833	12.0830
165	16.8491	36.2562	24.4646	12.0750
150	16.8189	36.1556	24.4184	12.0652
135	16.7397	36.0471	24.3719	12.0474
120	16.6840	35.9339	24.3295	12.0319
105	16.6398	35.8344	24.2814	12.0272
90	16.6084	35.7581	24.2445	12.0343
75	16.5854	35.7068	24.2285	12.0491
60	16.5761	35.6788	24.2297	12.0609
45	16.5425	35.6682	24.1983	12.0543
30	16.5757	35.6610	24.1315	12.0305
15	16.5531	35.6464	24.1228	12.0094
0	16.4874	35.6366	24.1135	12.0035
$\Delta\alpha$	0.3706	0.6280	0.3698	0.0795

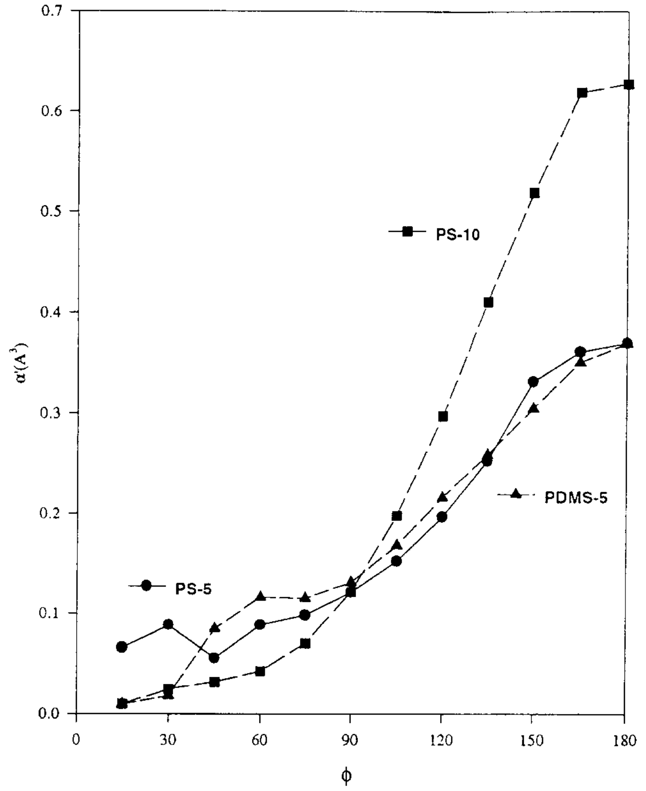

Figure 2 Calculated values of α' *versus* ϕ for the polysilane model compounds PS-5, PS-10 and PDMS-5

Estimation of V_D *for the polysilanes*

Schweizer deduced $V_D \approx 1.1\,\mathrm{kcal\,mol^{-1}}$ for a polyene in dilute solution of a typical non-polar organic solvent[70–72]. In the present application, V_D was estimated for the polysilanes under similar conditions using the data calculated above for PS-10. Adopting the form of the London dispersion equation[76,77] $E_{\mathrm{disp}} = c_{ij}/R^6$, an expression for V_D can be written

$$V_D = -\sum_{Z}[(-c_{ij}/R^6)_{trans} - (c_{ij}/R^6)_{\text{non-}trans\ \text{defect}}] \qquad (1)$$

where i refers to the Si atom in question and j refers to the atoms comprising the local solvent molecules, respectively. The summation is taken over the number of solvent molecules Z in the vicinity of the subject bond. (The leading minus sign in equation (1) has been added since an attractive V_D energy is defined as positive.) Equation (1) states that V_D is calculated as a difference in polymer–solvent dispersion energy between the all-*trans* conformation and the non-*trans* (i.e. defect-containing) conformation. The required c_{ij} parameters were deduced from the Slater–Kirkwood formula[73–75]:

$$c_{ij} = 360.0\alpha_i\alpha_j/[(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}] \qquad (2)$$

where α_i and α_j are, respectively, the polarizabilities of the Si atom and of the atoms comprising the solvent molecules. The parameters N_i and N_j represent the effective number of outer-shell electrons N_{eff} in atoms i and j. The factor 360.0 produces c_{ij} in kcal Å^6 mol^{-1} for α expressed in Å^3.

