Ring-Opening Polymerization of Cyclotetrasilanes: Microstructure and Mechanism

Eric Fossum and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received September 28, 1994; Revised Manuscript Received December 16, 1994®

ABSTRACT: Ring-opening polymerization of the all-trans isomer of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane (**1**) using $(PhMe_2Si)_2Cu(CN)Li_2$ affords nearly quantitative conversion to polymer with 75% heterotactic and 25% isotactic triads as determined by ^{29}Si NMR spectroscopy. Polymerization of a mixture of the stereoisomers of **1** leads to a polymer with 58% heterotactic, 15% syndiotactic, and 27% isotactic triads. The polymerization initiated with silyl cuprates occurs with inversion of configuration at both the attacked silicon atom and the newly formed reactive center. The polymers have molecular weights up to 30 000 depending on the ratio of $[M]_0/[I]_0$ with $M_w/M_n \geq 1.5$. Kinetic measurements show a first-order dependence on monomer concentration and also on initiator concentration.

Introduction

Polysilylenes (polysilanes) are an interesting class of polymers which consist of a linear chain of silicon atoms carrying two substituents, generally alkyl or aryl.[1-3] Interest in these materials stems from their unique properties such as σ-catenation and thermochromic behavior. They have potential applications as photoresists, as electrooptical and nonlinear optical materials, and also as precursors to silicon carbide.

The electronic properties of polysilylenes depend on the conformation of the silicon backbone, which can be affected by the configuration of the substituents. Temperature also plays an important role in the conformation of the backbone as evidenced by the many cases in which thermochromic behavior has been observed.[4-6] Polysilylenes have been prepared by several methods including (1) the reductive coupling of dichlorosilanes,[1-3,7,8] (2) dehydrogenative coupling of hydridosilanes,[9-11] (3) anionic polymerization of masked disilenes,[12] and (4) ring-opening polymerization of cyclotetrasilanes.[13,14] Each of these methods possesses its own advantages and disadvantages. In ring-opening polymerization, the resulting polymer microstructure depends on the configuration of the monomer used for polymerization and also on the mechanism of the polymerization, which in turn depends on the catalyst or initiator used and the polymerization conditions.

Recent reports have described the synthesis and characterization of the isomeric 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilanes (**1**), the first all-silicon-containing rings which have been polymerized.[13] Ring-opening polymerization (ROP) of these monomers allows the preparation of well-defined polysilanes with controlled molecular weights, relatively low polydispersities, and defect-free structures. ROP allows for potential control over the resulting microstructure if the monomers, with known configurations of substituents, can be opened in a controlled manner. In addition, ROP of cyclotetrasilanes affords the possibility of preparing polymers with functionalities which would not survive other polymerization techniques as well as the preparation of well-defined copolymers and block copolymers.[15]

Experimental Section

1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. The stereoisomeric forms were prepared by previously reported methods.[13] Upon recrystallization from cold hexane isomer **1a** was obtained 95% purity. The monomer was stored in hexane and dried before use.

Silyl Cuprate. $(PhMe_2Si)_2Cu(CN)Li_2$ was prepared by the addition of 2 equiv of $PhMe_2SiLi$ to a stirred suspension of CuCN in THF at −40 °C, similar to literature procedures.[16]

A typical polymerization experiment involved dissolving 0.100 g of **1a** in 1 mL of THF. To this stirred solution was added 2 mol % of cuprate initiator. The solution turned light brown and the color persisted for 1 h, at which time ^1H NMR showed 99% conversion to polymer. The polymer was precipitated into 2-propanol and the filtered product dried in a vacuum oven, yielding 0.070 g of white powder (70% gravimetrically). All analyses were carried out with the precipitated and dried polymer.

Wide-angle X-ray scattering (WAXS) measurements were performed on a Siemens D-500 refractometer with a 0.3° slit size using a 1.541-Å Cu Kα X-ray source with a graphite monochromator and a scintillation counter detector with a step size of 0.04° from $2 \leq 2\theta \leq 32°$ and a measuring time of 4 s. WAXS samples were prepared in a Cu boat as pressed powder and heated at 130 °C for 20 min before acquisition.

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters 510 HPLC equipped with a 410 differential refractometer and a Waters 991 photodiode array detector with THF as an eluent and a flow rate of 1.0 mL min^{-1}. Three Ultrastyragel columns (100 Å, 500 Å, and linear) were used in series. The molecular weights are reported relative to a calibration curve obtained using polystyrene standards. Previous results obtained by Devaux et al. using an on-line light scattering detector indicated that in the molecular weight range from 5000 to 100 000 the molecular weights determined for PMPS relative to polystyrene standards corresponded relatively well to absolute molecular weights.[17]

NMR measurements were performed using an IBM NR-300 spectrometer. ^1H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra at 75.4 MHz, and ^{29}Si NMR spectra at 59.6 MHz, using a standard Bruker DEPT microprogram. All spectra were obtained using C_6D_6 as the solvent and C_6H_6 as an internal reference for ^1H and ^{13}C; TMS was used as an external standard for ^{29}Si.

Kinetic measurements were performed in NMR tubes using THF-d_8 as the solvent. $Me_4Ph_4Si_4$ was dissolved in THF-d_8, transferred to an NMR tube, and sealed with a septum and Teflon tape. The initiator was taken into a syringe and then the syringe needle placed through the septum, but not injected. The initiator was injected, the sample was shaken well, and then NMR experiments were performed immediately, with the first spectrum being taken after a calculated 80 s had elapsed. Conversion was followed by ^1H NMR spectroscopy on a GE 300-MHz spectrometer.

® Abstract published in *Advance ACS Abstracts,* February 15, 1995.

