became heterogeneous. After cooling, the tube's viscous contents were added to stirring ether, and a dark-red solid separated. This precipitate was collected on a frit, washed with chloroform, and reprecipitated several times from DMF into ether to afford a dark-red amorphous polymer–metal complex: 200 mg (17% conversion of monomers); IR (KBr) ν_{OH} 3650–3150 (m), ν_{CH} 3090, 3070, 3010, and 2910 (m), $\nu_{C=N}$ 1600 (m), $\nu_{PF_6^-}$ 840 cm^{-1} (s); λ_{max} (CH_3CN) 482, 310, 275, 235 nm.

Anal. Calcd for $(C_{9.24}H_{8.86}N_{0.285}P_{0.0952}F_{0.571}Ru_{0.0476}\cdot 0.0476H_2O)_n$ where [sty]/([sty] + [Ru^{2+} complex]) = 0.952: C, 77.38; H, 6.37; N, 2.79. Found: C, 77.13; H, 6.35; N, 2.79.

Registry No. **2**, 108295-34-7; **3**, 114532-87-5; **4**, 114532-88-6; (**4**)(styrene) (copolymer), 114532-89-7; (**13**)(styrene) (copolymer), 114532-90-0; (**15**)(styrene) (copolymer), 114532-92-2; styrene, 100-42-5.

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Cyclopolymerization of Dipropargylsilanes by Transition-Metal Catalysts

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ABSTRACT: Polymerization of dipropargylsilanes [$RR'Si(CH_2C{\equiv}CH)_2$; R, R′ = CH_3 or Ph] was examined for various transition-metal catalyst systems. A molybdenum complex was found to be a particularly effective catalyst for the cyclopolymerization of dipropargylsilanes. Polymerization of methylphenyldipropargylsilane and diphenyldipropargylsilane by various catalysts leads to soluble, highly colored polymers of average molecular weight 7000–15 000. Polymerization of dimethyldipropargylsilane under the same conditions, however, gives only a partially soluble polymer. IR, ^1H NMR, and UV–visible spectroscopies showed that poly(methylphenyldipropargylsilane) and poly(diphenyldipropargylsilane) possess polyene structures having cyclic recurring units in the polymer backbone. Poly(dipropargylsilane)s have been investigated in terms of physical properties, the nature of the doping process, electrical conductivity, and thermal and oxidative stability. The size of substituents was important for the cyclopolymerization tendency and for the resulting polymer properties.

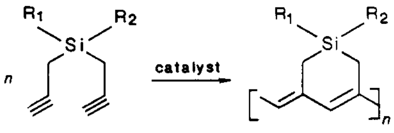
Introduction

There have been many studies of polyacetylene[1] because of its unique properties. Polyacetylene is, however, unstable in air and insoluble in the usual organic solvents. Thus, though the electrical conductivity is somewhat low, a study of the synthesis and properties of substituted polyacetylene has been intensively investigated.[2]

Since various substituted acetylenes have been polymerized by transition-metal catalysts to olefinic polymers, the cyclopolymerizations of nonconjugated diynes were investigated in an attempt to prepare a polymer that would contain alternating double and single bonds along the polymer backbone and a cyclic recurring unit.[3] Recently, Gibson et al. reported that the polymerization of 1,6-heptadiyne by a special method using a Ziegler–Natta catalyst [$Ti(OBu)_4/Et_3Al$] leads to insoluble polymer films.[4]

In another work,[5] we have found that $MoCl_5$- and WCl_6-based catalyst systems are very effective for the cyclopolymerization of dipropargyl sulfide and dipropargyl ether.

The present paper deals with the cyclopolymerization by Mo- and W-based catalysts of dipropargylsilanes, which often has an interesting character (see eq 1).