Values of $(c_{ij})_{trans}$ and $(c_{ij})_{\text{non-}trans\text{ defect}}$ required for equation (1) were computed by inserting the appropriate value of α_i into equation (2) for the type of Si atom in each case. For $(c_{ij})_{\text{non-}trans\text{ defect}}$, α_i was assigned the standard value of 2.8Å^3 for a typical Si atom devoid of any extra delocalization effects[43,45,54,83]. For $(c_{ij})_{trans}$, this α_i value is augmented by $\Delta\alpha$ to reflect the enhancement in polarizability due to electron delocalization. The value $\Delta\alpha = 0.63$ Å^3 calculated for PS-10 (*Table 2*) was taken as a reasonable estimate for this quantity. Accordingly, the augmented value of α_i associated with $(c_{ij})_{trans}$ is 3.43 Å^3. Following Schweizer[70–72], it was assumed that the maximum change in polarizability of PS-10 can be assigned to a single Si atom in the rotating backbone bond.

To estimate V_D for the polyenes, Schweizer assumed a first solvent shell of $Z = 8$ molecules (each with $\alpha_s \sim 10.4$ Å^3) located at a distance $R = 4.5$ Å from the polyene CH group under consideration[70–72]. In the present derivation of V_D, equations (1) and (2) have been formulated in terms of the atomic polarizabilities α_j of the atom composing the solvent molecules. Organic solvent molecules like hexane, benzene and toluene contain 6–7 carbon atoms, so $Z = 8$ solvent molecules would yield approximately $8 \times 6 = 48$ highly polarizable carbon atoms. Each of these carbon atoms was assigned the parameters $\alpha_j = 0.93$ Å^3 and $N_j = 5.0$[83]. The corresponding parameters for the Si atom in PS-10 are $N_i \cong 13$ and either $\alpha_i = 3.43$ Å^3 or 2.8 Å^3 depending on whether the electron delocalization along the silicon backbone is included or not.

Assuming that each solvent atom is located an average distance R from the Si atom, equation (1) can be simplified by factorizing out the variable R to give:

$$V_D = -(1/R^6)ZN_a[(-c_{ij})_{trans} - (-c_{ij})_{\text{non-}trans\text{ defect}}] \quad (3)$$

where Z is the number of solvent molecules and N_a is the number of polarizable (carbon) atoms in each solvent molecule. The appropriate values of α_i, α_j, N_i and N_j were inserted into equation (2) to obtain $(c_{ij})_{trans} = 1215$ kcal Å^6 mol^{-1} and $(c_{ij})_{\text{non-}trans\text{ defect}} = 1047$ kcal Å^6 mol^{-1}, which, in turn, were inserted into equation (3) to obtain values for V_D. V_D is strongly dependent on R, as illustrated by a plot V_D *versus* R based on equation (3) for the case $Z = 8$ and $N_a = 6$ (Figure 3). For the value $R = 4.5$ Å adopted by Schweizer, equation (3) yields $V_D = 0.97$ kcal mol^{-1} for the polysilanes. Although these calculations are admittedly crude, they provide evidence that V_D may be sufficiently large in the polysilanes to support Schweizer's theory of abrupt thermochromism based on solvent-induced conformational changes of the polymer backbone.

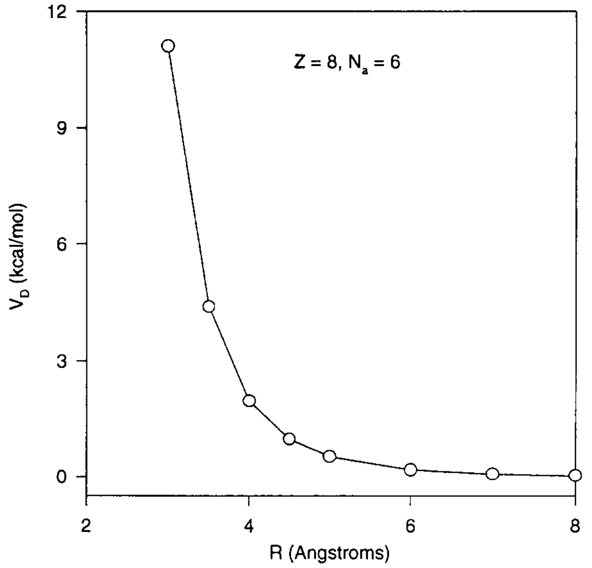

Figure 3 Plot of V_D *versus* R based on equation (3) for the case $Z = 8$ and $N_a = 6$