0024-9297/95/2228-1618$09.00/0

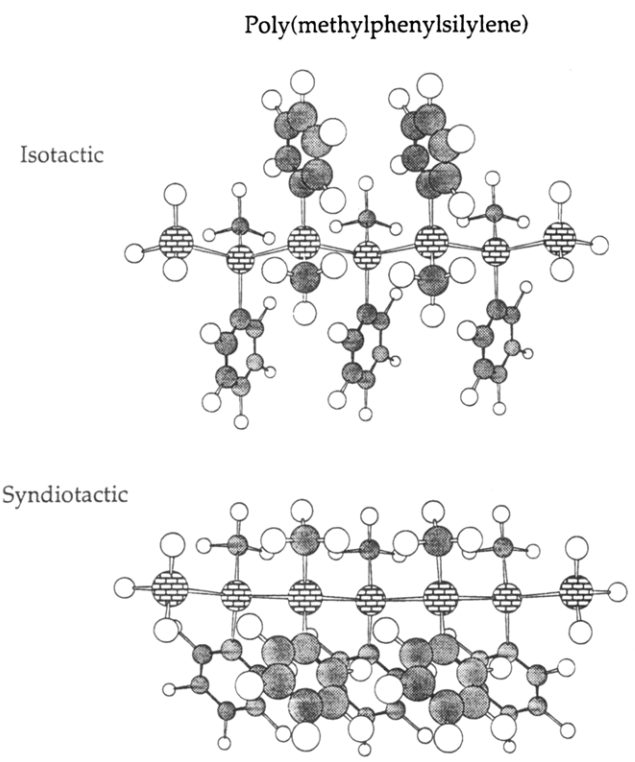


Figure 1. Short segments of (a) isotactic and (b) syndiotactic PMPS depicted in the planar, all-trans zigzag conformation. View is from the top looking down on the backbone.

Materials. Hexane was dried over LAH and distilled prior to use. THF was dried over sodium benzophenone, distilled, and then vacuum transferred from Na/K alloy prior to use. Benzene was refluxed over potassium and distilled under argon prior to use. *n*-BuLi (1.6 M in hexanes; Aldrich) was used as received.

Results and Discussion

Microstructure of Poly(methylphenylsilylene) (PMPS). In poly(methylphenylsilylene) (PMPS) each silicon atom in the chain is pseudoasymmetric,[18] and therefore the stereochemistry can be used to describe the microstructure of the chain. The simplest picture of the microstructure can be given by an analysis of triads, or three silicon atom sequences. The configurations of the two neighboring atoms relative to the stereochemistry at the observed silicon atom determine the microstructure of the triad. A mm triad, corresponding to isotactic sequences, results when the configurations of the two neighboring silicon atoms are meso relative to the configuration of the central silicon atom. A rr triad, corresponding to syndiotactic sequences, results when the configurations of the two neighboring silicon atoms are both racemic relative to the configuration of the central silicon atom. A rm or mr triad, corresponding to heterotactic sequences, results when the configurations of the two neighboring silicon atoms are racemic and meso, or vice versa with respect to the configuration of the central silicon atom.

Pictorial descriptions of syndiotactic and isotactic triads are shown in Figure 1. It must be stressed that in syndiotactic PMPS, existing in the fully extended planar zigzag conformation, all of the phenyl groups are on one side and all of the methyl groups are on the other side of a plane passing through the backbone. This is in contrast to a typical vinyl polymer, where the stereocenters are separated by methylene units and the substituents would be on one side in the isotactic polymer. However, in both systems mm and rr sequences correspond to isotactic and syndiotactic structures, respectively.

^{1}H NMR spectra of PMPS possess broad peaks with very little detail for both the aromatic and methyl regions, which may be due to the shielding effects of the aromatic groups. ^{29}Si NMR spectra contain information which can be analyzed more successfully to determine the microstructure of the polymer. For PMPS prepared via the reductive coupling route, three broad resonances, in the ratio of 3:3:4, are present between −38.5 and −41.0 ppm. The peaks have been previously tentatively assigned to isotactic, syndiotactic, and heterotactic triads, respectively.[19] The assignments were based upon the corresponding six-membered rings where the molecules are forced into cis and gauche conformations as opposed to trans and gauche for the linear chains. Shielding effects of the phenyl rings depend on the conformation and therefore in the cyclics may be different from those in the polymer chains.

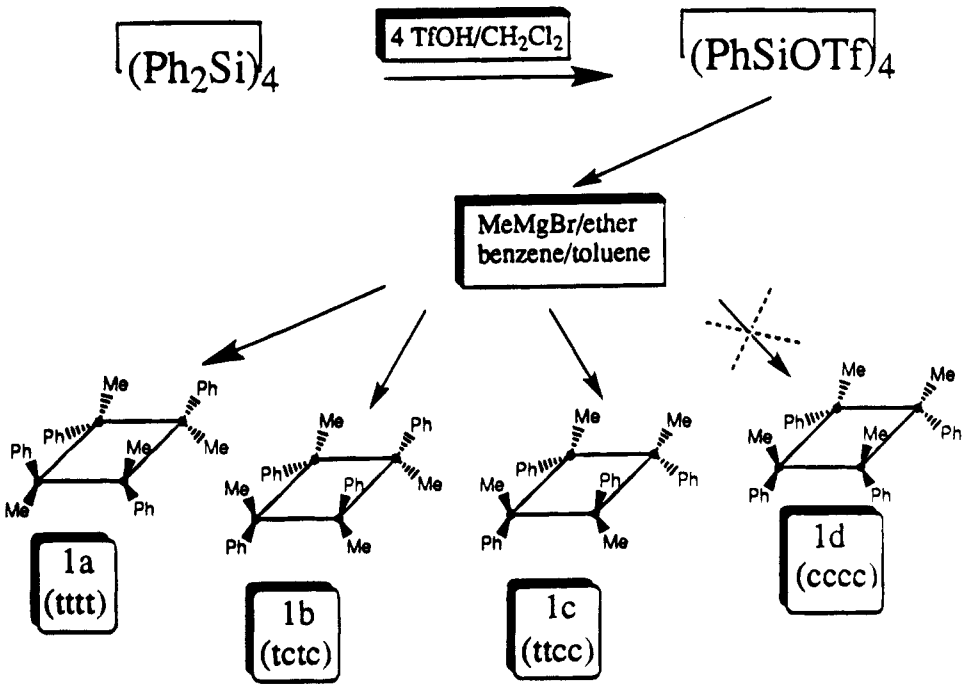
Synthesis and Characterization of Monomers. The monomers used for the ring-opening polymerization of cyclotetrasilanes are prepared via the route shown in Scheme 1. Polymerization of octaphenylcyclotetrasilane is not possible due to several factors including high crystallinity which causes very low solubility (<1% in most organic solvents) resulting in monomer concentrations below the equilibrium monomer concentration, repulsive interactions of the bulky phenyl groups upon ring opening to a linear structure which offset the release of angular ring strain, and slow attack at the Ph_2Si units that leads to the formation of the relatively stable Ph_2Si anion. However, replacing some of the bulky phenyl groups with methyl groups results in a monomer in which the ring strain is preserved, but smaller repulsive interactions are present in the ring-opened product. The new monomer is less crystalline and thus results in higher solubilities. Additionally, attack of a propagating chain at a PhMeSi unit is faster than that at a Ph_2Si unit.

