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Synthesis and characterization of cyano-substituted disilacyclobutane rings and poly(silylenemethylene) polymers

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Abstract

The synthesis, and characterization by nuclear magnetic resonance (NMR) spectroscopy, of two cyano-substituted 1,3-disilacyclobutanes, 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane, $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_2$, and 1,1,3,3-tetracyano-1,3-disilacyclobutane, $[\text{Si}(\text{CN})_2\text{CH}_2]_2$, are reported. Evidence for a *trans/cis* exchange process in solution was obtained in the case of $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_2$, where the initially obtained all-*trans* isomer was observed, by NMR spectroscopy, to rearrange to a mixture of the *cis* and *trans* isomers. The corresponding poly(silylenemethylene) (PSM) polymers, $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_n$ and $[\text{Si}(\text{CN})_2\text{CH}_2]_n$, were obtained in, respectively, fully and partially substituted form by means of exchange reactions carried out on the corresponding chloro-PSMs with trimethylsilyl cyanide. The $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_n$ polymer, which is a silicon analog of poly(methacrylonitrile), was found to exhibit a glass transition at 33 °C.

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1. Introduction

The poly(silylenemethylene)s (PSMs) $[\text{SiRR}'\text{CH}_2]_n$ are a unique class of linear organic/inorganic hybrid polymers that effectively bridge the gap between the all-carbon backbone polyolefins and such inorganic polymers as the poly(silane)s, poly(siloxane)s (PSOs) and poly(phosphazene)s (PPPs) [1]. Analogous to the PPPs, substitution reactions on preformed (Si)–X (X = Cl, Br, OR) polymers can be used to obtain a wide range of new polymers that contain various organic or inorganic groups directly bonded to the main chain Si atoms [2]. For example, we have previously reported the use of the X = OR group in this manner to obtain the first (Si)–F polymers, $[\text{SiF}(\text{Me})\text{CH}_2]_n$ [3] and $[\text{SiF}_2\text{CH}_2]_n$ [4] (PFSM). PFSM is of particular interest, since by analogy to poly(vinylidenedifluoride), [5] an appropriately poled sample with the polymeric chains aligned in

the all-*trans* conformation could potentially possess piezoelectric and pyroelectric activity. When considering other electronegative substituents for analogous PSMs we became interested in the possibility of producing cyano-substituted polymers because the dipole moment of Si–CN is also expected to be quite large.

While organic polymers containing CN groups bonded directly to the polymeric backbone have been thoroughly investigated and are important for their industrial utility (e.g. poly(acrylonitriles) for synthetic textiles, elastomeric material and as precursors to carbon fibers), relatively little is known about their inorganic counterparts [6]. This stems, in part, from the lack of suitable synthetic routes to these polymers. The cyanide ligand is classified as soft by the classical hard/soft Lewis acid/base concept of chemical bonding. As a consequence, nucleophilic substitution of CN^- for the harder Cl^- atom, usually associated with preformed inorganic polymers having hard main chain atoms such as P and Si, is likely to be thermodynamically unfavorable. There has been a report on a synthetic route to stable cyclic phosphazene trimers, $[\text{PR}_2=\text{N}]_3$, with partial CN substitution, but the synthesis of the corresponding cyano-substituted polymers using the

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same methodology resulted in a complex mixture of unstable products [7]. As part of our continuing efforts to prepare and study PSM analogs of important poly(olefins), PSOs and PPPs, we report herein the results of our efforts to prepare the cyano-substituted disilacyclobutanes $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_2$ and $[\text{Si}(\text{CN})_2\text{CH}_2]_2$, and the PSMs $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_n$ and $[\text{Si}(\text{CN})_2\text{CH}_2]_n$.

2. Results and discussion

There are two potential routes to functional PSMs, both of which involve the ring-opening polymerization (ROP) of a 1,3-disilacyclobutane monomer. In one case (Scheme 1, Method A) cyano substituted DSCBs could be prepared and potentially ring-opened to produce the desired cyano-polymers, or alternately, synthetic chemistry on a suitably functionalized preformed polymer could lead to the desired cyano-substituted PSMs (Scheme 1, Method B). Both routes were explored and the results are presented herein.

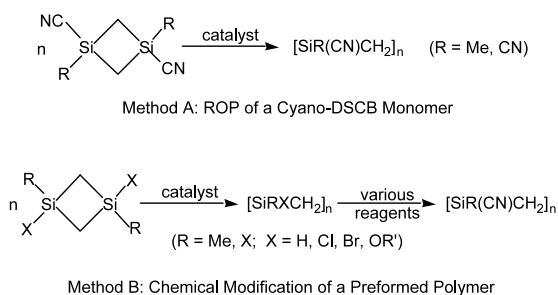
Our initial focus was on the synthesis of the 1,3-(di- and tetra-)cyano-1,3-disilacyclobutanes, $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_2$ and $[\text{Si}(\text{CN})_2\text{CH}_2]_2$, with the expectation that these small molecules would be easier to synthesize, purify and characterize than the corresponding polymers. In addition, the cyano-substituted DSCBs might be expected to yield the desired fully substituted polymers upon ROP, whereas the identical substitution reactions on preformed polymers often lead to incomplete substitution for several reasons, including in this case the hydrolytic instability of both the starting polymer and intended product. Even a small percentage of Si–X groups undergoing hydrolysis would likely lead to the formation of Si–O–Si crosslinks, which would substantially decrease the solubility of the product, thereby limiting the accessibility of reactive sites and hindering complete substitution.

The most attractive synthetic route described in the literature that could be adapted to the production of cyano-substituted DSCBs, is the direct replacement of an alkoxy group on silicon with CN^- using an acetylcyanide [8], since the synthetic route that we

employ to make DSCBs produces them initially with alkoxy substituents [3,9]. However, several attempts to carry out reactions of 1,1,3,3-tetraethoxy-1,3-disilacyclobutane and 1,3-isopropoxy-1,3-methyl-1,3-disilacyclobutane with either pyruvitrile (acetyl cyanide) or *tert*-butylacetyl cyanide, using AlCl_3 as catalyst, were not successful in producing the desired Si–CN substituted reaction products. The inability to recover any of the starting material, or other volatile Si-containing products from the reaction mixture, and the presence of multiple broad resonances that we were unable to assign in the ^{29}Si -nuclear magnetic resonance (NMR) of the reaction mixture, indicates that ring-opening of the starting material and formation of a complex mixture of high molecular weight reaction products likely occurred.