(1)

R1	R2
CH_3	CH_3
CH_3	C_6H_5
C_6H_5	C_6H_5

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Table I
Polymerization of Dimethyldipropargylsilane by $MoCl_5$-Based Catalysts[a]

expt no.	catal system[b] (mole ratio)	DMPS/catal mole ratio	polym yield, %
1	$MoCl_5$	50	48
2	$MoCl_5$	100	46
3	$MoCl_5$	200	33
4	$MoCl_5$-$(n\text{-}Bu)_4Sn$ (1:2)	50	42
5	$MoCl_5$-$(n\text{-}Bu)_4Sn$ (1:4)	50	43
6	$MoCl_5$-$EtAlCl_2$ (1:2)	50	8

[a] Polymerization was carried out 60 °C for 24 h in chlorobenzene. Initial monomer concentration ($[M_0]$) was 2 M. [b] Mixture of $MoCl_5$ and cocatalyst in chlorobenzene was aged at 30 °C for 15 min before use as catalyst.

Table II
Effect of Various Catalyst Systems[a] in the Polymerization of Dimethyldipropargylsilane

expt no.	catal system (mole ratio)	DMPS/catal mole ratio	time, h	polym yield, %
1	WCl_6	50	24	9
2	WCl_6-$(n\text{-}Bu)_4Sn$ (1:4)	50	24	16
3	WCl_6-$EtAlCl_2$ (1:2)	50	24	21
4	WCl_6-$EtAlCl_2$ (1:4)	50	24	38
5	$TiCl_4$-$EtAlCl_2$ (1:4)	50	24	16
6	$NbCl_5$	50	24	0
7	$TaCl_5$	50	24	0
8	$PdCl_2$[b]	30	48	10
8	$PdCl_2$[b]	30	48	22

[a] Polymerization was carried at 60 °C in chlorobenzene. Initial monomer concentration ($[M]_0$) was 2 M. [b] Polymerization solvent was dimethylformamide.

Table III
Solvent Effect in the Polymerization of Dimethyldipropargylsilane[a]

expt no.	solvent	polym yield, %
1	chlorobenzene	40
2	benzene	35
3	toluene	31
4	tetrahydrofuran	58
5	dichloromethane[b]	17
6	1,2-dichloroethane	8
7	chloroform	8
8	nitrobenzene	0

[a] Polymerization was carried out by $MoCl_5$ at 60 °C for 24 h. Monomer to catalyst mole ratio (M/C) and initial monomer concentration ($[M]_0$) were 50 and 1 M, respectively. [b] Polymerization temperature was 30 °C.

Table IV
Substituent Effect in the Polymerization of Dipropargylsilane Derivatives[a]

expt no.	catal system (mole ratio)	polymer yield, %		
		$R_1 = CH_3$; $R_2 = CH_3$	$R_1 = CH_3$; $R_2 = C_6H_5$	$R_1 = C_6H_5$; $R_2 = C_6H_5$
1	$MoCl_5$	48	55	100
2	$MoCl_5$-$(n\text{-}Bu)_4Sn$ (1:4)	43	47	95
3	WCl_6-$EtAlCl_2$ (1:4)	38	42	47
4	WCl_6-Et_2AlCl (1:4)	7	27	87
5	$TiCl_4$-$EtAlCl_2$ (1:4)	16	23	55

[a] Polymerization was carried out at 60 °C for 24 h. Initial monomer concentration ($[M_0]$) was 2 M. Monomer to catalyst mole ratio was 50.

Experimental Section

Monomers were prepared by a Grignard reaction according to the literature.[6] Dimethyldipropargylsilane (DMPS), 1.22 mol of magnesium turnings, and 1.49 mol of propargyl bromide were reacted with 0.31 mol of dichlorodimethylsilane, yielding dimethyldipropargylsilane [yield 67%; bp 50–51 °C (10 mmHg) (lit.[6] bp 62 °C A (35 mmHg)); ^1H NMR ($CDCl_3$) δ 1.82 (t, 1 H), 1.58 (d, 2 H), 0.18 (s, 3 H); IR (NaCl) 3320, 2980, 2140, 850 cm^{-1}].