Replacement of phenyl groups with methyl groups is accomplished in a two-step process, the first of which is a dearylation reaction using trifluoromethanesulfonic acid (triflic acid). Four equivalents of the acid are used to remove four of the phenyl groups, resulting in the 1,2,3,4-tetrakis(trifluoromethanesulfonato)-1,2,3,4-tetraphenylcyclotetrasilane derivative.[20] Nucleophilic substitution of the trifluoromethanesulfonate groups using methylmagnesium bromide yields 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane in high yields (95%).

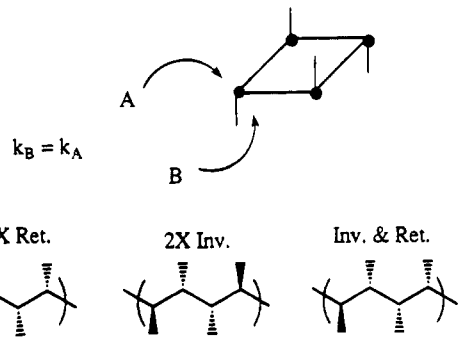
The synthesis results in a mixture of three different isomers: **1a**, **1b**, and **1c**. The dominating isomer is present in 55% abundance and can be enriched to 95% by repeated crystallizations from cold hexanes. The dominating isomer has been shown to possess an all-trans structure of substituents and was assigned to **1a**.[21] The mother liquor contains a different proportion of **1a**, **1b**, and **1c** (28%, 14%, 58%, respectively). The other two isomers, **1b** and **1c**, have been assigned as well by NMR analysis but to date have not been separated into individual components.

The ROP method has several disadvantages including the difficult synthesis of monomers, purification and isolation of individual isomers, and the low oxygen and moisture stability of the compounds. However, the method is valuable for the preparation of well-defined materials, enabling one to correlate properties with structures.

Scheme 1



Scheme 2



	[(rrr)r/m]$_n$	[(mmm)m/r]$_n$	[(mrr)m/r]n
	2 X RET	2 X INV	INV & RET.
% syndio (rr)	75	-	37.5
% iso (mm)	-	25	12.5
% atact (mr=rm)	25	75	50

Possibilities for Resulting Microstructures. Ring-opening polymerization of **1a** to form the linear polymer **2** can result in a variety of different microstructures depending on the mechanism. Scheme 2 depicts three different scenarios based on different combinations of retentions and inversions of configuration. These possibilities assume that attack of the growing chain can occur with equal probability on either of the two equivalent prochiral faces in the monomer unit.

If the polymerization occurs with retentions of configuration at both the attacked silicon atom and the newly formed reactive center, then a series of racemic sequences will be formed. Since there is an equal probability of attack at either of the two prochiral faces of each silicon atom in the monomer, connections between individual monomer units may be either racemic or meso in nature. The probability for a meso juncture may be equal to that for a racemic one, resulting in a microstructure sequence of [(rrr)r/m]. This sequence would lead to a polymer with 75% syndiotactic triads, 25% heterotactic triads, and 0% isotactic triads. If ring opening occurs with inversions of configuration at both the attacked silicon atom and the newly formed active site, a series of heterotactic triads is formed. A similar statistical analysis leads to a microstructure sequence of [(mrm)r/m], and a polymer with 75% heterotactic, 25% isotactic, and 0% syndiotactic triads results. If the polymerization occurs with a combination of inversions and retentions of configuration at the attacked silicon atom and the new active center, formation of all three triads is possible. The end result would be a polymer with 37.5% syndiotactic triads, 12.5% isotactic triads, and 50% heterotactic triads. If the polymerization occurs with a combination of any of the three described scenarios, it becomes more difficult to determine the microstructures and therefore the mechanism by which it is formed. Nevertheless, successful fits of the ^{29}Si NMR spectra of more complex polymerization routes have been made and will be discussed later.

Nomenclature. To simplify the following discussion of microstructure in PMPS prepared by the various routes, a series of abbreviations will be used. For polysilylene, PS, prepared by the reductive coupling (RC) route, will be referred to as PSRC; for the polymer prepared by the *n*-BuLi (**Li**) initiated polymerization of the all-trans (T) isomer and the mixture (M) of stereoisomers, PSTLi and PSMLi will be used, respectively. For polymers prepared by polymerizations of the all-trans isomer and the mixture of stereoisomers using silyl cuprates, Cu, PSTCu, and PSMCu will be used, respectively.

