bridges between chain segments) as well as the morphological perfection of its environment. Roginskii et al. have shown that peroxyl radical reactivity drops with increased levels of polymer oxidation.[5] We suggest that in the initial macroperoxyl population, a fraction of the radicals behave as if they are in motionally restricted domains and are unable to propagate. They can however terminate when another radical passes close by, moving by a combination of physical site transport (e.g., segmental oscillation, reptation etc.) and reactive migration (sequences of reactions 2a and 2b). The change in ESR line shape of $PP^{16}O_2\cdot$ at room temperature as the popultion "ages" is consistent with the concept of mobile and trapped radicals. For example, after protracted decay time at 23 °C, the ESR line shape is a sharp anisotropic singlet (Figure 1) identical with all $PP^{16}O_2\cdot$ spectra at 77 K, when there is negligible mobility.[15] The concept of peroxyl radicals trapped in "crystalline" domains has frequently been invoked.[4,7] However, it must be emphasized that only peroxyl radical signals are detected immediately after γ-irradiation of semicrystalline PPH in air or within 2 min after admitting O_2 to a PPH sample irradiated under vacuum. This means that all macroalkyls (the precursors of the peroxyl radicals) generated by γ-irradiation are O_2 accessible, either because "crystalline" domains in normal PPH samples (i.e., not exhaustively annealed) are highly defective and so O_2 permeable or because macroalkyl sites migrate rapidly into the amorphous regions by a hydrogen-transfer process.

The failure of $PP^{17}O_2\cdot$ radicals to propagate in the Reuben and Mahlman study probably stems from the nature of their sample (as-polymerized PPH powder gave much slower rates of radical decay than melt-quenched film in air experiments) and the history of their radicals.[10] Unfortunately, little precise information on irradiation conditions and postirradiation conditions was given in their paper, but it is reasonable to expect some sample heating during their 10-s electron beam exposure, which would cause a dramatic drop in radical population before the sample reached the ESR spectrometer "shortly after irradiation". Consequently, only the relatively immobile and unreactive ("aged") fraction of the population would be detected.

Although the formation of macroalkyl radicals from peroxyl radicals and the $PP^{17}O_2\cdot$ to $PP^{16}O_2\cdot$ conversion are consistent with the classical oxidative propagation step (reaction 2a), both effects could result from the complex interaction of *tert*-peroxyl radicals, the fate of over 60% the initial peroxyl population.[11] In an attempt to resolve this problem, we are currently combining ESR and Fourier transform infrared spectroscopy to examine the products generated during the decay of a $PPO_2\cdot$ population.

In summary our overall conclusions are that macroperoxyl radical reactivity is controlled by mobility factors, so that the radicals may be highly reactive to propagation or termination or extremely unreactive. The proportions of each type of radical present will depend markedly on the precise morphology of the sample, irradiation conditions, and subsequent thermal history of the radical ("aged") population. All of the diverse $PPO_2\cdot$ behavior reported in the literature can be reproduced by the correct combination of the above factors. Both the highly reactive "mobile" $PPO_2\cdot$ and the less reactive "trapped" radicals appear to contribute to the degradation of the polymer. However, we believe that the thermal decomposition of the macrohydroperoxide groups becomes the dominant initiation mechanism for the prolonged oxidation which develops subsequent to γ-irradiation.[16]

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Conformational Analysis of Poly(di-*n*-hexylsilylene)

Polysilane polymers are a scientifically interesting class of materials for which numerous applications have been described.[1] Of special interest is the remarkable ultraviolet (UV) absorption spectra exhibited by these polymers.[2] Alkyl-substituted polysilanes absorb strongly in the mid-UV, with λ_{max} typically residing within the 305-326-nm range.[1-4] The location of this absorption maxima at room temperature ($\lambda_{max,RT}$) shows an interesting correlation with the relative steric bulk of the alkyl substituent. The observed UV $\lambda_{max,RT}$ occurs at longer wavelengths when the alkyl substituents are more sterically demanding. A recent addition to this list of interesting spectral properties is the observation that polysilane polymers are thermochromic both in solution and in thin films.[5] Bathochromic shifts for UV λ_{max} upon cooling are found to be as large as 44 nm in solution and 55 nm in films. The present study was undertaken in order to explore possible relationships between the ground-state molecular structure of polysilane polymers and their observed thermochromic behavior.

