terpretation above, only the interactions between the TBLG terminal unit and incoming monomer have been taken into account for the sake of simplification. Penultimate and even more remote untis may contribute, to some extent, to the enantiomer selection at the growing chain end, but their effects cannot be evaluated by the aforementioned analytical procedure.

In summary, asymmetric-selective copolymerization *rac*-4(e)-BrDBO with optically active TBLG was achieved in dichloromethane at −60 °C without using a chiral initiator. In this copolymerization, the D enantiomer of 4-(e)-BrDBO, whose chirality was the same as that of the optically active comonomer TBLG, was preferentially incorporated in the copolymer chain. Such asymmetric selection originates from the difference in the reactivities of the growing chain end of the chiral TBLG unit toward the D and L enantiomers of 4(e)-BrDBO, and it is principally ascribable to the steric and electronic interactions between the asymmetric environment created by the chiral terminal TBLG unit and the rigid bicyclic 4(e)-BrDBO monomer having three asymmetric centers in addition to the polar bromine substituent.

Registry No. TBLG, 10548-46-6; (TBLG)·(4(*e*)-bromo-6,8-dioxabicyclo[3.2.1]octane) (copolymer), 98819-28-4; 4(*e*)-bromo-6,8-dioxabicyclo[3.2.1]octane, 84621-97-6.

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(21) The molar ratio of the D- and L-enantiomeric 4(e)-BrDBO units in the copolymer, D/L, is represented by eq i

$$\frac{D}{L} = \frac{(M_2/2) - Af_D}{(M_2/2) - A(1 - f_D)} \quad \text{(i)}$$

where M_2, A, and f_D are the weight of 4(e)-BrDBO in feed, the weight of unreacted 4(e)-BrDBO and the fraction of the D enantiomer in the unreacted 4(e)-BrDBO. (A is calculated by the equation shown below eq 1.) Since f_D is given by eq ii

$$f_D = \frac{1}{2}\left(1 - \frac{[\alpha]}{[\alpha]_0}\right) \quad \text{(ii)}$$

one obtains eq 1 from eq i and ii.
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(24) Skeist, I. *J. Am. Chem. Soc.* **1946**, *68*, 1781. Change in copolymer composition with conversion is given by eq iii

$$\ln (1 - m) = \int_{f_1^0}^{f_1} \frac{df_1}{F_1 - f_1} \quad \text{(iii)}$$

where m, f_1 and F_1 are conversion, monomer composition, and instantaneous copolymer composition, respectively. This equation is applicable to any copolymerization and terpolymerization as long as the relation between f_1 and F_1 is given.
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(26) The curves in Figure 3 were calculated as follows: With the use of monomer reactivity ratios given in the text, copolymer composition at any conversion and therefore the D/L ratio can be determined by Skeist's equation in combination with Alfrey and Goldfinger's equation. The optical purity of the remaining 4(e)-BrDBO can be readily calculated from the copolymer composition and conversion.

Polysilane High Polymers with Olefinic Side Groups: Syntheses, Properties, and Addition of Hydrogen Halides

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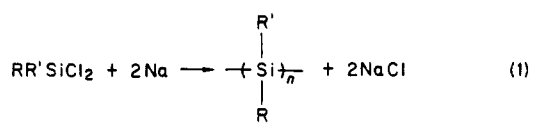
ABSTRACT: Three polysilane polymers containing alkene substituent groups were prepared by sodium condensation of dichlorosilanes: poly[(2-(3-cyclohexenyl)ethyl)methylsilylene] (**3**) and copolymers of this with phenylmethylsilylene (**1**) and *n*-propylmethylsilylene units (**2**). These polymers undergo cross-linking when irradiated with UV light or heated to 200 °C in vacuo. Addition of HCl or HBr to **1** or **2** in the presence of Lewis acid catalysts gave the corresponding chlorine- or bromine-containing polymers, with little degradation of the polysilane backbone.