Ring-Opening Polymerization. Si–Si bonds can be cleaved by a variety of nucleophiles.[22] Polysilylene chains can be degraded in the presence of strong nucleophiles to give mixtures of five- and six-membered rings, which are the thermodynamic products.[23] Since the linear polymers are kinetic products, only polymerization conditions which favor the kinetic products can be used. 1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilanes were polymerized using anionic or nucleophilic initiators including *n*-BuLi/[2.1.1]cryptand and silyl cuprates. Initial results using *n*-BuLi in benzene with [2.1.1]cryptand indicated that 100% con-

Table 1. Cuprate Initiators Utilized for the Polymerization of $Me_4Ph_4Si_4$ in THF Solution

initiator	temp (°C)	$[M]_0/[I]_0$	polymer	M_n	M_w/M_n
n-$Bu_2Cu(CN)Li_2$	20	0.20/0.002	yes	29 900	2.8
n-BuCu(CN)Li	−30	0.16/0.001	no		
$(Ph_2MeSi)_2Cu(CN)Li_2$	20	0.21/0.004	yes	11 800	2.1
$(PhMe_2Si)_2Cu(CN)Li_2$	20	0.11/0.002	yes	11 500	1.5
$(PhMe_2Si)_2Cu(CN)Li_2$	−30	0.28/0.003	yes	20 700	1.7
$(PhMe_2Si)MeThCu(CN)Li_2$[a]	20	0.21/0.004	yes	24 700	1.7
$(PhMe_2Si)Cu(CN)Li$	20	0.59/0.006	no		
n-Bu_2CuLi	20	1.0/0.01	no		
n-BuMeThCuLi[a]	20	0.27/0.003	no		

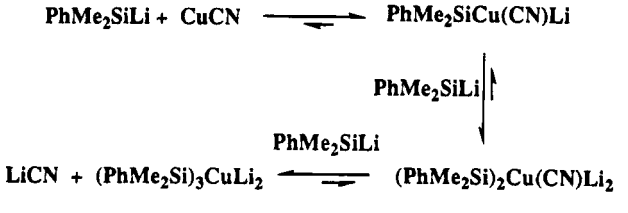
[a] MeTh = 3-methylthienyl.

version to PSMLi was possible without degradation to five- and six-membered rings via a backbiting process as long as the reactions were terminated after 1 h (the backbiting process was not evidenced until 3 h). However, if n-BuLi is used in tetrahydrofuran (THF), degradation competes with propagation, giving rise to a mixture of cyclic products.

The ^1H NMR spectrum for PSMLi contains broad and nearly featureless resonances for both the methyl and phenyl protons; similar to the spectrum obtained for PSRC. The ^{29}Si NMR spectrum of PSTLi displays three resonances in the ratio 4:1:3 present at −38.5, −39.2, and −40.7 ppm, respectively. The three resonances are identical in chemical shift to those reported by West et al. for PSRC,[19] but the ratio is considerably different.

Because it was apparent that using Li^+ as the counterion did not lead to the desired level of control over the polymer microstructure, other systems were explored. The use of cuprates for the anionic polymerization of methyl methacrylate has been reported and resulted in poly(methyl methacrylate) with regular structures.[24] A silyl cuprate, $(PhMe_2Si)_2Cu(CN)Li_2$, has been used for the ring-opening polymerization of 1,2-disilacyclopentane, yielding nearly quantitative conversion of the monomer to linear polymer with molecular weight distributions as low as 1.3.[25] These results prompted the use of cuprates for the polymerization of cyclotetrasilanes.

Ring-Opening Polymerization with Silyl Cuprates. Cuprates are generally complex systems which can aggregate and form dimers and higher aggregates.[26] The structures of cuprates are not widely understood, but some systems have been studied in detail. Silyl cuprates, $(PhMe_2Si)_nCu(CN)Li_n$, studied in detail by Oehlschlager,[16] display equilibria between the higher and lower order cuprates, with equilibrium constants depending on the ratio of R_3SiLi to Cu. No free R_3SiLi was observed:



A series of cuprates and silyl cuprates were prepared and used as initiators for the ROP of **1**. The polymerization results are listed in Table 1. The results varied widely, with the silyl cuprates affording the best results with regard to the conversion of monomer and the molecular weight distributions. The use of $(PhMe_2Si)_2Cu(CN)Li_2$ (**3**) in THF yielded the most effective initiator for polymerization and resulted in nearly quantitative (>95% in most cases) conversion to polymer, PSMCu. However, when the lower order analogue, $PhMe_2SiCu(CN)Li$ (**4**), was used, no polymerization was observed.

Despite using **3** in THF, no depolymerization or transsilylation to form cyclic compounds is observed, even after allowing the solution to stand for 12 h, in contrast to the BuLi system in THF, where degradation competes with propagation. Another feature of this initiation system is the apparently higher tolerance to impurities. Considerably lower concentrations of cuprates as initiators compared to BuLi could be used (3.3×10^{-3} vs 1.0×10^{-2} mol/L), which affords the possibility of obtaining higher molecular weight polymers. Finally, the molecular weight distributions are considerably narrower as compared to those of BuLi-initiated polymerizations, $M_w/M_n \geq 1.5$ versus approximately ≈ 2.0 at comparable molecular weights.

Microstructure of PMPS Prepared with Silyl Cuprates. The polymerization of **1** initiated by **3** provided a significant improvement over normal anionic systems, with respect to molecular weights and molecular weight distribution, but the most dramatic difference was in the polymer microstructure. ^1H NMR spectra of PSTLi, PSRC, PSTCu, and PSMCu are shown in Figure 2. The methyl region of the spectrum for PSTCu shows more clearly defined peaks and covers a narrower chemical shift range than is observed for PSRC and PSTLi, 0.7 versus 1.0 ppm, respectively. The sharper lines indicate some degree of regularity imparted into the system and indicate a different microstructure for PSTCu than for PSTLi or PSRC. The aromatic regions of all of the polymers are quite similar.

^{13}C NMR spectra for PSTLi, PSRC, PSTCu, and PSMCu are given in Figure 3. The methyl region of the spectrum of PSTLi is similar to that for PSRC; however, the methyl region of PSTCu contains one dominating signal, which is an indication of one particular type of microstructure. The intensity ratio and number of the peaks in the ^{13}C NMR spectrum do not correlate well with the ratio of peaks in the ^1H NMR spectrum. This discrepancy may be due to the promixity of the methyl carbons to the backbone causing them to be more sensitive to longer structural sequences, such as tetrads, pentads, etc., in PMPS than are the methyl protons.

Figure 4 contains the ^{29}Si NMR spectra for PSTLi, PSRC, PSTCu, and PSMCu. There are three broad resonances present in different ratios in the spectra for PSTLi and PSRC, but the spectrum for PSTCu contains only two resonances. Even though reliable integration is not possible for spectra obtained using the DEPT program, silicon atoms with identical substituents should be enhanced to the same degree; therefore, the relative intensities should give an indication of the percentages of the particular signals. The two peaks in the spectrum of PSTCu are in a 3:1 ratio.