An alternate reaction pathway explored involves the replacement of a silicon halide with CN^- using silver cyanide [10]. Because of the low yield of this exchange reaction expected with the relatively small, hard, Si– Cl_x ($x = 1, 2$) compounds [11] the preparation of the corresponding bromo-DSCB derivatives was undertaken in an effort to provide large, soft anions for subsequent exchange with CN^- upon reaction with AgCN . These previously unreported Si–Br compounds were obtained by utilizing a synthetic route analogous to that used for the preparation of chloro-DSCBs [12]. In this method, the alkoxy-DSCBs are added to acetyl bromide with a small amount of FeCl_3 catalyst, resulting in the production of the desired bromo compounds in high yields. The ^{29}Si -NMR spectra of these compounds are presented in Fig. 1. Of particular interest is the 3:1 ratio of *trans* to *cis* isomers found for the 1,3-dibromo-1,3-dimethyl-1,3-disilacyclobutane, which compares to the 2.3:1 ratio found for the corresponding 1,3-dichloro-1,3-dimethyl-DSCBs produced in the same manner. The higher ratio of the *trans* isomer can be rationalized by the relative sizes of the substituent atoms; since bromine is larger than chlorine, production of the less sterically crowded *trans* isomer is favored, presumably the result of the lower activation energy of the transition state leading to the *trans* form.

Once the bromo-DSCBs were obtained, exchange reactions with AgCN were attempted. The bromo-DSCBs were dissolved in toluene and added to an excess of silver cyanide, and the reaction mixture was refluxed for several days. The visible color change of the silver salt from white (AgCN) to yellow (AgBr) indicated that the reaction was occurring. The compounds 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane (**I**) and 1,1,3,3-tetracyano-1,3-disilacyclobutane (**II**) were obtained in crude form (based on NMR before attempted purification) in 74 and 32% yield, respectively, in separate reactions involving a toluene suspension of AgCN with the corresponding bromide-substituted disilacyclobutanes. The reaction work up included remov-



Scheme 1. Possible routes to cyano-PSMs.

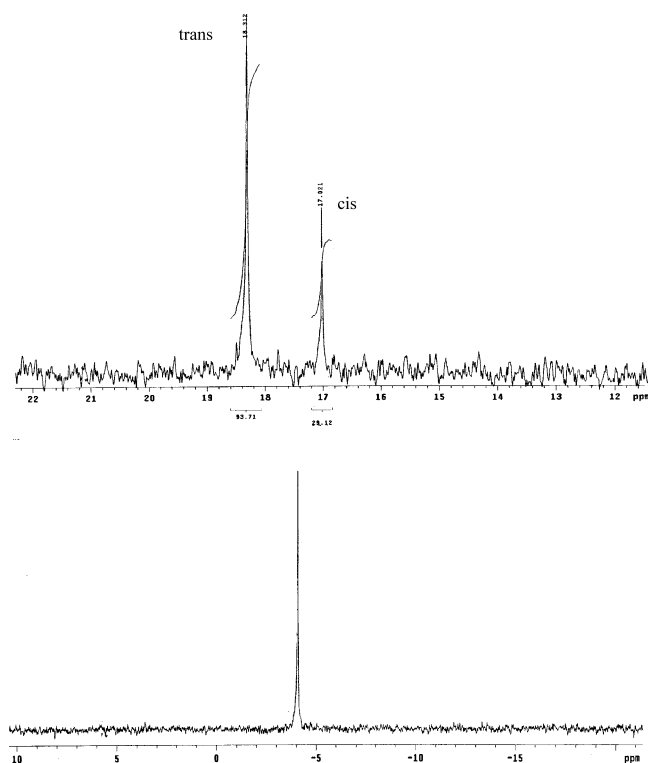


Fig. 1. ^{29}Si -NMR spectrum of (top) 1,3-dibromo-1,3-dimethyl-1,3-disilacyclobutane and (bottom) 1,1,3,3-tetrabromo-1,3-disilacyclobutane.

ing the solid AgCN/AgBr by filtration, and then separating the liquid fraction by distillation, initially removing the toluene at atmospheric pressure. When attempting to purify compound **I** by vacuum distillation, only a small amount of distillate was obtained, even at low pressure and high temperature, evoking the possibility that the compound is thermally unstable and decomposes before it becomes sufficiently volatile for distillation. However, the IR spectrum of the crude oily undistilled material was nearly identical to that obtained for the small amount of isolated liquid distillate, indicating that decomposition was not occurring. The presence of absorption bands at 2190 cm^{-1} and at 2090 cm^{-1} is consistent with those assigned to the Si-CN and Si-NC stretching modes in trimethylsilylcyanoide [8], and indicates that a cyano-substituted DSCB product was produced. Several subsequent attempts to purify the crude reaction products by elevated temperature dissolution followed by low temperature recrystallization from various solvents were attempted, and resulted in the eventual isolation of small amounts of white solid material. However, after standing for several weeks, a clear, colorless, crystalline solid formed from the crude reaction products, which was subsequently isolated. The observation of crystals suggests isolation of a single isomeric form of compound **I**. This supposition is supported by the ^1H -NMR spectrum of this