Introduction

Recently several different substituted polysilane polymers have been prepared[2] by the reaction of dichlorosilanes $RR'SiCl_2$ with sodium in refluxing toluene (eq 1). Properties, molecular weights, and yields of the products are strongly dependent on the substituents R and R′. All of these polymers are soluble in common organic solvents and can be formed into a variety of shapes by molding, casting, or potting. They also show strong UV absorption and are easily degraded by UV irradiation[3] or heating to high temperatures.[4] Some of them also can be cross-linked by UV irradiation[3] or by heating them in the presence of vinylsilanes and free radical initiators.[5] Because of these



(1)

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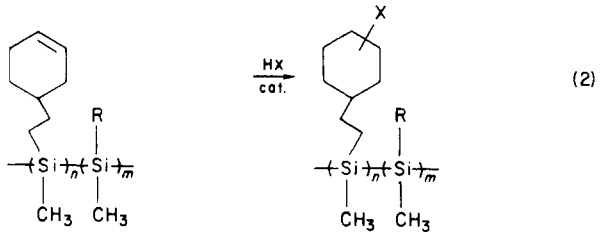
properties polysilane polymers are of considerable interest as UV photoresists,[6] as radical photoinitiators,[7] as impregnating agents for strengthening ceramics,[8] and as precursors for silicon carbide fibers.[9]

It would be desirable to introduce functional groups or heteroatoms into the side groups of the polysilanes, to provide a wider range of properties. However, the number of suitable substituents is limited by the severe reaction conditions (110 °C, sodium dispersion) used to prepare the polysilanes. Up to now only chlorosilanes with alkyl or aryl groups have given high molecular weight products.

Olefinic groups seemed likely to survive the reaction conditions and would provide the opportunity to introduce other functionality at the double bond, as well as to form cross-links. Initial experiments with vinylchlorosilanes showed, however, that they lead to extensive cross-linking during the sodium condensation. Allylchlorosilanes also gave only low yields of linear polymer (~3%). We turned to the 2-(3-cyclohexenyl)ethyl substituent, which proved to withstand the polymerization conditions.

In this paper we report the synthesis of poly[(2-(3-cyclohexenyl)ethyl)methylsilylene] (**3**) and copolymers of these with phenylmethylsilylene (**1**) and *n*-propylmethylsilylene (**2**) units. Addition of HCl and HBr to **1** and **2** gave the chlorine- or bromine-containing polymers **4**–**7** (eq 2).



(2)

1, R = phenyl
2, R = *n*-propyl
3, R = 2-(3-cyclohexenyl)ethyl

4, R = phenyl, X = Cl
5, R = *n*-propyl, X = Cl
6, R = phenyl, X = Br
7, R = *n*-propyl, X = Br

Experimental Section

General. Unless noted otherwise all reactions were carried out under an atmosphere of predried nitrogen. Light was excluded during all operations to prevent degradation of the polymer molecules. Chlorosilanes were purchased from Petrarch Systems, Inc., and distilled prior to use. Toluene was dried by refluxing it for 24 h over sodium and subsequent distillation. Chlorosilanes and dry toluene were transferred into reaction vessels with syringes previously flushed with dry nitrogen. Hydrogen halides were purchased from Matheson Gas Products. Hydrogen chloride, technical grade, was predried by passing it through a $CaCl_2$ drying tube. Hydrogen bromide (99.8%) and hydrogen iodide (98%) were used without further purification. Tin tetrachloride and boron tribromide were purchased from Aldrich Chemical Co. in the highest available purity and used as received.