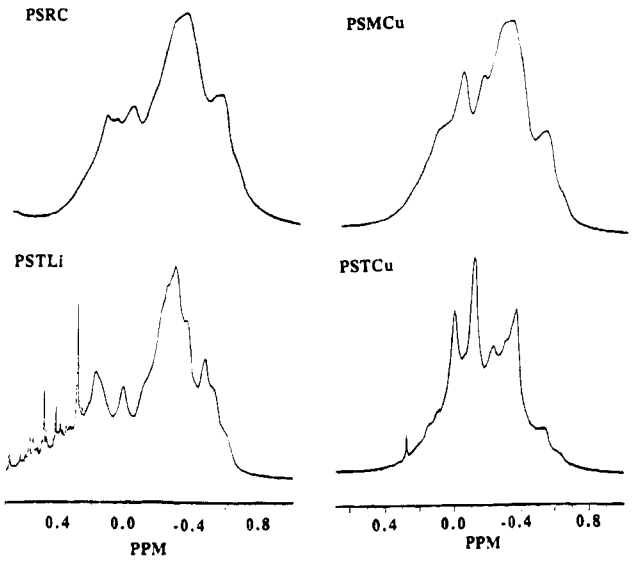


Figure 2. Methyl regions of the 300-MHz ^{1}H NMR spectra of (a) PSRC, (b) PSTLi, (c) PSMCu, and (d) PSTCu in C_6D_6. Residual C_6H_6 was used as an internal reference.

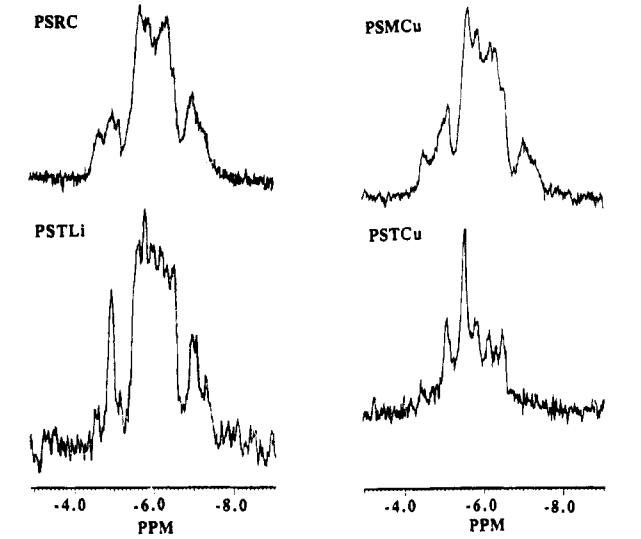


Figure 3. Methyl regions of the 75.4-MHz ^{13}C NMR spectra of (a) PSRC, (b) PSTLi, (c) PSMCu, and (d) PSTCu in C_6D_6. Spectra were obtained using a standard Bruker DEPT microprogram for carbon and are referenced internally to C_6H_6.

In Scheme 2, two possibilities for polymerization routes leading to 3:1 ratios of microstructures were presented. These mechanisms resulted in 75% syndiotactic and 25% heterotactic triads and 75% heterotactic and 25% isotactic triads. However, based on the previously reported assignments of configuration, the two peaks should correspond to 75% isotactic and 25% heterotactic triads.[19] Regardless, differentiating between the two possible mechanisms of polymerization is important because the different microstructures could have different effects on the electronic properties of the polymer. In fact, it has been predicted that syndiotactic PMPS is the most likely structure to exist in a planar, all-trans zigzag, which should give rise to a higher value of λ_{max}.[27]

Microstructural Assignments. Assignment of the ^{29}Si NMR signals to specific microstructures was achieved by comparison of the ^{29}Si NMR spectra of PSTCu and PSMCu. The possible microstructures resulting from the polymerization of **1a** and a mixture of **1a**, **1b**, and **1c** (28%, 14%, and 58%, respectively) are shown in Table

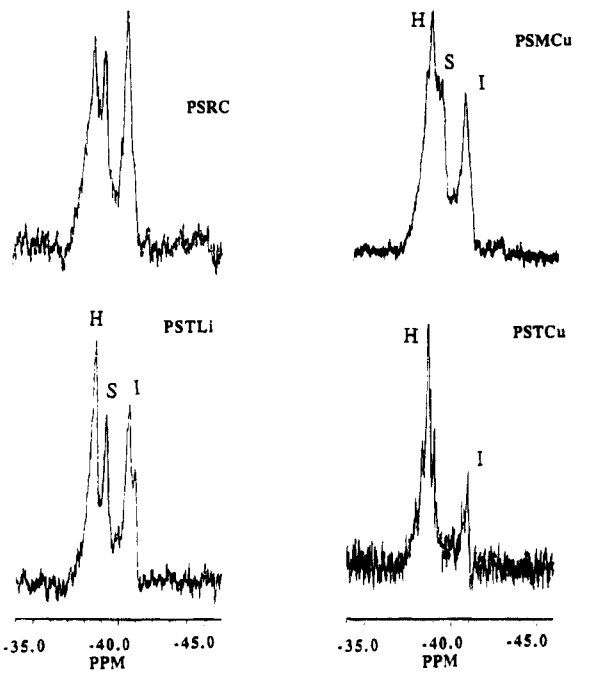
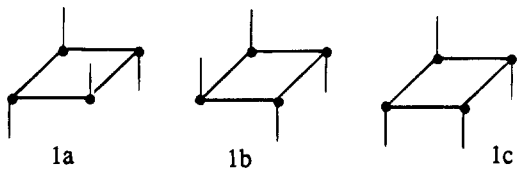


Figure 4. 59.6-MHz ^{29}Si NMR spectra of (a) PSRC, (b) PSTLi, (c) PSMCu, and (d) PSTCu in C_6D_6. Spectra were obtained using a standard Bruker DEPT microprogram. Spectra are referenced externally to TMS.