Bonding in polysilanes has been described previously in terms of a linear combination of atomic orbitals (LCAO) model.[6] This model predicts that the HOMO-LUMO energy separation for a polysilane chain will be smaller in the trans conformation than in the gauche. Based on this it has been suggested[5] that the thermochromic behavior exhibited by polysilane polymers is the result of a temperature-dependent conformational change along the polymer backbone. As the temperature decreases, the population of the trans conformation increases, resulting in the observed bathochromic shift in UV λ_{max}. Implicit in this interpretation is that the ground-state conformation for these polysilane polymers is trans. Unfortunately,

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Table I
Selected Bonding Parameters of Conformational Isomers of 1

av Si–Si bond lengths[a]		av Si–Si–Si bond angles[b]		Si–Si–Si–Si torsion angles[b]	
T	235.5	T	110.4	T[c]	180.0
GT	235.9	GT	114.2	GT (G)	58.8
G	235.4	G	113.2	GT (T)	178.3
				G[c]	55.1

[a] In picometer units. [b] In degrees. [c] Reported as the average of these angles.

however, only a very limited amount of structural information is presently available on polysilane polymers with which to test this hypothesis. While recent empirical force field (EFF) calculations[7] on polysilane and poly(dimethylsilylene) have indicated that these molecules adopt gauche conformations in the ground state, no information is as yet available on the ground-state structure of polysilane polymers containing alkyl groups which are more sterically demanding than methyl, a characteristic shared by all thermochromic polymers reported to date.[5] In order to partially fill this information gap and to allow for a test of the hypothesized relationship between polymer ground–state structure and thermochromic behavior, we now report the results of EFF calculations on poly(di-*n*-hexylsilylene), a representative polymer which exhibits thermochromic behavior.

Full-relaxation EFF calculations were performed with the program MM2[8] and the previously reported parameters[10] and approximations.[11] In addition, methylene and methyl groups were approximated as carbon atoms without hydrogens with van der Waals radii increased from the standard value to 1.95 Å.[12] Using this value for the van der Waals radius, we were able to calculate a gauche–trans energy difference in butane of 0.86 kcal/mol, in agreement with a standard (with hydrogen) calculation. All-trans (T), all-gauche (G), and gauche–trans (GT) backbone conformations were considered as input structures for the model[11] of poly(di-*n*-hexylsilylene) (**1**).[13] For each conformation of **1** the *n*-hexyl side chains were maintained in the all-trans conformation. In the G conformation, the lowest energy structure was that in which the *n*-hexyl groups along the internal edge of the helix were directed away from the helical axis, i.e., C–Si–C–C angles of approximately 0°. For the GT and T conformations the lowest energy structures had all C–Si–C–C angles approximately equal to 180°. Relative energies of the T, GT, and G conformations of **1** are 0.0, 1.5, and 3.0 kcal/mol, respectively. Selected bonding parameters are reported in Table I.

Inspection of the relative energies reveals that **1** is predicted to adopt the T conformation in the ground state. A view of this conformation is shown in Figure 1. These calculations thus reveal that the relative conformational energies of **1** follow a trend which is opposite to that obtained for poly(dimethylsilylene)[7] (**2**), in which the G conformation is predicted to be the ground state. We attribute this difference in conformational behavior between **1** and **2** to the added steric bulk of the *n*-hexyl side chains of **1** compared to the methyls in **2**. In addition to this difference in conformational energy ordering, it is also interesting to compare the relative magnitudes of the conformational energy differences in **1** and **2**. The relative energy range of 0.9 kcal/mol calculated for **2** is significantly smaller than the 3.0 kcal/mol range calculated for **1**, indicating that **1** is expected to be considerably less conformationally flexible than **2**. We infer from these results that as the steric bulk of the substituent at silicon increases, polysilane polymers will show an increasing tendency to adopt T conformations in the ground state and will, in general, exhibit decreasing conformational flexibility.[14]

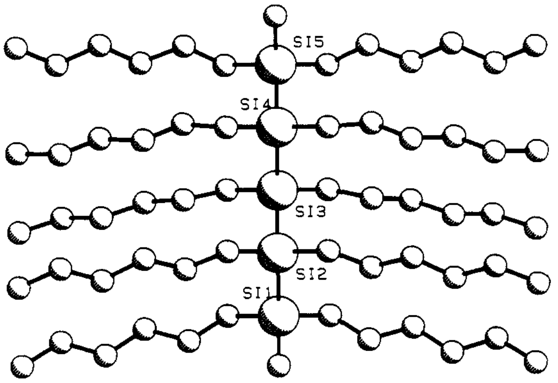

Figure 1. T conformation of **1** viewed along the least-squares plane of the backbone silicon atoms. Silicon and carbon atoms are represented by spheres which are proportional in size to the van der Waals radii of the atoms.

It is interesting to note that these results are consistent with the experimental observation that the UV $\lambda_{\max,RT}$ for high molecular weight polysilane polymers occurs at longer wavelengths when alkyl substituents are more sterically demanding. Evidently, even at room temperature, the population of trans conformational states is greatest in those polymers which have the most sterically demanding substituents. In addition, recent light scattering experiments[15] have indicated a decrease in polymer flexibility concomitant with the increasing steric bulk of the alkyl side chains. We are thus confident that these calculations present an accurate picture of the conformational behavior of **1**.