Syntheses of Polymers. A 500-mL, three-necked, round-bottom flask, fitted with a dropping funnel, a high-speed stirrer, and a condenser, was thoroughly dried and purged with dry nitrogen. To the flask were added 100 mL of dry toluene and 4.7 g (0.205 mol) of sodium metal. The mixture was heated to reflux and a sodium dispersion was created by high-speed stirring for about 15 min. Then a total of 0.1 mol of the chlorosilane monomers (0.05 mol of each monomer in the synthesis of **1** and **2**) was added dropwise with stirring at a rate to maintain gentle reflux. Addition required about 15 min, during which time the color of the mixture turned from gray to dark purple. The reaction mixture was refluxed for 30 min and then allowed to cool, and a slurry of 2 g of $NaHCO_3$ in 30 mL of 2-propanol was added to destroy excess sodium. The entire mixture was then poured into 2000 mL of 2-propanol to precipitate the polymer. To the solid (polymer and NaCl) was added 200 mL of toluene. The residual insoluble NaCl was filtered off and the toluene solution was extracted three times with 500 mL of water. The organic layer was separated and dried with anhydrous Na_2SO_4. The polymer was precipitated by addition of 2500 mL of 2-propanol, filtered, and dried in vacuo (0.1 torr) for 3 days at room temperature.

Table I
Yields, Molecular Weights, Compositions, and UV Absorption of Polymers Containing 2-(3-Cyclohexenyl)ethyl Groups

polymer	yield, %	$\bar{M}_w \times 10^{-3}$ max[a]	m[b]	$\lambda_{max,RT}$, nm	$\epsilon \times 10^{-3}$ [c]
1	20	300	0.8–1.2	333	8.05
		9		280	3.0
2	20	180	1.0	303	4.5
		20			
3	10	105	–	302	4.3
		13			
4	85	250	0.8–1.2	333	7.9
		11		280	3.0
5	80	140	1.0	303	4.4
		20			
6	85	240	0.8–1.2	333	7.9
		11		280	3.0
7	75	70	1.0	302	4.4
		20			

[a] Estimated by GPC relative to polystyrene standards. [b] Ratio of monomer units in copolymers. [c] Per average Si unit.

Addition of HX. To 500 mg of polymers **1** or **2** in a 50-mL, two-necked, round-bottom flask, fitted with a gas inlet tube, a nitrogen inlet and outlet, and a magnetic stir bar, was added 15 mL of dry toluene. The reaction mixture was stirred until all polymer had dissolved and then cooled to −78 °C. Then 0.1 mmol of the catalyst was added (25 mg of $SnCl_4$[10] for HCl addition or 26 mg of BBr_3 for HBr addition). Hydrogen halide gas was bubbled through the solution for 30 min, the excess HX gas was stripped off in vacuo at 0.1 torr, and the mixture was poured into 200 mL of 2-propanol, causing the polymers to precipitate. The products were dried in vacuo at room temperature for 3 days; they showed no indication of carbon–carbon double bonds in the IR and NMR spectra.

No reaction took place between HCl or HBr and the polymers in the absence of Lewis acid catalysis. In the HBr addition, $SnBr_4$ and $FeBr_3$ were inactive as catalysts; $SnCl_4$ catalyzed addition but was much less effective than BBr_3. Attempts to add HI to polymers **1** and **2** in the presence of AlI_3 led only to cross-linked materials that could not be characterized.

Characterization. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with four μ-Styragel columns calibrated by polystyrene standards (porosity ranges 10^3, 10^4, 10^5, and 10^6 Å). Eluant was THF at a flow rate of 2 mL/min; the detection system was a Waters Associates Model 440 ultraviolet absorption detector set at 254 nm. Values for molecular weights in Table I are relative to polystyrene. NMR spectra were recorded on a Bruker WP-200 spectrometer on polymer solutions in benzene-d_6 or methylene-d_2 chloride. Determination of m, the ratio of monomer units in the copolymers, was carried out by integration of the ^1H NMR signals for the different groups. Infrared spectra were determined for thin polymer films using a Beckman IR 4230 spectrometer. Ultraviolet spectra were recorded on a Cary Model 118 spectrometer in cyclohexane solution.