Methylphenyldipropargylsilane (MPPS) [yield 65%; bp 65 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 7.4–7.6 (m, 5 H), 1.83 (s, 6 H), 0.5 (s, 3 H); IR (NaCl) 3310, 3080, 2980, 2900, 2120, 820 cm^{-1}].

Diphenyldipropargylsilane (DPPS) [yield 60%; bp 168 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 7.4–7.8 (m, 5 H), 2.1 (d, 2 H), 1.8 (t, 1 H); IR (NaCl) 3310, 3080, 2900, 2110, 1240 cm^{-1}].

Other Materials. Tungsten(VI) and molybdenum(V) chloride (Aldrich, resublimed, 99.9%) were used without further purification. Tetraphenyltin (Aldrich, 97%) was purified by recrystallizing twice from carbon tetrachloide. Organoaluminum compounds (Aldrich, 25% solution in hexane) and tetrabutyltin (Aldrich, 99%) were used without further purification. All solvents were purified in the usual manner.

Polymerization. All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent before use as 0.05, 0.2, or 0.4 M solutions. A typical polymerization procedure is as follows: into a 20-mL ampule equipped with rubber septum, solvent, catalyst solution, and cocatalyst solution (in case of need) are injected in the order given. When cocatalyst was used, these catalyst systems were aged at 30 °C for 15 min to reduce WCl_6 and $MoCl_5$. Finally, monomer was injected into the polymerization ampule. After the mixture stood at 60 °C for 24 h, the polymerization was stopped by adding a small amount of methanol. The resulting polymer was dissolved in chloroform followed by precipitation with excess petroleum ether. The precipitated polymer was filtered from the solution and dried to a constant weight under vacuum at 40 °C for 24 h. The polymer yield was calculated by gravimetry.

Doping. Rectangular pellets of the resulting polymer were made by exerting 15 000 lb of pressure with a Perkin-Elmer Caver laboratory press. Pressed pellets of these polymers were doped by exposure to the vapor of iodine in a vacuum desiccator. The doping levels were determined by the weight uptake method.

Instruments for Characterization. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian T-60A spectrometer and a Bruker AM-200 spectrometer. Infrared spectra were taken on a Perkin-Elmer 283B spectrometer with a potassium bromide pellet. Ultraviolet–visible spectra were obtained with a Carey 17 spectrometer. Thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere at a heating rate of 20 °C/min with a du Pont 1090 analyzer. Number average molecular weights (M_n) were determined in THF solution by a Waters GPC-150C with a calibration curve for polystyrene. Electrical conductivities were measured by four-point probe DC method with a Hewlett-Packard 3435A digital multimeter.

Results and Discussion

Effectiveness of Catalyst in the Polymerization of Dimethyldipropargylsilane (DMPS). Table I lists the results for the polymerization of DMPS by $MoCl_5$-based catalysts. DMPS was effectively polymerized by $MoCl_5$. Though $(n\text{-}Bu)_4Sn$ is an excellent cocatalyst for the polymerization of mono- and disubstituted acetylenes,[7,8] cyclopolymerization of DMPS is hardly affected. $EtAlCl_2$ rather decreased catalytic activity of $MoCl_5$. Table II shows that WCl_6 exhibits less effective catalytic activity by itself than does $MoCl_5$. However, WCl_6 and cocatalyst were effective. Especially, $EtAlCl_2$ exhibited high cocatalyst activity. These results were consistent with cyclopolymerization of other dipropargyl derivatives.[5] Polymer was not obtained by using $NbCl_5$ and $TaCl_5$.