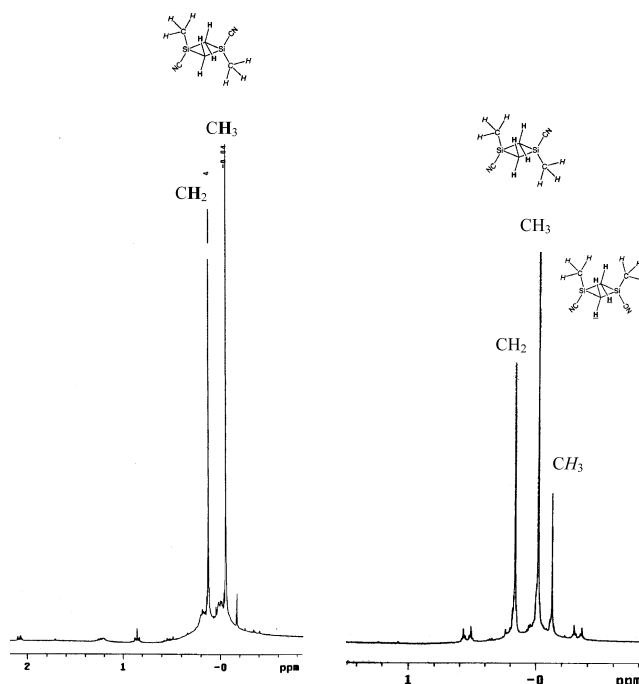


Fig. 2. ^1H -NMR Spectra of 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane immediately after dissolution in CDCl_3 (left) and 1 h later (right).

crystalline solid (Fig. 2, left) obtained within several minutes of dissolution in deuteriochloroform. This ^1H -NMR spectrum shows two distinct proton environments in a 3:2 ratio, as would be expected for a single isomer with both sets of methyl protons in identical chemical environments ($6H$, CH_3 : -0.04 ppm) and both sets of methylene protons in identical chemical environments ($4H$, CH_2 : 0.14 ppm). Interpretation of this spectrum indicates that the isolated crystalline material is the *trans* form, where geometry dictates that geminal methylene protons (one H above and below the plane of the ring) are in identical environments, therefore producing a singlet in the ^1H -NMR spectrum.

After 1 h in solution the ^1H -NMR spectrum shows the initial two chemical environments plus two additional ones in a 3:2 relative intensity ratio. Observation of these new resonances indicates formation of the *cis* isomer (Fig. 2, right). In this *cis* form, the geminal methylene protons are spatially located in different chemical environments; the protons above the plane of the ring have a local environment effected by the two adjacent methyl groups whereas the protons below the plane of the ring have two adjacent CN groups. Since the geminal protons are in different chemical environments, they also undergo geminal ^1H splitting. Thus there are two separate environments for the geminal protons, and since they split each other, the obtained pattern is a doublet of doublets (with a 1:1:1:1 relative ratio).

Because of the long acquisition times and high concentrations required for both ^{29}Si - and ^{13}C -NMR, the spectra of compound **I** were obtained for the isomeric mixture. The ^1H -decoupled ^{29}Si -NMR spectrum had resonances at -14.4 and -14.7 ppm, corresponding to the *trans* and *cis* forms respectively. The ^{13}C -NMR spectrum (Fig. 3) was run without ^1H -decoupling for assignment of the resonances of each of the carbon atoms. The methylene carbons appear as a triplet and the methyl carbons appear as a quartet (due to coupling with the attached ^1H), while the carbon in the cyano group appears as a singlet. The assigned value of -124.8 ppm is in agreement with values reported for cyanosilanes. The NMR spectra do not show separate resonances for Si–NC units; this could be due to the fact that the chemical shifts of Si–CN and Si–NC are so close they are unresolvable and/or that the timescale of the exchange reaction is fast compared to the NMR timescale. However, the observation of distinct resonances for the geminal methylene protons (Fig. 2, right) appears to rule out the latter (fast exchange) possibility.

The combined NMR and IR data obtained for compound **I** support the existence of the cyano/isocyno exchange mechanism analogous to that previously proposed for cyanosilanes [8]. Since we identify formation of both *cis* and *trans* isomers in a solution initially

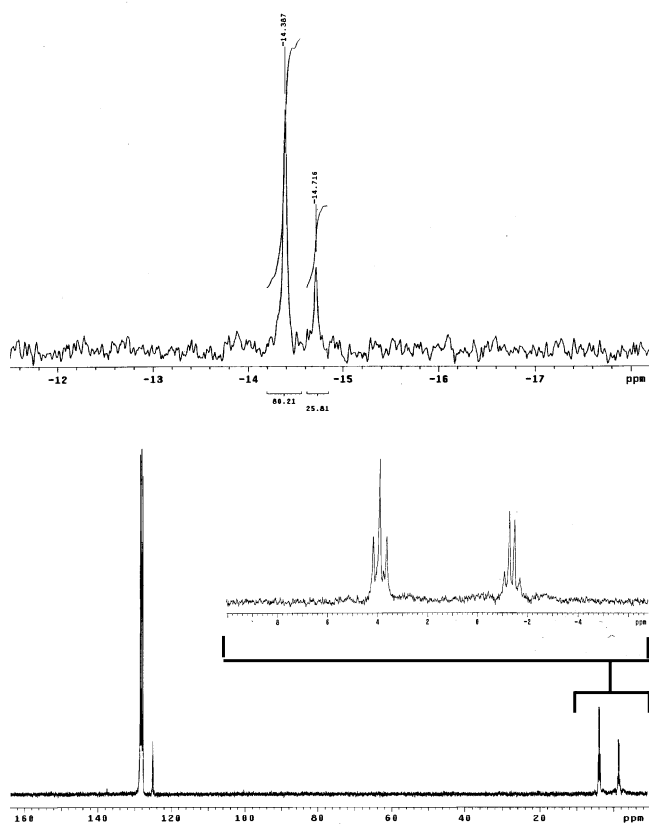
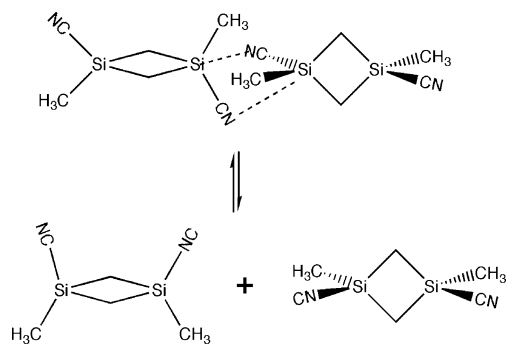


Fig. 3. ^{29}Si -NMR spectrum (top) and ^{13}C -NMR spectrum (bottom) of 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane.

consisting of a single isomeric form, molecular rearrangement obviously occurs in solution. The presence of a small band attributable to Si–NC stretching ($<5\%$ relative intensity) in the IR spectrum [8], coupled with the ^1H -NMR data, suggests that the exchange process occurs through a four-centered transition state (Scheme 2). For formation of the alternate isomer (*cis* to *trans* or *trans* to *cis*) the transition state must allow for inversion of configuration at the silicon atom, indicating that the exchange may follow a $\text{S}_{\text{N}}2$ type nucleophilic substitution mechanism.