Table 2. Expected Tacticities for Cuprate Polymerization of 1a and a Mixture of Isomers: 28% 1a, 14% 1b, and 58% 1c



Mixt. **1a**	% hetero.	% syndio.	% iso.
2 X Ret.	*46.5* **25.0**	*37.25* **75.0**	*16.25* **0.0**
2 X Inv.	*53.5* **75.0**	*19.75* **0.0**	*26.75* **25.0**
Inv./Ret.	*35.5* **50.0**	*35.75* **37.5**	*28.75* **12.5**
Ret./Inv.	*64.5* **50.0**	*21.25* **37.5**	*14.25* **12.5**
Obs. mix.	*58.0*	*15.0*	*27.0*
Obs. 1a	**75.0**	**0.0**	**25.0**

2. The numbers in the upper left-hand corner of each box are for the polymerization of the mixture of stereoisomers, and the numbers in the lower right-hand corner correspond to the polymerization of **1a**. The following assumptions were made in calculations of the values for Table 2: (1) the stereoselectivity of ring opening is not affected by the configuration of the individual rings, (2) the reactivities of the rings are similar, and (3) the probability of attack at either of the faces of each silicon atom in the rings is equivalent. It should be noted that the absence of the all-cis isomer, **1d**, results in a nonstatistical distribution of triads (i.e., not 50% heterotactic, 25% syndiotactic, and 25% isotactic).

Because **1c** dominates the monomer mixture, it should also dominate the resultant microstructure. According to the predictions in Table 2, the highest

intensity peak in the ^{29}Si NMR spectrum for PSMCu (the most downfield peak; Figure 4) should be assigned to the heterotactic triads. The most upfield peak can be assigned by analysis of the spectrum of PSTCu. Because the spectrum of PSTCu contains only two peaks and the most downfield peak is assigned to heterotactic triads, the upfield peak must be assigned to the isotactic triads (Scheme 2). Therefore, the third peak in the spectrum for PSMCu between the heterotactic and isotactic triads must be assigned to the syndiotactic triads. In summary, the polymerization of **1a** and the mixture of **1a**, **1b**, and **1c** appear to proceed with two inversions of configuration at both the attacked silicon atom in the ring and the newly formed reactive center. Previous reports from our group have indicated that the most likely microstructure was predominantly syndiotactic based on two retentions of configuration.[28] This polymerization mechanism was expected by intuitive arguments involving the steric interactions of the cuprate and the more covalent Cu–Si bond compared to the Si–Li bond in the presence of cryptand. The reasons for two inversions of configuration will be discussed later.

For PSTLi, the ratio of intensities corresponds the closest to the polymerization mechanism in which there is a combination of inversions and retentions of configuration. This indicates that the control over the stereochemistry at the newly formed reactive site is lower with Li as the counterion solvated by [2.1.1]cryptand than with silyl cuprates. The reaction appears to occur with an inversion of configuration at the attacked silicon atom and incomplete racemization at the newly formed reactive center.

Kinetic Studies

Kinetic measurements were performed with this system to gain a further understanding of the reaction mechanism. Kinetic measurements were performed using ^1H NMR spectroscopy to follow the conversion of monomer to polymer. The first spectrum, in all experiments, was acquired after approximately 80 s, at which time up to 20% conversion had already taken place in some cases (at the higher $[I]_0$ values). A representative time–conversion plot is shown in Figure 5 and indicates first-order behavior with respect to monomer and the overall kinetics obeying the equation:

$$-\mathrm{d}[M]/\mathrm{d}t = k_{app}[M][I]_0^{\,n}$$

Similar plots were obtained for all kinetic runs.

Figure 6 displays a logarithmic apparent rate constant of propagation versus initiator concentration. The slope of the fit is nearly equal to $n = 1.0$, which indicates a first-order relationship with respect to initiator concentration. The first-order dependence indicates that either the aggregation state remains constant over this concentration range or the reactivities of different aggregation states are similar. An Arrhenius plot is shown in Figure 7. An activation energy, $E_a = 8.1$ kcal/mol, was calculated for this system.

Proposed Mechanism. Determination of the microstructure of PSTCu along with the kinetic data allows a tentative proposal for a polymerization mechanism using silyl cuprates which is depicted in Scheme 3. A pentacoordinate silicon intermediate is proposed, with the incoming chain and the exiting reactive center in apical positions. Because of the potential aggregation of the cuprate, attack, with inversion of configuration,

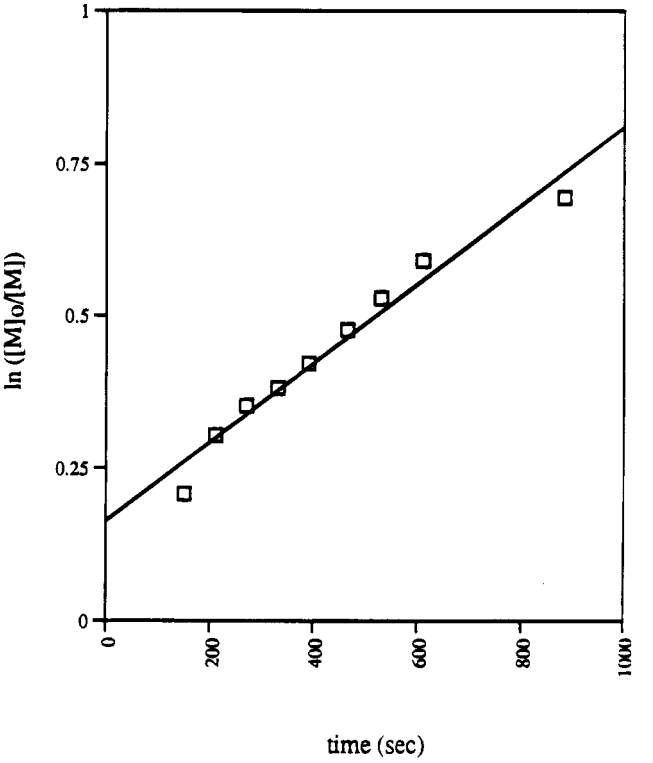


Figure 5. Time–conversion plot for the polymerization of **1a** in THF-d_8 (0.26 mol/L) initiated with $(PhMe_2Si)_2Cu(CN)Li_2$ (0.005 mol/L) at 22 °C. Conversions were determined by comparison of the integration of the methyl region for the monomer with the polymer.