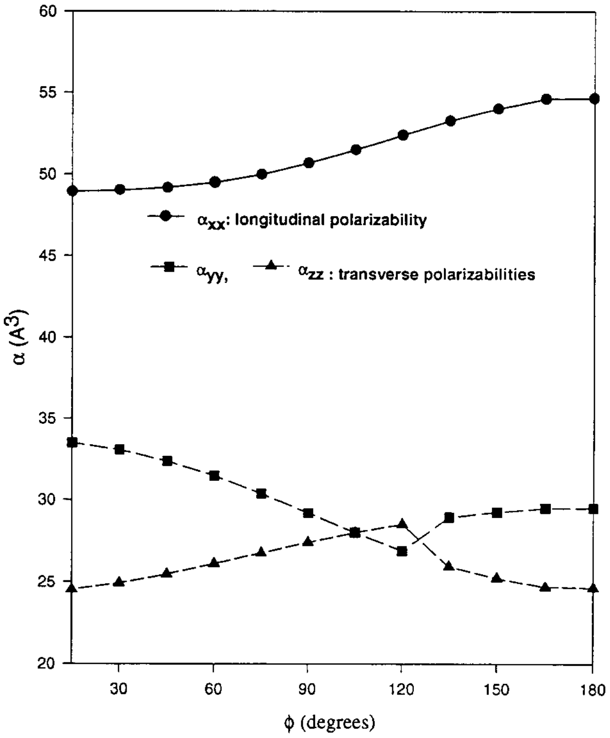

Figure 4 Calculated values of the longitudinal polarizability α_{xx} and the transverse polarizabilities α_{yy} and α_{zz} *versus* ϕ for PS-10

Component polarizabilities versus ϕ

The variation of the component polarizabilities α_{xx}, α_{yy} and α_{zz} with ϕ, as plotted for PS-10 in *Figure 4*, reveals that the sum of the transverse components α_{yy} and α_{zz} is very nearly constant (i.e. $\alpha_{yy} + \alpha_{zz} \cong$ constant). This relationship implies the $\Delta\alpha_{yy} \cong -\Delta\alpha_{zz}$; therefore the changes in the transverse polarizabilities with ϕ essentially cancel out. Only the longitudinal component α_{xx} contributes substantially to the variation of α with ϕ. Since $\Delta\alpha = (\Delta\alpha_{xx} + \Delta\alpha_{yy} + \Delta\alpha_{zz})/3$, it follows that $\Delta\alpha \cong \Delta\alpha_{xx}/3$ in the present case.

Values of α_{xx} are nearly double those of α_{yy} or α_{zz} (*Figure 4*). This result is as expected since the molecular polarizability will be significantly larger parallel than perpendicular to the chain direction. The α_{xx} per SiH$_2$ unit is about 3.63 Å^3 (or 31 a.u.) according to AM1 for

PS-10 in the all-*trans* conformation. This compares reasonably well with the range of STO-3G (Slater-type orbitals, three Gaussians) values ($\cong 32$ a.u.) reported by Kirtman and Hasan[80]. Both AM1 and STO-3G underestimate the 6-31G (plus diffuse functions) values reported by the same authors. However, use of AM1 was consistent with the major goal of the present study, which was to recognize trends rather than to calculate α with absolute numerical accuracy.

Polysilane electronic structure

An increase in electron delocalization, as found for the polysilanes and other conjugated polymers as the backbone approaches all-*trans*, is expected to cause the molecular polarizability α to increase and the electronic band-gap energy E_g (i.e. $E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) to decrease. Plots of the AM1-calculated values of E_g *versus* ϕ (*Figure 5*) for PS-5, PS-10 and PDMS-5 confirm that E_g decreases monotonically with increasing ϕ to a minimum at *trans* ($\phi = 180°$). A plot of E_g *versus* α for corresponding values of ϕ yielded a strong second-order fit with correlation coefficient $r = 0.98$ (inset to *Figure 5*).

The AM1-calculated energies of the six frontier orbitals HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1 and LUMO+2 for PS-10 are plotted *versus* ϕ in *Figure 6*. Consistent with the E_g *versus* ϕ data plotted in *Figure 5*, the HOMO energy increases and the LUMO energy decreases as ϕ approaches 180°. The HOMO energy changes somewhat more than the LUMO energy, suggesting that the HOMO orbitals are perturbed more so by changes in the backbone conformation. The variations in energy of the HOMO and LUMO with ϕ are strongly correlated with those of the respective penultimate orbitals HOMO−1 and LUMO+1. As the HOMO is destabilized with increasing ϕ, the HOMO−1 is stabilized by almost an equal amount; likewise, as the LUMO is stabilized with increasing ϕ, the LUMO+1 is destabilized almost equally. In contrast, the HOMO−2 and LUMO+2 orbitals remain almost unperturbed by variations in ϕ. This general behaviour of the frontier orbitals conveys the sense that electron delocalization is achieved by donation from the HOMO into the LUMO.