Photo-Cross-Linking. Polymer samples (20 mg) were dissolved in 5 mL of cyclohexane, and 0.5-mL portions of these solutions were placed on a glass plate and the solvent was evaporated while the glass plate was protected from light. The resulting thin polymer films were irradiated under argon for 16 h with an Oriel 100-W high-pressure mercury lamp, fitted with a glass filter, cutting off light of wavelengths shorter than 300 nm. After this treatment the films were immersed in toluene for 2 h. Cross-linking was judged to have taken place if the film was insoluble in toluene.

Thermal Cross-Linking. Sample preparation was the same as for photo-cross-linking experiments. The polymer films were heated in air to 200 °C for 15 min and then transferred into toluene for 2 h to check gel formation. To examine thermal cross-linking in vacuo, polymer films on a glass plate were placed

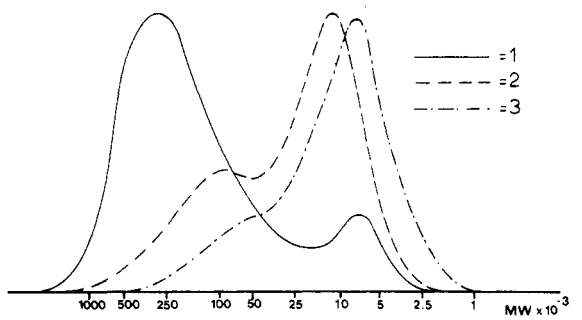


Figure 1. GPC elution profiles of polymers 1, 2, and 3.

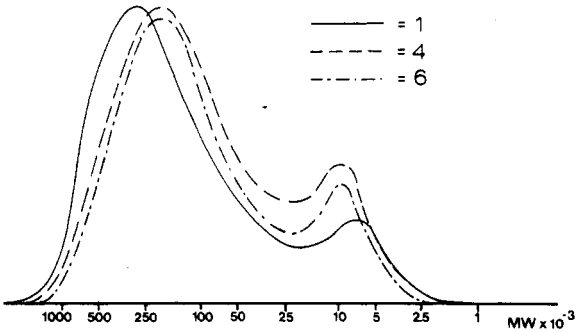


Figure 2. GPC elution profiles of polymers 1, 4, and 6.

in a round-bottom flask. The whole system was evacuated and heated to 200 °C for 4 h. Cross-linking was again determined by immersing the polymer films in toluene. In both cases light was carefully excluded during the heating period.

Results and Discussion

Synthesis of Alkenylpolysilanes. The properties of 1–3 are summarized in Table I. The polymers are obtained in 20% yield, the remainder being low molecular weight oligomers. The copolymers have a molar composition ratio near 1, similar to the molar ratio of the starting chlorosilanes, showing that the cyclohexenylethyl groups are not destroyed during condensation. Like most polysilane copolymers, 1–3 show bimodal molecular weight distributions. GPC elution curves for these polymers are shown in Figure 1.

Copolymer 1 is more stable than 2 or 3. Even when stored below 0 °C under nitrogen, 3 undergoes considerable cross-linking within a few days, and 2 within a few weeks, whereas 1 appears to be stable indefinitely under these conditions. Also, from the GPC curves for the polymers in Figure 1, the amount of high molecular weight fraction is highest for 1 and lowest for 3.

Addition of HX. Although normally hydrogen halides add rapidly to C=C double bonds, solutions of polymers 1–3 did not react with HCl or HBr at 30 °C in the absence of catalysts. However, in the presence of suitable Lewis acids, $SnCl_4$[10] for HCl and BBr_3 for HBr, addition took place smoothly and quantitatively even at −78 °C. The GPC elution profiles for the halogenated polymers compared with those of their parent alkenyl polymers are shown in Figures 2 and 3. The results indicate that very little chain degradation took place during the HX addition reactions.