A similar procedure to the one previously discussed for the isolation and purification of compound **I** was employed for the purification of compound **II**. Compound **II** has only a single isomeric form and is expected to be a crystalline material in pure form. Low pressure trap-to-trap distillation/recrystallization of the reaction products led to the recovery of a white solid. The presence of multiple peaks in the ^1H - and ^{29}Si -NMR spectrum of this material indicated that it was impure and contained unreacted Si–Br units. This result is consistent with the increased difficulty for difunctional Si to undergo nucleophilic substitution at both sites. Fortunately, after allowing the material to stand for several months in a sealed container, small crystal platelets formed and were subsequently isolated. The ^{29}Si -, ^{13}C -NMR and ^1H -NMR spectra of this material are consistent with a $[\text{Si}(\text{CN})_2\text{CH}_2]$ structure and the IR of this compound shows the expected Si–CN/Si–NC absorptions at 2190 and 2090 cm^{-1} , respectively, with the latter, again, at $<5\%$ the intensity of the former.

Attempts to polymerize these cyano substituted DSCBs (compounds **I** and **II**) by ROP with Pt catalysts $[(\text{C}_6\text{H}_{10})_2\text{Pt}_2\text{Cl}_4$ and chloroplatinic acid] were unsuccessful, even after prolonged heating to elevated temperatures (ca. 110°C). The inability of these monomers to undergo ROP can be explained by CNs efficacy as an ambidentate ligand, which can coordinate with the Pt catalyst, tying up available coordination sites, thus rendering the catalyst ineffective for opening the DSCB ring. Alternately, CN^- could exchange for Cl^-



Scheme 2. Illustration of the proposed mechanism for the silicon-cyano/isocyno exchange process that occurs in solution for 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane.

in the catalyst, making the $\text{Pt}(\text{CN})_x$ complex inactive for ROP.

Due to our inability to prepare the cyano-substituted PSMs by ROP, we shifted our attention to reactions on preformed PSMs in an attempt to produce the desired cyano-substituted polymers. In our initial attempts, the bromo-DSCBs were successfully polymerized by ROP with a platinum catalyst, but were not characterized due to their hydrolytic instability. Instead the bromo polymers were dissolved in toluene and allowed to react with AgCN by refluxing the mixture for a period of several days. As evidence that the exchange was proceeding, the AgCN was turning yellow, indicating the presence of AgBr . The absence of ^{29}Si -NMR resonances in the filtered liquids revealed that the polymers were not soluble and therefore had not separated from the solid materials (AgCN/AgBr particles). Heating the solid products in several solvents (CH_2Cl_2 , diethyl ether, trifluorotoluene) did not result in any soluble Si-containing products. Although some degree of CN substitution of the bromo polymers likely occurred, the polymeric products could not be fully characterized due to their admixture with the solid reaction byproducts. A likely cause of the insolubility of the resulting polymers could be the introduction of a small degree of Si–O–Si crosslinking by hydrolysis.

As an alternate synthetic pathway, we attempted an exchange reaction between Si–Cl and Si–CN by reacting the preformed chloro-PSMs with trimethylsilylcyanide [13]. In this case, the fact that the byproduct trimethylchlorosilane boils at a considerably lower temperature than either the starting trimethylsilyl cyanide or the toluene used as the solvent, provides a driving force for complete exchange through the removal of the chloro-byproduct. First, both 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane and 1,1,3,3-tetrachloro-1,3-disilacyclobutane were polymerized under neat conditions using chloroplatinic acid. The two polymers were then separately dissolved in a solvent (toluene or toluene–acetonitrile mixture), and a large stoichiometric excess of $(\text{CH}_3)_3\text{SiCN}$ was added and the reaction mixture brought to reflux. The exchange reaction byproduct [$(\text{CH}_3)_3\text{SiCl}$ (b.p. 66°C)] was removed from the reaction mixture by distillation using a packed column to a head temperature of 110°C (b.p. of the solvent toluene). In both cases, a white (polymer I) to orange colored (polymer II) solid precipitated out of solution during the exchange reaction.

An initial attempt at the preparation of the cyano-methyl-PSM, $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_n$, resulted in a clear viscous material that was insoluble in toluene, hexane, diethyl ether, methylene chloride and DMSO (polymer I–A). The IR spectrum of this polymer showed the characteristic Si–CN and Si–NC stretching bands (2190 and 2090 cm^{-1}) indicating some degree of cyano-substitution. Due to the insolubility of the polymer,

SS-NMR was employed for its characterization. The ^{29}Si SS-NMR spectra of this initial preparation showed four distinct Si resonances (Fig. 4). The peak at -14.8 ppm was assigned to the C_3SiCN moiety based on comparison with the ^{29}Si chemical shift obtained for compound I, $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_2$. The minor peak at -27 ppm was assigned to C_3SiCl units based on a comparison to $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_2$, while the peak at 8.3 ppm was assigned to SiOC_3 units. The remaining peaks at -57.1 and 17.6 ppm are spinning side bands of the peak at -14.8 ppm (due to the offset of ± 3 kHz, which corresponded to the sample spinning speed). These results indicated that the substitution of CN^- for Cl^- did occur, but was incomplete. To demonstrate that this polymer is hydrolytically unstable, and confirm the assignment of the C_3SiO units, the clear gummy sample was removed from the sealed NMR rotor, and exposed to the atmosphere overnight. The result was a hard black material suggesting abstraction of CN^- and the formation of residual cyanogen. The ^{29}Si -NMR of this material showed only a single broad resonance at -14.8 ppm indicating that only C_3SiO units were present, and that the material was indeed hydrolytically unstable, with both Si–Cl and Si–CN bonds reacting with atmospheric moisture to form Si–O–Si crosslinks.