Solvent Effect. As it was found that $MoCl_5$ is an effective catalyst for the polymerization of DMPS, the influence of solvents was examined by using $MoCl_5$ (Table III). Aromatic hydrocarbons such as chlorobenzene, benzene, and toluene are favorable solvents since they are good solvents for both catalyst and polymer. DMPS is not polymerized in nitrobenzene but is effectively polymerized

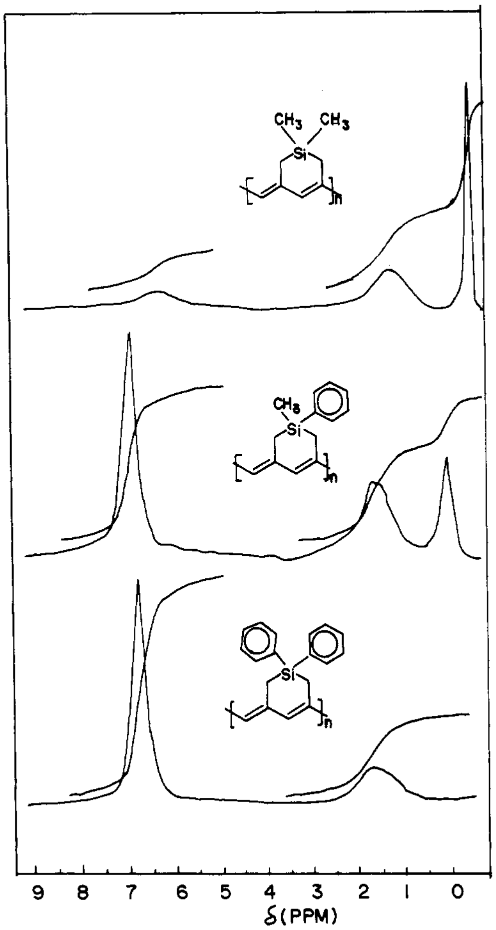

Figure 1. ^{1}H NMR spectra of poly(dipropargylsilane)s.

in an oxygen-containing solvent such as THF.

Comparison of the Polymerizability of Dipropargylsilanes. The substituent effects in the cyclopolymerization of dipropargylsilanes were studied (Table IV). The reaction was catalyzed by $MoCl_5$, $MoCl_5$–$(n\text{-}Bu)_4Sn$, WCl_6, WCl_6–Et_2AlCl, and TiC_4–$EtAlCl_2$.

Catalytic activity order was hardly affected by substituent bulkiness. However, monomer reactivities increase in the following order: DMPS < MPPS < DPPS. These observations indicated that substituent bulkiness considerably influences the cyclopolymerization of dipropargylsilanes. It seems that the bulkier the substituent, the greater the probability of cyclopolymerization. This tendency is similar to that in the cyclopolymerization of diallylsilane derivatives.[9,10]

Structure Analysis. The ^{1}H NMR spectra of poly(dipropargylsilane)s are shown in Figure 1. The new peaks that appeared at 6.2 ppm in the ^{1}H NMR spectrum of poly(DMPS) are assignable to the protons on the conjugated double bond. Vinylic protons of poly(MPPS) and poly(DPPS) appeared at 6–7.3 ppm with phenylic protons. Figure 2 shows the IR spectra of poly(dipropargylsilane)s. The infrared spectra of the polymer showed neither the acetylenic hydrogen stretching nor the carbon–carbon triple bond stretching presented in the IR spectra of the monomer. Instead, the carbon–carbon double bond stretching frequency at 1590–1650 cm^{-1} indicates a highly conjugated unsaturation. The UV–visible spectra of the polymers were obtained in 1,2-dichloroethane (Figure 3). A characteristic peak of conjugated polymers, broad $\pi \rightarrow \pi^*$ absorption, appeared in the visible region. The UV–visible spectrum of partially soluble PDMPS exhibits a weak absorption in the 300–500-nm region. On the other hand, the absorptions of completely soluble PMPPS and PDPPS were extended to the 600-nm region [PMPPS λ_{max} = 445 nm, ϵ = 3133; PDPPS λ_{max} = 445 nm, ϵ = 2466]. Figure 4 shows the ^{13}C NMR spectra of poly(MPPS) and MPPS. While the 81.26 and 68.85 ppm acetylenic carbon peaks disappeared, carbon peaks on the conjugated double bond appear at 136–141 ppm. The peak of the methylene carbon adjacent to the silicon is shifted from 4.13 to 18–25 ppm by polymerization.