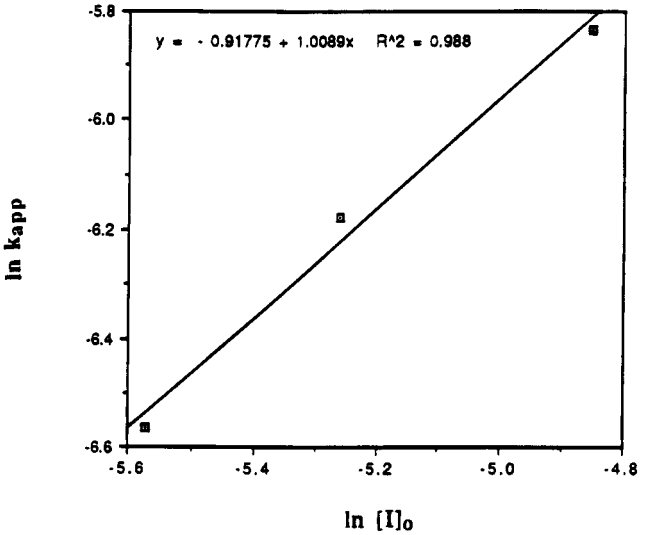


Figure 6. Plot of k_{app} versus initiator concentration for the polymerization of **1a** initiated with $(PhMe_2Si)_2Cu(CN)Li_2$ in THF-d_8 at 22 °C.

at one of the ring silicon atoms may result from the presence of other metal centers, Cu or Li, which could aid inversion of the newly formed reactive center. The first-order dependence of the polymerization rate on monomer indicates that the first step, attack of the growing species at one of the silicon atoms in the incoming monomer ring, is the rate-determining step.

Attack of the propagating center on the monomer has a significant effect on the resultant microstructure. As described earlier, the attack can occur with equal probability on either of the two prochiral faces of each silicon atom in the ring and, therefore, the connections between monomer units are random. Low-temperature

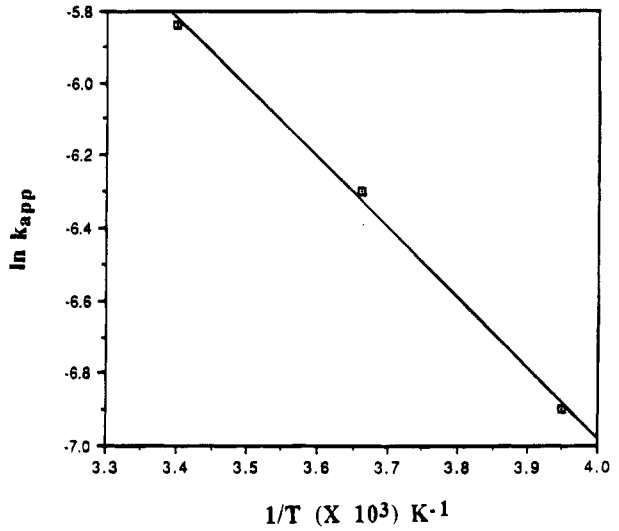
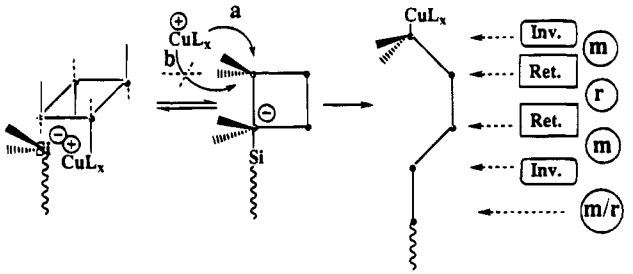


Figure 7. Arrhenius plot for the polymerization of **1a** initiated with $(PhMe_2Si)_2Cu(CN)Li_2$ in THF-d_8. E_a = 8.1 kcal/mol.

Scheme 3



$CuL_x \Rightarrow$ a>>b; $Li^+/[1.1.2] \Rightarrow$ a≈b

experiments, −40 °C, were performed to examine the energetic difference between the two arrangements, but no effects were observed, indicating the energy difference is very low.

In the polymerization using *n*-BuLi, the mechanism is proposed to occur with inversion of configuration at the attacked silicon atom and racemization at the newly formed reactive center. This may result because of the highly ionic character imparted to the Si−Li bond by the cryptand which could allow the silicon anion to undergo pyrimidal inversion much easier than with silyl cuprates where the Si−Cu bond is more covalent.

Polymer Characterization. The polymers prepared using silyl cuprates and mixed cuprates were characterized by a variety of methods including GPC, DSC, WAXS, UV−vis, fluorescence, and the previously mentioned NMR spectroscopy. The λ_{max} for the PSTCu was found to be 336 nm. This value is 2−4 nm lower than the literature value for PMPS (338−340 nm).[1,2] The lower value can arise because of relatively short isotactic segments which may result in short segments of the trans backbone conformation. This may also give rise to a shorter persistence length for the polymer. Theoretical predictions suggest that the actual chromophores are all-trans chain segments separated by gauche links;[29] therefore, it is likely that the polymer prepared by ROP possesses much shorter segments of all-trans conformations.

Figure 8 contains a plot of WAXS results for PSTCu at various temperatures. DSC had shown no detectable transitions up to 300 °C, whereas the WAXS measurements indicated a transition near 137 °C. The room temperature plot displayed one sharp peak present at

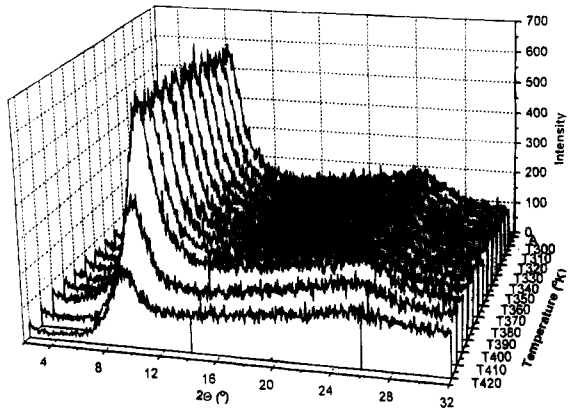


Figure 8. Variable-temperature WAXS data for PSTCu.