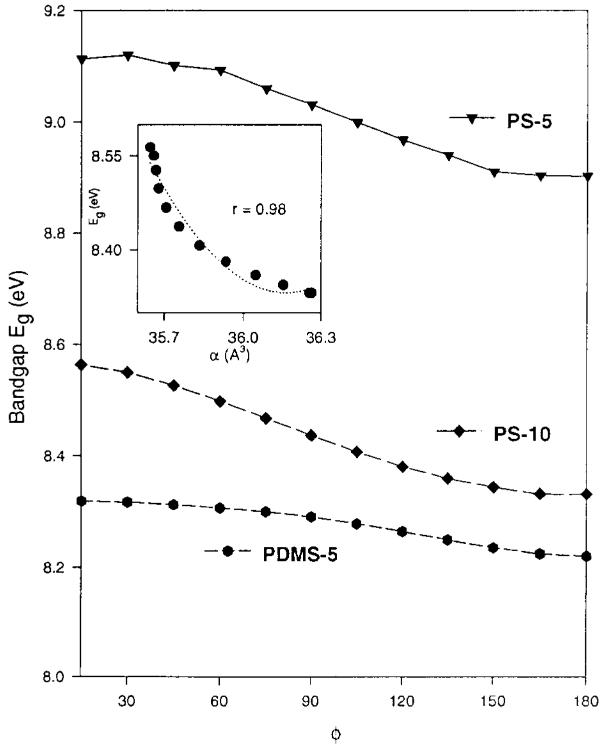

Figure 5 AM1-calculated values of the electronic band-gap energy E_g *versus* ϕ for PS-5, PS-10 and PDMS-5. Inset: plot of E_g *versus* α at corresponding values of ϕ. The curve shows a second-order regression fit

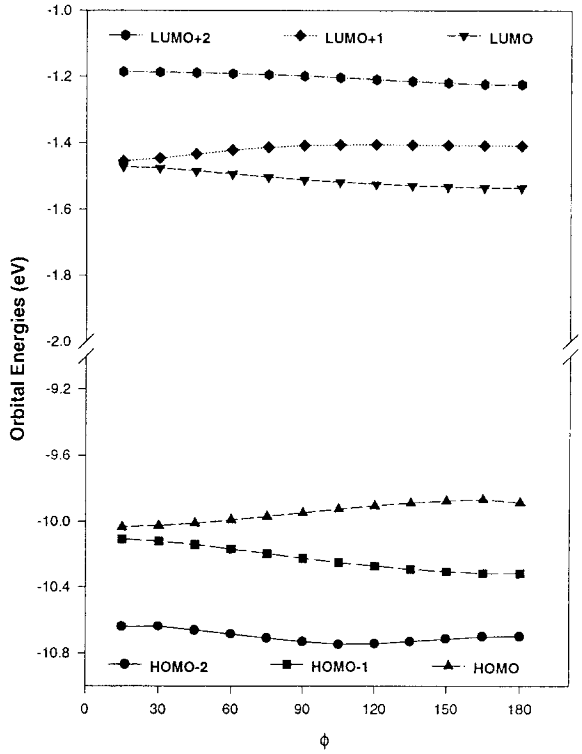

Figure 6 Energies of the frontier molecular orbitals HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1 and LUMO+2 *versus* ϕ, as calcuated by AM1

CONCLUDING REMARKS

Perhaps the most thoroughly investigated polysilanes from the standpoint of thermochromism are the homologous series of symmetrically substituted polysilanes [$-\mathrm{SiR}_2-$], particularly PDBS (R = n-butyl), PDPS (R = n-pentyl) and PDHS (R = n-hexyl). Despite the similarity of their molecular structures, PDBS, PDPS and PDHS exhibit significant differences with respect to their conformational preferences and thermochromic behaviour (*Table 1*). In the solid state, PDHS adopts an all-*trans* backbone conformation and exhibits abrupt thermochromism; PDBS and PDPS adopt a 7/3 helical backbone conformation and do not exhibit abrupt thermochromism[33–35]. (Evidence suggests that the all-*trans* backbone is induced by attractive interchain side chain···side chain interactions, which are stronger for PDHS than for PDBS and PDPS.) The clear implication drawn from these comparisons is that the all-*trans* backbone plays an instrumental role in polysilane abrupt thermochromism. There appears to be general agreement that the long runs of all-*trans* backbone are responsible for the red-shifted $\lambda_{\max}$ observed below T_c. Accordingly, the sudden disruption of these all-*trans* sequences at T_c causes $\lambda_{\max}$ to shift to the blue. This interpretation is largely supported by a significant body of theoretical and experimental data on a wide range of polysilanes[1-15].