A subsequent synthetic preparation by the same route was attempted (polymer I–B), with extra care to protect the sample from traces of moisture, particularly during sample handling. This included machining tightly fitting teflon endcaps to make sure the sample was sealed in an inert atmosphere in the NMR rotor. The ^{29}Si spectrum of this sample indicated 83% Si–CN units and 17% unreacted Si–Cl by integration of the corresponding ^{29}Si peaks at -14.8 and 28.6 ppm, respectively. The spectrum also included several sharp peaks of low intensity that correspond to unassigned small, volatile, Si-containing, reaction byproducts. This partially cyano-substituted polymer sample was then re-treated with $(\text{CH}_3)_3\text{SiCN}$, by refluxing the solid polymer in a large excess of pure $(\text{CH}_3)_3\text{SiCN}$ for several hours, followed

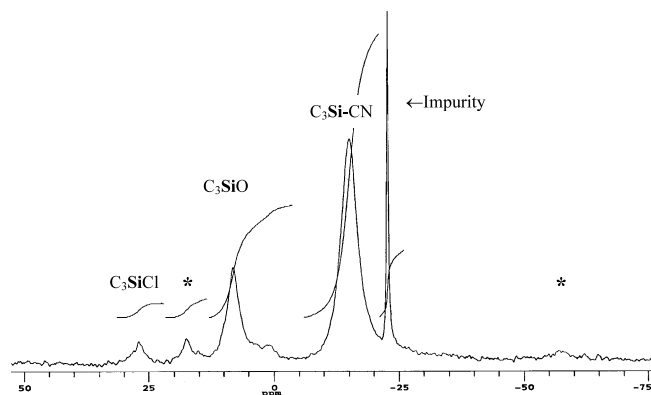


Fig. 4. ^{29}Si SS-NMR spectrum of the partially substituted $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_n$ polymer I–A (*, indicates a spinning side band).

by atmospheric distillation to a head temperature of 120 °C (corresponding to the b.p. of (CH₃)₃SiCN) to ensure that all the (CH₃)₃SiCl (b.p. 66 °C) was removed. This material was worked up by evacuation on a vacuum line at 10⁻⁴ Torr for 24 h at 100 °C to remove all volatile reactants/byproducts, resulting in polymer I–C as a white solid. The ²⁹Si SS-NMR spectra of this sample (Fig. 5) produced a single resonance. The intense broad resonance at –14.8 ppm (C₃Si–CN), with the absence of a resonance at 28.6 ppm (C₃Si–Cl) indicates that an apparently completely substituted polymer with the chemical structure [–Si(CH₃)(CN)CH₂–]_n was obtained. The ¹³C 4 kHz CPMAS spectrum of the fully substituted sample consists of three principal resonances; a manifold of spinning sidebands centered about 128 ppm, which is assigned to the cyano carbon, (Si–CN), and a broad peak at 1.1 ppm which consists of overlapping CH₂ and CH₃ resonances which decomposed by linefit to 1.7 and –0.2 ppm, respectively. The ¹H spectrum of this polymer consisted of a single resonance at 0.5 ppm with the CH₃ and CH₂ protons overlapping.

The DSC curve for the fully substituted [Si(CN)(CH₃)CH₂]_n, polymer I–C, indicates a T_g of 33 °C, which was reproducibly observed on both heating and cooling cycles. This T_g compares to a T_g of 120 °C for the corresponding polyolefin, poly(methylacrylonitrile), [C(CN)(CH₃)CH₂]_n. The lower T_g of the cyano-PSM is consistent with the comparatively longer Si–C bond length in the PSMs, leading to decreased torsional barriers for the polymer chain. However, the T_g of this cyano-PSMs is high when compared to other similarly substituted PSMs (e.g. the T_g of [SiF(Me)CH₂]_n is –70 °C) [3] suggesting that dipolar interaction between adjacent CN groups and/or their large size significantly

increases the barrier for the main chain torsional motion.

An initial attempt to synthesize the corresponding dicyano polymer from the chloro-PSM prepolymer [SiCl₂CH₂]_n was performed. 1,1,3,3-tetrachloro-1,3-disilacyclobutane was dissolved in toluene and polymerized using chloroplatinic acid to produce [SiCl₂CH₂]_n, which was then dissolved in toluene. After the first treatment with (CH₃)₃SiCN a solid orange material precipitated out of solution, which was retreated with neat (CH₃)₃SiCN in an attempt to obtain a fully substituted polymer. The final synthetic treatment resulted in a solid orange colored material (polymer II), that was found to be insoluble in all solvents tried. The ²⁹Si SS-NMR spectrum of this material is shown in Fig. 6. The spectrum is complicated by the presence of spinning side bands. The peaks are assigned as follows: –49 ppm CH₂Si(CN)₂CH₂; –13.5 ppm CH₂Si(CN)ClCH₂; –22 ppm CH₂SiO₂CH₂; and 12 ppm CH₂Si(Cl)₂CH₂. From the integrated intensity of the ²⁹Si peaks of this material, the apparent polymeric structure consists of 46% Si(CN)₂, 26% SiCl(CN) units, 14% unreacted SiCl₂ units, and 14% of Si–O–Si crosslinks. The observation of a substantial amount of SiO₂C₂ units by SS-NMR may indicate that exposure to moisture during synthesis prevented full substitution from occurring.