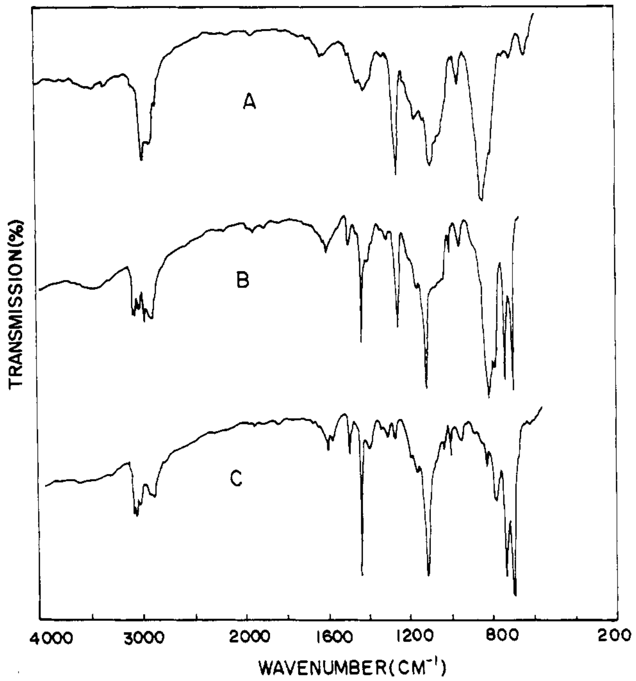

Figure 2. IR spectra of poly(dipropargylsilane)s: A, PDMPS; B, PMPPS; C, PDPPS.

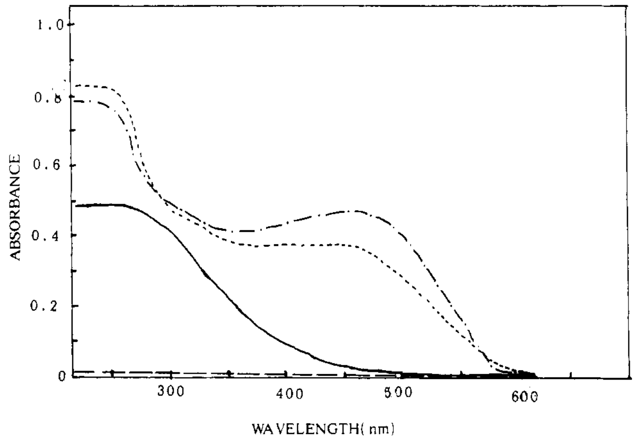

Figure 3. UV–visible spectra of poly(dipropargylsilane)s in (– – –) 1,2-dichloroethane, (—) PDMPS, (–·–) PMPPS (1.5 × 10^{-4} M), and (- - -) PDPPS (1.5 × 10^{-4} M).

Table V
Number Average Molecular Weights (M_n) of Poly(dipropargylsilane)s

polym	catal system	M_n[a]
PMPPS	$MoCl_5$	10 000
PMPPS	$MoCl_5$–$(n\text{-}Bu)_4Sn$ (1:4)	10 600
PDPPS	$MoCl_5$	14 300
PDPPS	$MoCl_5$–$(n\text{-}Bu)_4Sn$ (1:4)	16 500

[a] Polystyrene standard.