The controversy over the molecular origins of abrupt thermochromism in the polysilanes has centred largely on the thermochromisms of PDBS, PDPS and PDHS in dilute solution. Remarkably, all three polysilanes exhibit abrupt thermochromism in dilute solution (*Table 1*)[39-42]. The immediate question that arises relates to the backbone conformation below T_c, which, according to the above explanation of the solid-state data, is all-*trans* or nearly so. The crux of this issue deals with finding a mechanism by which PDBS, PDPS and PDHS can adopt this conformation. According to the solid-state data, the all-*trans* backbone is hardly that preferred by PDBS and PDPS and is adopted by PDHS only through the action of interchain forces that presumably are absent in dilute solution. Both the 'aggregation' model[39-42] and the 'single chain' model[38,70-72] attempt to provide the mechanism by which the all-*trans* backbone in PDBS, PDPS and PDHS (and other polysilanes) is stabilized in solution below T_c.

The 'aggregation' model maintains the primacy of side chain···side chain interactions to explain both the solid-state and dilute-solution phenomena. In the solid state, these interchain interactions promote crystallization of the side-chain substructure below T_c, which locks in the all-*trans* backbone responsible for the red-shifted $\lambda_{\max}$. This substructure abruptly 'melts' at T_c, thereby releasing the backbone to adopt the disordered form responsible for the blue-shifted $\lambda_{\max}$. In dilute solution, side chain···side chain interactions within a single chain may stimulate at low temperatures a process described as intramolecular polymer collapse[39-42], which induces adoption of the all-*trans* backbone. This 'seed' chain may then template the aggregation of other chains also in the all-*trans* backbone conformation.

The alternative 'single chain' or 'rod-to-coil' model seeks to explain the same phenomena in terms of the intrinsic electron delocalization in conjugated polymers, which should act to stabilize the all-*trans* backbone conformation[1-15,38,70-72]. Schweizer's theory provides a cogent argument in favour of the 'single chain' model and establishes a feasible mechanism by which the all-*trans* backbone conformation is accessible to PDBS, PDPS and PDHS (and other polysilanes). The 'single chain' model obviates the need for chain···chain interactions, and hence it is especially pertinent to the situation found in dilute solution. On the other hand, the 'aggregation' model provides a lucid picture of circumstances in the solid state.

Consistent with Schweizer's theory, the present calculations suggest that the magnitude of V_D for the polysilanes is sufficiently large to stabilize the all-*trans* backbone conformation. The size of the rotational barriers in the polysilanes is highly dependent on the type, length and symmetry of the side chain R; hence the value of ε will vary considerably from one polysilane to another. For this reason, a direct calculation of Schweizer's V_D/ε parameter has not been attempted here. Compared with typical π-conjugated polymers, polysilanes can more easily populate helical (i.e. non-*trans*) backbone conformations. This increased accessibility to non-*trans* backbone conformations implies small or even negative values of ε. As a consequence, V_D/ε is likely to be larger for the polysilanes than for the π-conjugated polymers considered by Schweizer in his analysis[70-72]. It is worth noting that a recent experimental study on the thermochromism of a series of unsymmetrically substituted poly(n-alkylmethylsilane)s has provided additional support for Schweizer's model[84].

Although applicable to all polysilanes, Schweizer's theory of the 'single chain' model may be difficult to reconcile with the absence of abrupt thermochromism observed for some polysilanes with branched-chain substituents (e.g. poly(di-4-methylpentylsilane))[40]. One would not expect branching to impair abrupt thermochromism within the scheme of a 'single chain' model. On the other hand, this behaviour is consistent with the 'aggregation' model insofar as side-chain branching could thwart the formation of intramolecular and/or intermolecular aggregates. These apparent inconsistencies suggest that the 'aggregation' model of abrupt thermochromism cannot be ruled out. This particularly applies to the abrupt thermochromism observed for some polysilanes in the solid state (*Table 1*)[1-15].

The magnitude of $\Delta\alpha$ and, correspondingly, V_D depends on the specific conformation of the Si–Si bonds astride the Si–Si bond containing the defect. If one non-*trans* defect breaks an otherwise long all-*trans* sequence, that non-*trans* defect would experience the full magnitude of V_D calculated in the present study. If, instead, this non-*trans* defect breaks a shorter all-*trans* sequence, the operative magnitude of V_D would be something less than this upper limit. Thus, each and every Si–Si bond along the polysilane possesses a unique magnitude of V_D; V_D is, in turn, a dynamic variable of the backbone conformation astride the Si–Si bond in question.