The ¹³C 4 kHz-CPMAS spectrum of this material consists of two principal resonances, one a manifold of spinning sidebands centered about 122 ppm, corresponding to the cyano carbons and a peak at 0.9 ppm corresponding to the methylene carbons. The methylene peak can be decomposed into two components; a broad and a narrow component that can be attributed to the chemical-shift-dispersion of the amorphous domains and the ordered-crystalline domains respectively. With a contact time of 5 ms, the data can be considered semi-quantitative and an estimate of 20–30% crystallinity can be made for this material from a two component linefit of the methylene resonance.

The DSC of this polymer showed no evidence of melting or glass transitions. Nonetheless, a sample of

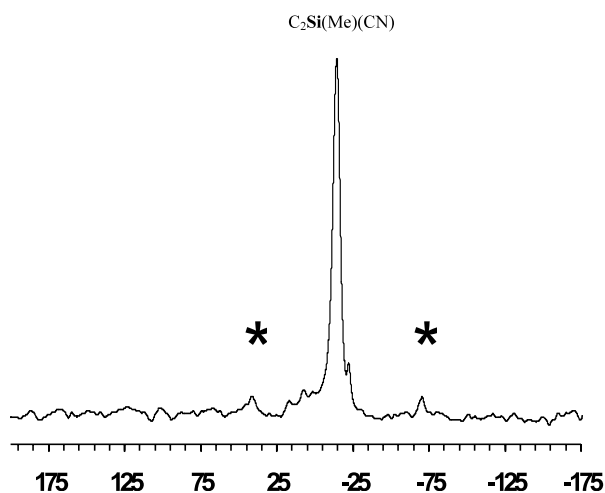


Fig. 5. ¹H decoupled ²⁹Si single pulse SS-NMR spectrum of the fully substituted [Si(CN)(CH₃)CH₂]_n, polymer I–C (*, indicates a spinning side band).

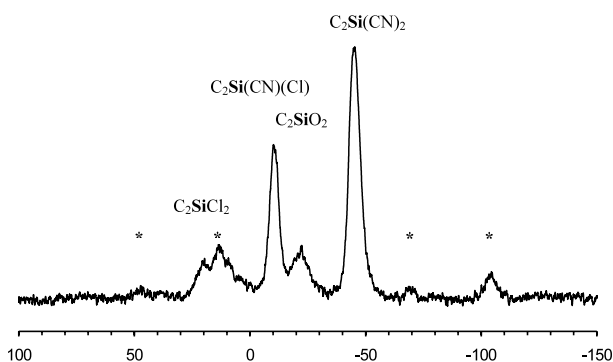


Fig. 6. ²⁹Si SS-NMR spectrum of the partially substituted [Si(CN)₂CH₂]_n, polymer II (*, indicates a spinning side band).

this polymer was affixed to a glass slide and sealed inside a plastic bag inside the glove box, for powder XRD analysis. The observation of a distinct diffraction pattern showed that the material was at least partially crystalline.

3. Conclusions

Starting from the previously unreported bromo-derivatives, the first cyano-substituted disilacyclobutanes, 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_2$ and 1,1,3,3-tetracyano-1,3-disilacyclobutane $[\text{Si}(\text{CN})_2\text{CH}_2]_2$, were prepared by reaction with AgCN in refluxing toluene. These colorless, crystalline, compounds were characterized by ^1H -, ^{13}C - and ^{29}Si -NMR spectroscopy in CDCl_3 solution. In the case of the $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_2$ compound, which can exist in *cis* and *trans* isomeric forms, ^1H -NMR spectra obtained immediately on dissolution in CDCl_3 indicated the presence of almost entirely the *trans* form; however, after 1 h in solution, a mixture of the two isomers was observed, evidencing a molecular exchange process. Based on IR spectral evidence for Si–NC groups, coupled with the results of prior studies of Si–CN exchange in cyanosilanes, a four-centered transition state mechanism for the *trans/cis* exchange process was proposed. Efforts to obtain cyano-substituted PSMs by ROP of these disilacyclobutanes proved unsuccessful; however, substitution reactions carried out on the preformed chloro-PSMs by exchange with $(\text{CH}_3)_3\text{SiCN}$ did yield the desired (by SS-NMR) fully substituted $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_n$ polymer and a partially substituted copolymer, with ca. 46% $\text{Si}(\text{CN})_2$ units. Both polymers were found to be insoluble in all solvents tried; however, the $[\text{Si}(\text{CN})(\text{CH}_3)\text{CH}_2]_n$ polymer exhibited a glass transition at 33 °C, which was considerably lower than that of its all-carbon backbone analog, poly(methacrylonitrile), and the $[\text{Si}(\text{CN})_2\text{CH}_2]_x$ - $[\text{SiCl}_2\text{CH}_2]_{1-x}$ copolymer was found to be partially crystalline by both SS-NMR and XRD studies.

4. Experimental

4.1. Materials

All reagents were obtained from Aldrich and used as received. All glassware was oven dried for at least 12 h at 140 °C before use. Solvents were dried by using standard drying reagents and freshly distilled before use. Synthetic procedures were carried out by using standard N_2 atmosphere/Schlenk-line techniques or inside a dry N_2 filled glovebox.

4.1.1. Attempted preparation of cyano-DSCBs by reaction of alkoxy-DSCBs with acetyl cyanides

In to a 50 ml three-necked round bottom flask equipped with a condenser, addition funnel, and magnetic stirbar, 3.0 g (0.011 mol) 1,1,3,3-tetraethoxy-1,3-disilacyclobutane, TEDSCB [3] was added dropwise using the addition funnel to a mixture of 3.5 g (0.05 mol, 20% excess) pyruvonnitrile and 10 mg of AlCl_3 (catalyst) over 15 min. The reaction mixture was heated to reflux overnight, yielding a dark brown, turbid liquid. Atmospheric pressure distillation to 95 °C was performed to remove the excess pyruvonnitrile and ethyl acetate. Reduced pressure distillation at 5 Torr to 110 °C yielded several drops of clear liquid that did not contain Si (based on the absence of peaks in its ^{29}Si -NMR spectrum). ^1H - and ^{29}Si -NMR spectral analysis of the brown solid residue remaining after distillation resulted in complex spectra that were not assigned. A similar reaction performed with *tert*-butylacetyl cyanide produced analogous results.