Characteristics. The ^1H NMR spectra of compounds 1–7 (Table II) show unusually broad resonance peaks, especially when phenyl groups are attached to the silicon chain. This was also observed for polysilane polymers prepared earlier.[2b-d] Very interesting is the appearance of more than one NMR signal for the protons attached to the same carbon atom as the halogen substituent in the cyclohexyl groups of compounds 4–7. This suggests that

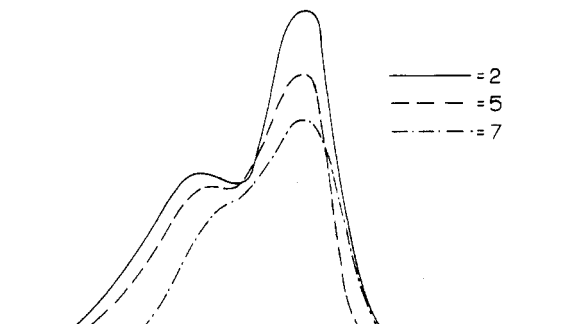
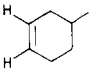
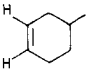


Figure 3. GPC elution profiles of polymers 2, 5, and 7.

Table II
^1H Chemical Shifts of Polymers 1–7[a]

polymer	δ	assignment
1[b]	0.3 (vb)	CH_3Si
	0.9 (b)	CH_2Si
	1.4 (vb), 1.7 (vb)	CH_2; CH
	2.0 (vb)	
	5.65 (b)	
	7.05 (vb)	
2[c]	0.6 (b)	CH_3Si
	1.2 (b)	CH_3C; CH_2Si
	1.4 (b), 1.7 (b), 1.95 (b)	CH_2; CH
	2.1 (b), 2.3 (b), 2.35 (b)	
	5.75 (b)	
3[c]	0.65 (b)	CH_3Si
	1.25 (b)	CH_2Si
	1.4 (b), 1.7 (b), 1.95 (b)	CH_2; CH
	2.1 (b), 2.3 (b), 2.35 (b)	
	5.75 (b)	
4[b]	0.3 (vb)	CH_3-Si
	0.9 (b)	-CH_2-Si
	1.3 (b), 1.6 (vb), 1.8 (b)	CH_2; CH
	2.0 (b), 2.3 (b)	
	3.8 (vb), 4.4 (vb)	
	7.1 (vb)	
5[c]	0.6 (b)	CH_3Si
	1.2 (b)	CH_3C; CH_2Si
	1.5 (sh), 1.65 (b), 1.9 (b)	CH_2; CH
	2.1 (b), 2.4 (b)	
	3.65 (b), 4.1 (b), 4.3 (b)	
6[b]	0.3 (vb)	CH_3Si
	0.9 (b)	CH_2Si
	1.3 (b), 1.65 (vb), 1.8 (sh)	CH_2; CH
	2.05 (sh), 2.3 (b)	
	3.95 (vb), 4.6 (vb)	
	7.15 (vb)	
7[c]	0.6 (b)	CH_3Si
	1.2 (b)	-CH_2Si; CH_3C
	1.55 (sh), 1.65 (b), 1.85 (sh)	CH_2; CH
	2.2 (b), 2.45 (b)	
	3.8 (b), 4.3 (b), 4.45 (b)	

[a] b = broad, vb = very broad, sh = shoulder. [b] In CD_2Cl_2 solution. [c] In C_6D_6 solution.

Table III
Cross-Linking Properties of Polymers[a]

polymer	thermal cross-linking in air[b]	thermal cross-linking in vacuo[c]	photolytic cross-linking[d]
1	+	+	+
2	+	+	+
4	o[e]	–[f]	–
5	+	–[f]	+
6	+	–[f]	+
6, $\bar{M}_w$ = 140 000	o[g]	–[f]	–

[a] "+" = cross-linking indicated by gel formation in toluene; "–" = polymer still soluble in toluene after treatment; "o" = cross-linking only upon long heating. [b] Heated for 15 min to 200 °C. [c] Heated 4 h to 200 °C. [d] Irradiated with 100-W Hg lamp overnight. [e] Cross-linked after 3 h. [f] No cross-linking even after heating overnight. [g] Cross-linking after 3 days.

different isomers are present in which the halogen atoms are in either axial or equatorial positions, sterically locked by the attached polymer chain.