Inspection of Table I reveals that the bond lengths in the conformations of **1** are all within the normal range and compare well with those obtained for **2**. The average Si–Si–Si bond angles in **1** are, however, ca. 3° smaller than those obtained for **2**[7] following a GT > G > T trend rather than the G > GT > T trend calculated for **2**. This difference in backbone structure between **1** and **2** does not, however, extend to the Si–Si–Si–Si torsion angles. As for **2** the average gauche torsion angle in the G conformation of **1** (55.1°) is smaller than the corresponding value (58.8°) calculated for the GT conformation. With gauche torsion angles which are less than 60°, the axial advancement per helical turn in these conformers is reduced relative to that expected for ideal G or GT structures. The alkyl chains in all conformations of **1** may properly be described as adopting all-trans conformations, with the most significant deviations from torsion angles of 180° occurring closest to the silicon backbone.

The present calculations are consistent with the hypothesis that the origin of thermochromic behavior in selected polysilane polymers resides in a change in population of conformational states along the silicon backbone with temperature.[5] Polymers such as **1**, with sterically demanding alkyl groups are expected to adopt trans conformations in the ground state.[16] At lower temperatures the population of this trans conformational state increases, resulting in the observed bathochromic shift. Further tests of this hypothesis await experimental efforts.

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(11) The polymer was modeled by 1,5-dimethyl-1,1,2,2,3,3,4,4,5,5-deca-*n*-hexylpentasilapentane.[7]

(12) For C_{sp^3}, R^* = 1.950 Å and EPS = 0.044.

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Monomer-Isomerization Radical Polymerization of Di-*tert*-butyl Maleate to High Molecular Weight Poly(di-*tert*-butyl fumarate)

We have found that di-*tert*-butyl fumarate (**1**) is obtained quantitatively through isomerization of di-*tert*-butyl maleate (**2**) in the presence of a catalytic amount of morpholine. Moreover, when the reactions of isobutene with fumaric acid and maleic acid were carried out in the presence of sulfuric acid catalyst in diethyl ether to prepare **1** and **2**, respectively, the yield of **2** was higher than that of **1**, because of high solubility of maleic acid in ether. As described in a previous paper,[1] **1** was polymerized quite easily with a radical initiator to give a high molecular weight nonflexible rodlike poly(di-*tert*-butyl fumarate), poly(*tert*-butoxycarbonylmethylene) (**3**), which is then converted to poly(fumaric acid), poly(hydroxycarbonylmethylene) (**4**) on heating **3** at 180 °C (see Scheme I).

Scheme I

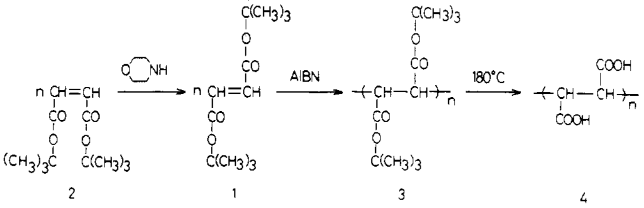

Table I
Results of Polymerization of 1 and 2[a]

compd	[morpholine], mol/L	yield, %	$\bar{M}_n \times 10^{-4}$ (GPC)
1	0	42	4.5
1	0.12	39	2.9
1	0.22	38	1.0
1	0.35	30	0.7
2	0	0	
2	0.08	17	1.1
2	0.16	25	1.0
2	0.22	27	0.9
2	0.27	25	0.8
2	0.35	23	0.7

[a] Polymerization conditions: [**1**] = [**2**] = 2.2 mol/L, [AIBN] = 2.2 × 10^{-2} mol/L in benzene; 60 °C; 10 h.

On the other hand, we have also found that dialkyl maleates do not homopolymerize with a radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN), but they undergo homopolymerization with a monomer isomerization in the presence of AIBN and morpholine as an isomerization catalyst to yield high molecular weight polymers, which consist of similar structure to those obtained from the corresponding dialkyl fumarates; i.e., the maleates isomerize first to the fumarates, which then homopolymerize.[2-4] Similar monomer-isomerization polymerizations have been reported for various internal olefins with Ziegler–Natta catalyst.[5-7]

The most important merit of such monomer-isomerization polymerization in polymer synthesis is that compounds that have been known to be not homopolymerized are used as a new polymerizable monomer.[8] If **2** is polymerized via a monomer-isomerization radical polymerization mechanism, this reaction is a one-pot synthesis of **3**, from which **4** is easily derived.

The results of polymerization of **2** are shown in Table I, in which those of **1** are also indicated.

As reported previously,[1] **1** readily polymerizes with AIBN in the absence of morpholine, but **2** does not give any polymer. In the presence of both AIBN and morpholine, **2** undergoes polymerization, and the polymer yields increase with increasing morpholine concentration below ca. 2.0 mol/L and then decrease at higher concentrations. During polymerization, the isomerization of **2** to **1** was also observed, though its rate was slow compared with that of diethyl maleate to diethyl fumarate.[7] The addition of morpholine to radical polymerization of **1** decreased the yield and the molecular weight of the polymers. Therefore, morpholine seemed to act as both an isomerization catalyst of **2** to **1** and a retarder of radical polymerization of **1**.

When time–conversion relations for the monomer-isomerization radical polymerization of **2** with both AIBN and

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