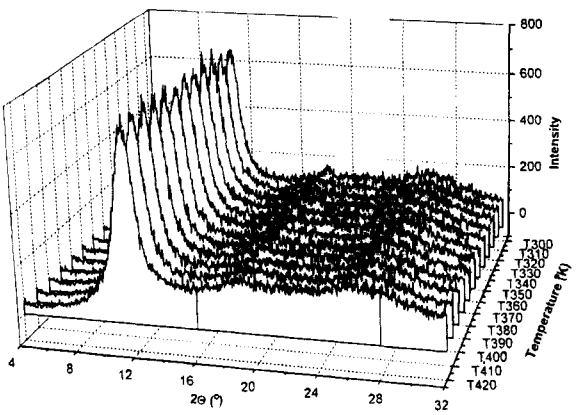


Figure 9. Variable-temperature WAXS data for PSTLi.

9.7 Å, which may be assigned to the interchain distance, and a broad peak centered at 3.7 Å. As the temperature is increased, no changes were observed until 137 °C was reached, at which point the intensity of both peaks began to decrease. By 147 °C the 9.7 Å peak was weaker and the broader peak at 3.7 Å was barely perceptible. The tentative assignment of the observed changes in WAXS is based on the loss of the long-range order in the polymer with sufficiently long $(mr)_n$ runs which might be able to crystallize.

WAXS measurements on PSTLi did not show a similar transition in the same temperature range (Figure 9). The room temperature diffraction pattern showed the same intensity for a peak at 9.7 Å as for PSTCu at lower temperatures; also present are two broader, but defined, peaks centered at 5.2 and 3.7 Å, respectively. PSTLi contains a larger proportion of isotactic and syndiotactic triads. However, they cannot form sufficiently long sequences to exhibit long-range order.

Conclusions

Ring-opening polymerization of the all-trans isomer of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane using silyl cuprates leads to poly(methylphenylsilylene) with a microstructure consisting of 75% heterotactic triads and 25% isotactic triads. Nearly quantitative conversions to polymer were observed without the presence of backbiting to cyclics. Molecular weights of up to 30 000 were achieved with molecular weight distributions, M_w/M_n, ≥1.5. Polymerization of a mixture of stereoisomers (28% **1a**, 14% **1b**, and 58% **1c**) with silyl cuprates leads to polymer with 58% heterotactic triads, 15% syndiotactic, and 27% isotactic triads. The polymerization mechanism proceeds via a route in

which two inversions of configuration occur at both the attacked silicon atom in the ring and the newly formed reactive center.

Acknowledgment. The authors than the National Science Foundation and the Office of Naval Research for financial support. Michael White is acknowledged for performing WAXS measurements on the samples of PMPS under the direction of Dr. T. Pakula at the Max-Planck-Institut, Mainz, Germany.

References and Notes

(1) Michl, J.; Miller, R. D. *Chem. Rev.* **1989**, *89*, 1359.
(2) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
(3) Matyjaszewski, K.; Cypryk, M.; Frey, H.; Hrkach, J.; Kim, H. K.; Moeller, M.; Ruehl, K.; White, M. *J. Macromol. Sci., Chem.* **1991**, *A28*, 1151.
(4) Miller, R. D.; Farmer, B. L.; Fleming, W. W.; Sooriyakumaran, R.; Rabolt, J. F. *J. Am. Chem. Soc.* **1987**, *109*, 2509.
(5) Schilling, F. C.; Lovinger, A. J.; Davis, D. D.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1989**, *22*, 3055.
(6) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1994**, *27*, 881.
(7) Biran, C.; Bordeau, M.; Pons, P.; Leger, M.-P.; Dunogues, J. *J. Organomet. Chem.* **1990**, *382*, C17.
(8) Kunai, A.; Toyoda, E.; Kawakami, T.; Ishikawa, M. *Organometallics* **1992**, *11*, 2899.
(9) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.
(10) Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11.
(11) Corey, J. Y.; Zhu, X. H. *Organometallics* **1992**, *11*, 672.
(12) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641.
(13) Cypryk, M.; Gupta, Y.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046.
(14) Matyjaszewski, K.; Chen, Y. L.; Kim, H. K. *ACS Symp. Ser.* **1988**, *360*, 78.
(15) Fossum, E.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, (2), 559.
(16) Sharma, S.; Oehlschlager, C. *Tetrahedron* **1989**, *45*, 557.
(17) Strazielle, C.; De Mahieu, A. F.; Daoust, D.; Devaux, J. *Polymer* **1992**, *33*, 4174.
(18) Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2309.
(19) Maxka, J.; Mitter, F. K.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 660.
(20) Chrusciel, J.; Cypryk, M.; Fossum, E.; Matyjaszewski, K. *Organometallics* **1992**, *11*, 3257.
(21) Fossum, E.; Gordon-Wylie, S. W.; Matyjaszewski, K. *Organometallics* **1994**, *13*, 1695.
(22) Ishikawa, M.; Kumada, M. *Chem. Commun.* **1970**, 612.
(23) Kim, H. K.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, C299.
(24) Dimonie, M.; Mardare, D.; Coca, S.; Hogen-Esch, T. E.; Zoller, J. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 175.
(25) Suzuki, M.; Obayashi, T.; Kotani, J.; Morishima, Y.; Saegusa, T. *Polym. Prepr. Jpn. (Engl. Trans.)* **1990**, *39*, E871.
(26) Posner, G. H. *An Introduction to Synthesis using Organocopper Reagents; Wiley-Interscience: New York*, 1980.
(27) Sundararajan, P. R. *Macromolecules* **1988**, *21*, 1256.
(28) Chrusciel, J.; Fossum, E.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 221.
(29) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7438.

MA9413249