The present study computed $\Delta\alpha$ and V_D by arbitrarily choosing the *cis* conformation ($\phi = 0°$) as the defect angle. The *cis* conformation will be energetically unfavourable for all substituted polysilanes, and consequently the occurrence of such a defect is highly unlikely in reality. The primary reason for choosing *cis* (i.e. the most extreme defect) was to determine whether the maximum values for $\Delta\alpha$ and V_D either supported or refuted Schweizer's model. The present results (*Figure 2*) reveal that the α *versus* ϕ curve for the polysilanes falls off sharply between $\phi = 180°$ (*trans*) and $\phi = 90°$, then only slowly between $\phi = 90°$ and $\phi = 0°$ (*cis*). Selecting a defect angle in the vicinity of $\phi = 90°$ would still have captured almost the full magnitude of $\Delta\alpha$ and V_D. In any case, it should not be construed that the *cis* conformation was adopted as the defect structure due to any special relevance to the actual case for the polysilanes.

ACKNOWLEDGEMENTS

The authors wish to thank the Research Board of the University of Missouri system for partial funding of this project. The authors also wish to acknowledge

Biosym Technologies, Inc., for access to the programs *Insight*, *Discover* and *DMol.*

REFERENCES

1 West, R. *J. Organomet. Chem.* 1986, **300**, 327

2 Harrah, L. A. and Ziegler, J. M. *Macromolecules* 1987, **20**, 2039

3 Zeigler, J. M. *Synth. Met.* 1989, **8**, C581

4 Miller, R. D. and Michl, J. *Chem. Rev.* 1989, **89**, 1359

5 West, R. in 'The Chemistry of Organic Silicon Compounds' (Eds. S. Patai and Z. Rappoport), Wiley, New York, 1989, Ch. 19, p. 1207

6 *Polym. Prepr.* 1990, **31**, August; 1991, **32**, April. A number of pertinent articles have been published in these issues based on symposia devoted to the subject area

7 Zeigler, J. M. *Mol. Cryst. Liq. Cryst.* 1990, **190**, 265

8 *Adv. Chem. Ser.* 324 'Silicon-Based Polymer Science: A Comprehensive Resource' (Eds. J. M. Zeigler and F. W. Fearon), American Chemical Society, Washington, DC, 1990

9 Harrah, L. A. and Ziegler, J. M. in 'Photophysics of Polymers' (Eds. C. E. Hoyle and J. M. Torkelson), *ACS Symp. Ser.* 358, American Chemical Society, Washington, DC, 1987, pp. 482–498

10 West, R. *J. Organomet. Chem.* 1986, **99**, 300

11 Miller, R. D., Wallraf, G. M., Bair, M., Cotts, P. M., Shukla, P., Russell, T. P., DeSchryver, F. C. and Declercq, D. *J. Inorg. Organomet. Polym.* 1991, **1**, 505

12 West, R., Menescal, R., Asuke, T. and Eveland, J. *J. Inorg. Organomet. Polym.* 1992, **2**, 29

13 Matyjaszewski, K. *J. Inorg. Organomet. Polym.* 1992, **2**, 5

14 Miller, R. D., Thompson, D., Sooriyakamaran, R. and Fickes, G. N. *J. Polym. Sci. (A) Polym. Chem.* 1991, **29**, 813

15 Michl, J. *Synth. Met.* 1992, **50**, 367

16 West, R., David, L. D., Djurovich, P. I., Stearly, K. L., Skinivasan, K. S. V. and Yu, H. *J. Am. Chem. Soc.* 1981, **103**, 7352

17 Kepler, R. G., Zeigler, J. M., Harrah, L. A. and Kurtz, S. R. *Bull. Am. Phys. Soc.* 1983, **28**, 362

18 Kepler, R. G., Zeigler, J. M., Harrah, L. A. and Kurtz, S. R. *Phys. Rev. (B)* 1987, **35**, 2818

19 Stolka, M., Yuh, H. J., McGrane, K. and Pai, D. M. *J. Polym. Sci. (A) Polym. Chem.* 1987, **25**, 823

20 Fujino, M. *Chem. Phys. Lett.* 1987, **136**, 451

21 Stolka, M., Yuh, H. J., McGrane, K. and Pai, D. M. *J. Polym. Sci. (A) Polym. Chem.* 1987, **25**, 823

22 Abkowitz, M., Knier, F. E., Yuh, H.-J., Weagley, R. J. and Stolka, M. *Solid State Commun.* 1987, **62**, 547

23 Samuel, L. M., Sanda, P. N. and Miller, R. D. *Chem. Phys. Lett.* 1989, **59**, 227

24 Miller, R. D., Baumert, J. C., Bjorklund, G. C., Jundt, J. H., Jurich, M. C., Looser, H., Rabolt, J. F., Sooriyakumaran, R., Swalen, J. D., Twieg, R. J., Cotts, P. M., Shulka, P., Torruellas, W. E., Schellenberg, F.M. and Byer, R.L. *Polym.* Prepr. 1990, **31**, 304.