Number Average Molecular Weights and Physical Properties. Table V represents number average molecular weights of poly(dipropargylsilane)s from use of $MoCl_5$

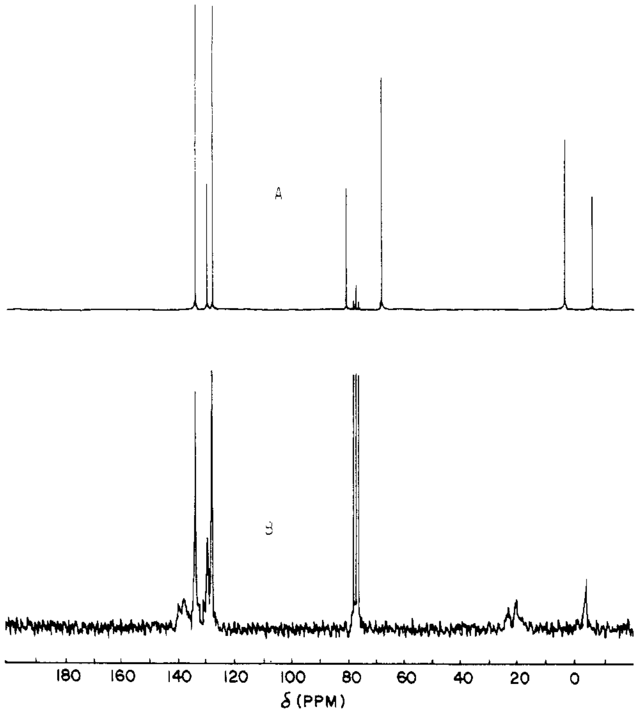

Figure 4. ^{13}C NMR spectra of methylphenyldipropargylsilane (A) and poly(methylphenyldipropargylsilane) (B).

Table VI
Solubility Behavior of Poly(dipropargylsilane) Derivatives[a]

solvent	polymer PDMPS	 PMPPS	 PDPPS
chloroform	+−	++	++
toluene	+−	++	++
1,2-dichloroethane	+−	++	++
CCl_4	+−	++	++
DMF	+−	++	++
THF	+−	++	++
chlorobenzene	−−	++	++
benzene	−−	++	++
m-cresol	−−	++	++
ethyl ether	+−	+−	+−
acetone	−−	+−	+−
methanol	−−	−−	−−
n-pentane	−−	−−	−−
formic acid	−−	−−	−−

[a] ++, soluble; +−, partially soluble; −−, insoluble.

and $MoCl_5$–$(n\text{-}Bu)_4Sn$. Though the addition of a reducing agent such as $(n\text{-}Bu)_4Sn$ decreases the polymer yields, there are slight increases in polymer molecular weights.

Table VI shows the solubility behavior of resulting polymers. Poly(MPPS) and poly(DPPS) are completely soluble in common organic solvents except for protic and hydrocarbon solvents such as methanol, formic acid, and *n*-heptane. We have recently found that poly(dipropargyl sulfide) and poly(dipropargyl ether) are insoluble in common organic solvents. However, poly(DMPS) is partially soluble and poly(DPPS) is completely soluble. Therefore, the bulkier the substituents, the better the solubility was exhibited. Thus, we suppose that (1) the bulkier the substituents, the more probabilities of the polymerization to ideal six-membered cyclic form and (2) the nature of the substituents influences solubility.[2]

Figure 5 shows the room-temperature electrical conductivity of poly(dipropargylsilane)s as a function of I_2 concentration. The concentration dependences observed in all cases are similar to those in Figure 5.

When pressed pellets of resulting polymers were doped by exposure to vapor of iodine in vacuo, polymers with smaller substituents were easily doped to high levels. Electrical conductivities of the pellet type polymer were 10^{-3}–10^{-2} Ω^{-1} cm^{-1} (Table VII).