4.1.2. Preparation of 1,1,3,3-tetrabromo-1,3-disilacyclobutane

Inside a 100 ml three-necked round bottom flask equipped with a condenser, addition funnel, and magnetic stirbar, 8.6 g (0.033 mol) of TEDSCB was added dropwise using the addition funnel to a mixture of 19.5 g (0.16 mol) [20% excess] of acetyl bromide and 5 mg of FeCl_3 (catalyst) over a period of 2 h. The reaction mixture was refluxed overnight, yielding a red solution with white precipitate. Atmospheric pressure distillation to a head temperature of 120 °C was performed to remove ethyl acetate and excess acetyl bromide. Trap to trap vacuum re-crystallization at 4 Torr with the receiver placed in an water/ice bath yielded 12.1 g (0.03 mol, 90.1% yield) of white crystalline TBDSCB. Purity > 98% (by NMR). IR (cm^{-1}): 2986 w, 2914 w, 1700 s, 1684 vs, 1560 s, 1066 br, 968 vs, 668 vs, 646 vs. 300 MHz ^1H -NMR (CDCl_3): δ 1.9 (CH_2); 75 MHz. ^{13}C -NMR (CDCl_3): δ 31.42 (CH_2); 99 MHz. ^{29}Si -NMR (CDCl_3): δ -4.08 (SiBr_2).

4.1.3. Preparation of 1,3-dibromo-1,3-dimethyl-1,3-disilacyclobutane

Inside a 100 ml three-necked round bottom flask equipped with a condenser, addition funnel, and magnetic stirbar 20.0 g (72 mM) of 1,3-diisopropoxy-1,3-dimethyl-1,3-disilacyclobutane [9] was added dropwise using the addition funnel to 19.5 g (156 mM, 20% excess) of acetyl bromide with 4–5 mg of FeCl_3 (catalyst) over a period of 1 h. The reaction mixture was refluxed overnight. Atmospheric pressure distillation to a head temperature of 120 °C was performed to remove ethyl acetate and excess acetyl bromide. Reduced pressure vacuum distillation at 10 Torr with the receiver placed in an water/ice bath yielded 18.6 g (68

mM, 94% yield) of 1,3-dibromo-1,3-dimethyl-1,3-disilacyclobutane at a head temperature between 49 and 52 °C. Purity: 98.6% by GC. IR (cm⁻¹): 2964 m, 2948 w, 1722 vs, 1369 vs, 1341 vs, 1253 w, 1017 vs, 867 m, 690 vs, 643 vs. 300 MHz ¹H-NMR (CDCl₃): δ 0.89 (CH₃), δ 1.34 (CH₃); 75 MHz; 99 MHz. ²⁹Si-NMR (CDCl₃): δ 18.3 (*trans*), δ 17.0 (*cis*).

4.1.4. Preparation of 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane

In a 100 ml one-neck round bottom flask equipped with a condenser and magnetic stirbar, a mixture of 10.0 g (36.5 mM) of 1,3-dimethyl-1,3-dibromo-1,3-disilacyclobutane and 50 ml of toluene was added to 11.6 g (8.66 mM, 20% excess) of AgCN. The mixture was brought to reflux and allowed to boil overnight. The crude reaction products were transferred to the glovebox, and the liquids were separated from the solid AgCN/AgBr reaction byproducts by filtration, rinsing the solids several times with hot (60 °C) toluene. The filtrate was distilled at atmospheric pressure to remove the toluene. Reduced pressure distillation at 4 Torr to a pot temperature of 120 °C only yielded several drops of clear liquid, which eventually formed a few clear crystals. NMR analysis of this product indicated that it was [Si(CN)(CH₃)CH₂]₂. However, allowing the remaining undistilled crude reaction products to stand at room temperature (r.t.) for several weeks afforded a clear crystalline product and a brown oily liquid. Inside a N₂ filled glovebox, the crystals were separated from the oil with tweezers and the residual oily byproduct was removed by wiping the crystals with a Kim-wipe and then briefly rinsing the crystals in a stream of freshly dried pentane. The pentane was removed by subjecting the crystals briefly to vacuum. 4.5 g (74% yield) of pure (based on their ¹H-NMR spectrum) crystals were thus obtained. 300 MHz ¹H-NMR (CDCl₃): δ 0.14 (CH₂), δ -0.04(CH₃); 75 MHz. ¹³C-NMR (CDCl₃): δ 124.8 (CN), δ -1.39 (CH₂); δ 3.9 (CH₃) 99 MHz. ²⁹Si-NMR (CDCl₃): δ -14.37 (*trans*), δ -14.72 (*cis*). IR (KBr) (cm⁻¹): 2990 (w), 2914 (s), 2190 (vs) [CN], 2090 (s) [NC], 1700 (s), 1560 (s) 1066 (br), 986 (s).

4.1.5. Preparation of 1,1,3,3-tetracyano-1,3-disilacyclobutane

Inside a 100 ml one-neck round bottom flask equipped with a condenser and magnetic stirbar, a mixture of 8.9 g (22 mM) of 1,1,3,3-tetrabromo-1,3-disilacyclobutane dissolved in 50 ml of toluene was added to 14.0 g (0.105 mol, 20% excess) of AgCN. The mixture was brought to reflux and allowed to boil overnight. The crude reaction products were transferred to a glovebox, and the liquids were separated from the solid AgCN/AgBr reaction byproducts by filtration, rinsing the solids several times with hot (60 °C) toluene. The filtrate was distilled at atmospheric pressure to

110 °C pressure to remove the toluene. Reduced pressure, trap-to-trap recrystallization yielded 2.3 g of an impure beige solid. Allowing the crude recrystallized material to stand for several weeks at r.t. resulted in small clear crystal platelets and a dark brown oil. The crystals were cleaned in the same manner as described for [Si(CN)(CH₃)CH₂]₂ yielding 1.3 g of pure (based on NMR analysis) product (32% yield). 300 MHz ¹H-NMR (CDCl₃): δ 2.2 (CH₂); 75 MHz. ¹³C-NMR (CDCl₃): δ 116.5 (CN), δ -2.95 (CH₂); 99 MHz. ²⁹Si-NMR (CDCl₃): δ -51.8.