25 Baumert, J. C., Bjorklund, G. C., Jundt, D. H. Jurich, M. C., Looser, H., Miller, R. D., Rabolt, J. F., Sooriyakumaran, R., Swalen, J. D. and Twieg, R. J. *Appl. Phys. Lett.* 1988, **53**, 1147

26 Kazjar, F., Messier, J. and Rosilio, C. J. *J. Appl. Phys.* 1986, **60**, 3040

27 Wang, L., Wang, Q. C., Ho, P. P., Dorsinville, R., Alfano, R. R., Zou, W. K. and Yang, N. L. *Appl. Phys. Lett.* 1988, **53**, 1245

28 McGraw, D. J., Siegman, A. E., Wallraf, G. M. and Miller, R. D. *Appl. Phys. Lett.* 1989, **54**, 1713

29 Schellenberg, F. M., Byer, R. L., Zavislan, J. and Miller, R. D. in 'Nonlinear Optics of Organics and Seimiconductors' (Ed. T. Kobayashi), Springer-Verlag, Berlin, 1989, p. 197

30 Schellenberg, F. M., Byer, R. L. and Miller, R. D. *Chem. Phys. Lett.* 1990, **166**, 331

31 For PDMS: Lovinger, A. J., Davis, D. D., Schilling, F. C., Padden, Jr, F. J., Bovey, F. A. and Zeigler, J. M. *Macromolecules* 1991, **24**, 132; *Polym. Prepr.* 1990, **31**, 263

32 For PDES and PDPrS: Lovinger, A. J., Davis, D. D., Schilling, F. C., Bovey, F. A. and Zeigler, J. M. *Polym. Commun.* 1989, **30**, 356

33 For PDBS and PDPS: Schilling, F. C., Lovinger, A. J., Zeigler, J. M., Davis, D. D. and Bovey, F. A. *Macromolecules* 1989, **22**, 3055. A form of PDBS with an all-*trans* backbone has been identified: Walsh, C. A., Schilling, F. C., Lovinger, A. J., Davis, D. D., Bovey, F. A. and Zeigler, J. M. *Macromolecules* 1990, **23**, 1742

34 For PDPS: Miller, R. D., Farmer, B. L., Fleming, W. W., Sooriyakumaran, R. and Rabolt, J. F. *J. Am. Chem. Soc.* 1987, **109**, 2509

35 For PDHS: Lovinger, A. J., Schilling, F. C., Bovey, F. A. and Zeigler, J. M. *Macromolecules* 1986, **19**, 2660; Kuzmany, H., Rabolt, J. F., Farmer, B. L. and Miller, R. D. *J. Chem. Phys.* 1986, **85**, 7413; Patnaik, S. S. and Farmer, B. L. *Polym. Prepr.* 1992, **33** (1), 272. Above $T_{\mathrm{c}} = 42^{\circ}\mathrm{C}$, PDHS appears as a liquid-crystalline material with hexagonal columnar structure: Weber, P., Guillon, D., Skoulios, A. and Miller, R. D. *J. Phys. Fr.* 1989, **50**, 703

36 For PDHepS and PDOS: Rabolt, J. F., Hofer, D., Miller, R. D. and Fickes, G. N. *Macromolecules* 1986, **19**, 611

37 For PDTDS: Farmer, B. L., Miller, R. D., Rabolt, J. F., Fleming, W. W. and Ficks, G. N. *Bull. Am. Phys. Soc.* 1988, **33**, 657

38 Harrah, L. A. and Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Edn.* 1985, **23**, 209

39 Trefonas, III, P., Damewood, Jr, J. R., West, R. and Miller, R. D. *Organometallics* 1985, **4**, 1318

40 Miller, R. D., Wallraf, G. M., Baier, M., Thompson, D., DeSchryver, F. C. and Declercq, D. *Polym. Prepr.* 1991, **32** (1), 437

41 Wallraff, G. M., Baier, M., Miller, R. D., Rabolt, J. F., Hallmark, V., Cotts, P. M. and Shukla, P. *Polym. Prepr.* 1989, **30**, 245

42 Shukla, P., Cotts, P. M., Miller, R. D., Russell, T. P., Smith, B. A., Wallraf, G. M. and Baier, M. *Macromolecules* 1991, **24**, 5606