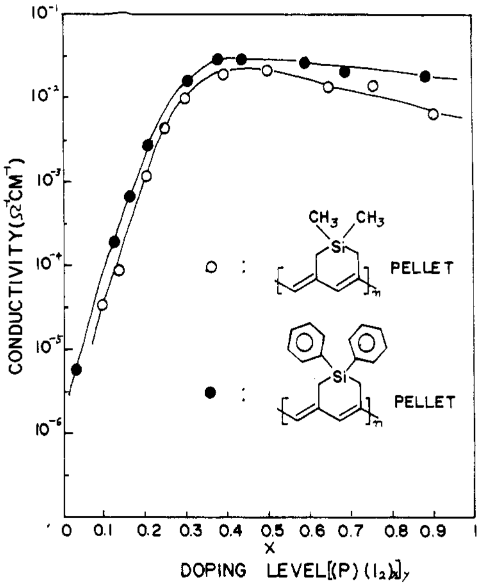

Figure 5. Electrical conductivities of poly(dimethyldipropargylsilane) and poly(diphenyldipropargylsilane) pellets as a function of I_2 doping level.

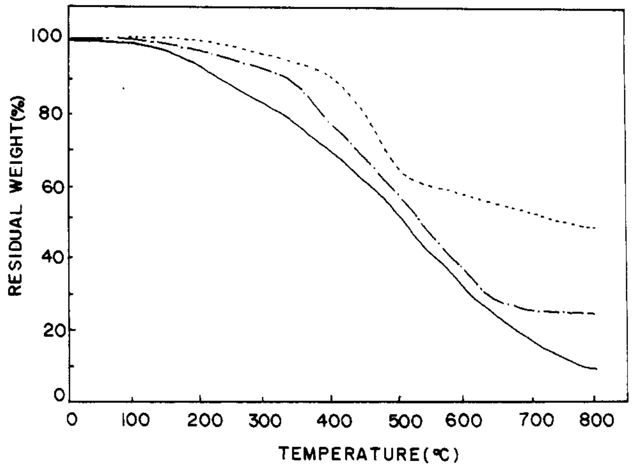

Figure 6. TGA curves of poly(dipropargylsilane)s: (—) PDMPS; (–·–) PMPPS; (---) PDPPS.

Table VII
Electrical Conductivity of Poly(dipropargylsilane)s[a]

polym	composition of doped polym[b]	conductivity,[c] Ω^{-1} cm^{-1}
PDMPS	$(C_8H_{12}Si)_1(I_2)_{0.76}$	9.1×10^{-3}–1.35×10^{-2}
PMPPS	$(C_{13}H_{14}Si)_1(I_2)_{0.74}$	1.6×10^{-2}–2.2×10^{-2}
PDPPS	$(C_{18}H_{16}Si)_1(I_2)_{0.79}$	2.6×10^{-2}–3.5×10^{-2}

[a] Pressed pellets of these polymer were doped by exposure to the vapor of iodine in a vacuum (10^{-1} mmHg). [b] Extent of doping was obtained by the weight uptake method. [c] Measured with the four-point probe method.

Stability. Figure 6 shows the TGA thermograms of poly(dipropargylsilane)s. Poly(DPPS) retained 99% of its original weight at 200 °C, 90% at 400 °C, and 60% at 500 °C. Air stability comparisons of poly(dipropargylsilane)s were examined by IR spectra in 4 successive weeks (Figure 7). When poly(DMPS) was left standing at room temperature in air for 1 week, a new carbonyl peak attributable to air oxidation appeared at 1700 cm^{-1}. However, the new carbonyl peak in poly(DPPS) appeared after 3 weeks of exposure. Thus, cyclopolymers having bulkier substituents