4.1.6. Attempted ROP of 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane

In a 50 ml one-neck round bottom flask equipped with a magnetic stirbar, 1.0 g. of 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane was heated to > 100 °C with 2 mg of (C₆H₁₀)₂Pt₂Cl₄ overnight. No increase in the viscosity of the solution was observed. chloroplatinic acid (2 mg) was added and the solution was heated with stirring to 120 °C overnight. Once again, no increase in the viscosity of the solution was observed.

4.1.7. Synthesis of poly(cyanomethylsilylenemethylene), [Si(CN)(CH₃)CH₂]_n

Inside a 50 ml one-neck round bottom flask equipped with a magnetic stirbar, 1.0 g. (5.4 mM) 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane was polymerized at 80 °C under neat conditions using 1 mg of chloroplatinic acid as the ROP catalyst. When the viscosity of the solution no longer permitted magnetic stirring (typically 3–4 h), polymerization was considered complete and the polymer was dissolved in ca. 20 ml of freshly dried toluene. 1.65 g. (16.6 mM, 50% excess) trimethylsilylcyanide was added and the solution brought to reflux for 1 h. Upon atmospheric distillation to a head temperature of 110 °C, a white solid precipitated from the solution. The liquids were decanted and the solids dried under vacuum (4 Torr) yielding polymer I–B. This polymer was subsequently determined by solid state NMR to be incompletely substituted, so it was re-treated with a large excess (4 g) of trimethylsilylcyanide and the reaction mixture was again brought to reflux for 1 h and then distilled to a head temperature of 120 °C. The liquids were decanted, and the resulting material dried at 100 °C under vacuum (10⁻⁴ Torr) for 24 h, yielding polymer I–C. ¹H SS-NMR: δ 0.4 (CH₂ and CH₃) ¹³C SS-NMR: δ 116.5 (CN), δ -1.1 (CH₂ and CH₃); ²⁹Si SS-NMR: δ -14.8.

4.1.8. Attempted synthesis of poly(dicyanosilylenemethylene), [Si(CN)₂CH₂]_n

Using a similar procedure to that described above, 1.0 g. (4.4 mM) of solid 1,1,3,3-tetrachloro-1,3-disilacyclobutane was dissolved in 1.0 g of toluene and polymerized with ca. 1 mg of chloroplatinic acid at 80 °C for 12

h, producing a viscous solution that did not permit magnetic stirring. The material was dissolved in toluene, treated with 3.5 g (35.3 mM, ca. 100% excess) of trimethylsilyl cyanide, brought to reflux and then distilled to a head temperature of 110 °C, at which point a bright orange precipitate formed. The liquids were decanted and the solids were retreated with 4 g of trimethylsilyl cyanide and the liquids distilled until a head temperature of 120 °C was reached. The liquids were decanted and the solids dried at 120 °C under vacuum (4 Torr) yielding an orange powder, polymer **II**. ^1H SS-NMR: δ 0.3 (CH_2 and CH_3) ^{13}C SS-NMR: δ 113.2 (CN), δ -1.1 (CH_2 and CH_3); ^{29}Si SS-NMR: δ -49 ($\text{C}_2\text{Si}(\text{CN})_2$), δ -13.5 ppm $\text{C}_2\text{Si}(\text{CN})\text{Cl}$, δ -22 C_2SiO_2 , δ 12 C_2SiCl_2 .

4.2. Liquid NMR studies

^1H -, ^{13}C -, and ^{29}Si -NMR spectroscopy was performed on liquid samples using a Varian 300 NMR or a Varian Unity 500 NMR spectrometer with samples dissolved in appropriate deuterated solvents. The spectra were referenced to the known chemical shifts of the residual protons in the solvent. For ^{29}Si proton-gated decoupling NMR experiments, the relaxation agent chromium(III) acetylacetonate was added to the sample, and a pulse delay (τ_1) of 15 s was employed; thus the integrated peak area for ^{29}Si -NMR spectra can be assumed to produce quantitative results for all peaks.

4.3. SS-NMR studies

In order to prevent exposure to atmospheric moisture, samples were loaded inside a glovebox into 7.5 mm diameter Zirconia Pencil™ rotors capped on both sides with custom machined teflon plugs. ^{29}Si -single-pulse-MAS spectra were recorded on a Chemagnetics CMX-360 Infinity spectrometer, with spinning speeds of 3.0 kHz \pm 2 Hz. ^{13}C -CPMAS spectra were recorded using a 55 kHz irradiation field, contact times of 5 ms, and spinning speeds of 4 kHz \pm 2 Hz.

4.4. Thermal analysis

DSC was performed by using a TA Instruments model 2920 DSC with a heating and cooling rate of 10 °C min⁻¹. Samples were sealed in hermetic aluminum sample pans inside a dry N₂ filled glovebox.

4.5. Powder XRD

In a dry N₂ filled glovebox, ca. 1.5 cm² area of powdered $[\text{Si}(\text{CN})_2\text{CH}_2]_n$ polymer was affixed to a glass

slide using petroleum jelly, and the slide sealed inside a heat sealable bag to avoid exposure to the atmosphere during transfer to the XRD apparatus. A powder XRD spectrum was run from $2\theta = 15^\circ$ to 75° using a Phillips X-Ray Diffractometer with an Al-K α X-ray source. Two broad diffraction lines were observed at $2\theta = 27.7^\circ$ and 37.4° .

4.6. IR spectral measurements

IR spectra were obtained on a Perkin–Elmer Paragon 1000 IR Spectrophotometer, on pressed KBr disks containing the solid samples (the CN-derivatives) or on a smear of the liquid samples (the bromo-DSCBs) between KBr plates. The samples were all prepared and mounted in the KBr press or between KBr plates in a dry, N₂-filled, glovebox.

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