43 Welsh, W. J., Ackerman, J. and Mark, J. E. *Polym. Prepr.* 1983, **24**, 131

44 Welsh, W. J., Debolt, L. and Mark, J. E. *Macromolecules 1986,* **19**, 2978

45 Welsh, W. J., Damewood, Jr, J. R. and West, R. *Macromolecules* 1989, **22**, 2947

46 Johnson, W. D. and Welsh, W. J. *PMSE J.* 1989, **61**, 222

47 Welsh, W. J. and Johnson, W. D. *Macromolecules* 1990, **23**, 1881

48 Welsh, W. J. *Polym. Prepr.* 1990, **31**, 232

49 Welsh, W. J. in 'Inorganic and Metal-Containing Polymeric Materials' (Eds. J. Sheats, C. Carraher, M. Zeldin, B. Currell and C. Pittman Jr), Plenum, New York, 1990, p. 197

50 Tersigni, S., Ritter, P. and Welsh, W. J. *J. Inorg. Org. Polym.* 1991, **1**, 377

51 Tersigni, S. and Welsh, W. J. *Comput. Polym. Sci.* 1991, **1**, 225

52 Durham, J., Corey, J. Y. and Welsh, W. J. *Macromolecules* 1991, **24**, 4823

53 Tersigni, S. and Welsh, W. J. *Comput. Polym. Sci.* 1992, **2**, 1

54 Welsh, W. J. *Adv. Polym. Tech.* 1993, **12**, 379

55 Damewood, Jr, J. R. *Macromolecules* 1985, **18**, 1795

56 Damewood, Jr, J. R. and West, R. *Macromolecules* 1985, **18**, 159

57 Farmer, B. L., Rabolt, J. F. and Miller, R. D. *Macromolecules* 1987, **20**, 1169

58 Ortiz, J. V. and Mintmire, J. W. *J. Am. Chem. Soc.* 1988, **110**, 4522

59 Mintmire, J. W. and Ortiz, J. V. *Macromolecules* 1988, **21**, 1191

60 Teramac, H. and Takeda, K. *J. Am. Chem. Soc.* 1989, **111**, 1281

61 Cui, C. X. and Kertesz, M. *J. Am. Chem. Soc.* 1989, **111**, 4216

62 Mintmire, J. W. and Ortiz, J. V. *Polym. Prepr.* 1990, **31**, 234

63 Cui, C. X., Karpfen, A. and Kertesz, M. *Macromolecules* 1990, **23**, 3302

64 Chapman, B. R., Patnaik, S. S. and Farmer, B. L. *Polym. Prepr.* 1990, **31**, 265

65 Chapman, B. R., and Farmer, B. L. *Polym. Prepr.* 1990, **31**, 288

66 Ortiz, J. V. *J. Chem. Phys.* 1991, **94**, 6064

67 Cui, C. X. and Kertesz, M. *Macromolecules* 1992, **25**, 1103

68 KariKari, E. K., Gresco, A. J., Farmer, B. L., Miller, R. D. and Rabolt, J. F. *Macromolecules* 1993, **26**, 3937

69 Sun, H. *Macromolecules* 1995, **28**, 701

70 Schweizer, K. S. *J. Chem. Phys.* 1996, **85**, 1156, 1176

71 Schweizer, K. S. *Synth. Met.* 1989, **28**, C565

72 Schweizer, K. S., Harrah, L. A. and Zeigler, J. M. in *Adv. Chem. Ser.* 324 (Eds. J. M. Zeigler and F. W. Gordon Fearon), American Chemical Society, Washington, DC, 1990, p. 379

73 Scott, R. H. and Scheraga, H. A *J. Chem. Phys.* 1965, **42**, 2209

74 Pitzer, K. S. *Adv. Chem. Phys.* 1959, **2**, 59

75 Slater, J. C. and Kirkwood, J. G. *Phys. Rev.* 1931, **37**, 682

76 Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B. 'Molecular Theory of Gases and Liquids,' Wiley, New York, 1954

77 Maitland, G. C., Rigby, M., Smith, E. B. and Wakeman, W. A. 'Intermolecular Forces' (Eds. R. Breslow, J. B. Goodenough, J. Halpern and J. S. Rowlinson), Clarendon Press, Oxford, 1987

78 Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. and Stewart, J. J. P. *J. Am. Chem. Soc.* 1985, **107**, 3902

79 Kurtz, H. A., Stewart, J. J. P. and Dieter, K. M. *J. Comput. Chem.* 1990, **11**, 82

80 Kirtman, B. and Hasan, M. *J. Chem. Phys.* 1992, **96**, 470

81 Welsh, W. J. and Yang, Y. *Comput. Polym. Sci.* 1991, **1**, 139

82 Kanis, D. R., Ratner, M. A. and Marks, T. J. *Chem. Rev.* 1994, **94**, 195

83 Welsh, W. J. in 'Computational Modeling of Polymers' (Ed. J. Bicerano), Marcel Dekker, New York, 1992, p. 127

84 Yuan, C.-H. and West, R. *Macromolecules* 1994, **27**, 629