The IR spectra are consistent with those reported earlier for other polysilane polymers bearing various alkyl and phenyl substituents.[2b-d] The spectra of **1**, **2**, and **3** exhibit additional bands at 3020 and 1650 cm^{-1} due to stretching modes of the olefinic C–H and C=C linkages in the cyclohexylenyl substituents. These bands are absent in the spectra of compounds **4–7**. This fact, together with the absence of vinylic proton resonances in the NMR spectra of **4–7**, indicates that addition of HX is nearly quantitative. Table I also presents the UV spectra of compounds **1–7**. Positions as well as intensity of the absorption maxima are typical for polysilane polymers.[2c,3a] Polymers **1–7** are completely soluble in toluene, cyclohexane, and THF; **2**, **4**, and **6** are also soluble in hexane.

Cross-Linking. In order to examine cross-linking properties, we carried out a comparative study of compounds **1–7** and of poly(phenylmethylsilylene-*co*-dimethylsilylene), "polysilastyrene" (**8**).[1,4] Films of all polymers were irradiated with UV light under argon and separately heated to 200 °C both in air and in vacuo. Cross-linking was tested by immersing these films in toluene and observing solubility or swelling. Results are outlined in Table III, where cross-linking samples are indicated by "+".[11]

Heating in air leads to rapid cross-linking. During this process silicon–oxygen bonds are formed, as indicated by the IR spectra of the polymers after heating which showed a strong band near 1050 cm^{-1}, typical for Si–O–Si linkages. The precise mechanism for cross-linking in air is not known, but probably oxygen reacts with the polymers to produce siloxy radicals (or traps silyl radicals that would otherwise recombine). Some of the siloxy radicals may then initiate chain processes leading to cross-linking, while others form Si–O–Si linkages along the polymer chain. Heating of the polymers in the absence of oxygen may lead to thermal homolysis producing silyl radicals, which can also initiate cross-linking chain reactions at the double bonds. This process is however much slower at 200 °C than oxidative cross-linking. When polymers **1–7** were heated in vacuo, only **1** and **2** yielded cross-linked products, and these only after longer heating (in this case no Si–O–Si bonds could be observed in the IR spectrum).

Irradiation of films of **1–7** with UV light with $\lambda > 300$ nm in argon resulted in cross-linking of all polymers, most rapidly for **1** and **2**. Polymer **8** however showed no cross-linking under any of the conditions applied (for cross-linking, heating to 200 °C in air for 3 days was necessary).

These results clearly indicate strong enhancement of cross-linking abilities of polysilane polymers by introduction of carbon–carbon double bonds. Polymers **1** and **2**, which cross-link most rapidly, are perhaps good candidates for the formation of negative photoresist by UV irradiation. The halogenated polymers also appear to undergo thermal or photochemical cross-linking somewhat more rapidly than typical polysilanes.

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Registry No. Poly[(2-(3-cyclohexenyl)ethyl)methyldichlorosilane] (homopolymer), 98800-88-5; poly[(2-(3-cyclohexenyl)ethyl)methyldichlorosilane] (SRU), 98800-54-5; ((2-(3-cyclohexenyl)ethyl)methyldichlorosilane)·(methylphenyldichlorosilane) (copolymer), 98800-89-6; ((2-(3-cyclohexenyl)ethyl)methyldichlorosilane)·(propylmethyldichlorosilane) (copolymer), 98820-31-6.

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(11) Under the conditions given in the table, samples recorded as "+" underwent no observable swelling in toluene. Photolysis or thermolysis for shorter times lead to partially cross-linked polymers that, although insoluble, were swelled by toluene.