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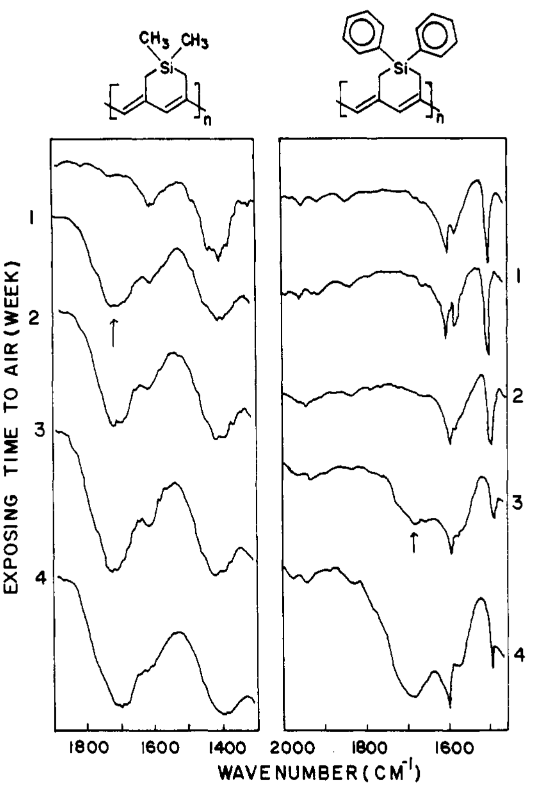

Figure 7. Comparison of oxidation stability to air at room temperature of poly(dimethyldipropargylsilane) and poly(diphenyldipropargylsilane).

were also more stable to oxidation than those having a smaller substituent.

In conclusion, (1) the catalytic activity of $MoCl_5$ was generally greater than that of WCl_6 in this cyclopolymerization; (2) $MoCl_5$ alone was the most effective catalyst for the cyclopolymerization; (3) cyclopolymers having bulkier substituents have better properties such as solubility, air stability, and thermal stability than those having smaller substituents.

In the present study, we found that these polymers had good solubilities in common organic solvents. We are now attempting to increase electric conductivity by homogeneous film casting.

Registry No. PDMPS, 114199-11-0; PMPPS, 114199-13-2; PDPPS, 114199-14-3; $MoCl_5$, 10241-05-1; Bu_4Sn, 1461-25-2; $EtAlCl_2$, 563-43-9; WCl_6, 13283-01-7; $TiCl_4$, 7550-45-0; $PdCl_2$, 7647-10-1; I_2, 7553-56-2.

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Site-Selective Derivatization of Oligoethylenimines Using Five-Membered-Ring Protection Method

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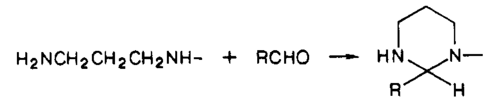
ABSTRACT: Application of modified Ganem's method was found to be effective for derivatization of oligoethylenimines (diethylenetriamine, triethylenetetramine, and pentaethylenehexamine) to site-selectively substituted products. The method involves protection of amino groups with aldehydes by formation of five-membered rings, resulting in only necessary NH groups remaining at which substituents should be introduced. The protective five-membered ring was readily deprotected to recover the amino groups after the necessary substitution reactions were carried out. This protecting method was applied to site-selective thiourea derivatizations and synthesis of completely linear heptaethyleneoctamine. The results suggest the protecting method to be highly promising in designing oligoethylenimine derivatives for a variety of applications including monomers in condensation polymerization.

Introduction

Selective reactions of $-NH_2$ and $=NH$ groups in oligoethylenimines have been a challenging problem in organic and polymer chemistry. It has been highly difficult to derivatize oligoethylenimines at the desired amino groups. The reason is that the basicities of primary (NH_2) and secondary (NH) amino groups differ only slightly, i.e., by 2 pK_a units at most.[1,2] Recently, Ganem[3,4] opened a new route to site-specific derivatization of naturally occurring oligoamines, i.e., spermine, spermidine, and other related amines, by reacting aldehydes to form six-membered protecting rings (eq 1). His basic concept is based on the stability of the six-membered ring that is the highest compared with those of the rings containing other numbers of member.



(1)

Since oligoethylenimines are commercially available, their potential importance on an industrial scale as well

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