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Syntheses of polysilanes having cyclodisilazane units in the backbone

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SUMMARY

Polysilanes containing cyclodisilazane units in the backbone were synthesized by the modified Wurtz-type coupling of available dichlorosilanes with N,N′-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in the mixture of solvents. The effect of solvent additives on the polymerization process was examined. These polymers are soluble in common solvents and very easily handled by molding or casting.

INTRODUCTION

Because polysilanes, linear polymers possessing an all Si-Si bonded backbone, have displayed some unusual properties and a number of potential applications,[1-10] the preparation of soluble derivatives of this type of polymer has been continuing today. Up to now, polysilanes have been investigated as (a) thermal precursors to β-silicon carbide[2-4]; (b) a new class of polymeric photoconductors and charge transport media[5-7]; (c) new materials for a variety of microlithographic[1,8]; (d) photoinitiator in the vinyl polymerization[2,9]; (e) nonlinear optical materials[1,10]. Polysilanes containing silicon-nitrogen groups had good thermostability and would be good materials for producing mixed SiC/Si_3N_4 ceramic compositions[11-13]. We described here our detailed studies of polysilanes (1)-(4) having cyclodisilazane units in the backbone by the modified Wurtz-type coupling of dichlorosilanes with N,N′-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in the mixture of toluene and solvent additives. The effect of solvent additives on the polymerization process was examined. The structure and properties of these polymers were also studied

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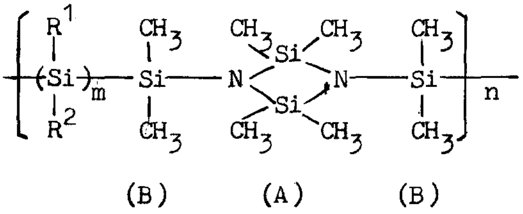

(1) $R^1 = R^2 = CH_3$ (3) $R^1 = CH_3$; $R^2 = C_6H_5$

(2) $R^1 = R^2 = C_6H_5$ (4) $R^1 = CH_3$; $R^2 = H$

EXPERIMENTAL

Materials

Toluene and diglyme were dried by refluxing over sodium and distilled before use. Dioxane was distilled from NaK alloy. Dichlorosilanes were distilled from calcium hydride before use. N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (5) was synthesized according to Fink's method[14]. The melting point, IR and ^{1}H-NMR spectra of (5) are in agreement with those of the reference[15].

Polymer Characterization

Molecular weights of these polymers were determined by GPC with three Microstyragel columns calibrated by polystyrene standards (porosity ranges $10^2, 10^3, 10^4$ Å) and with THF as eluant at a flow rate of 2mL/min. ^{1}H-NMR spectra were obtained on a FX-90Q spectrometer in $CDCl_3$. The IR spectra were examined using a Nicolet-5DX spetrometer. UV spectra were measured in THF with a Shimadze UV-260 spectrometer. Elemental analyses were obtained on a Perkin-Elmer 240C elemental analyzer.

Polymer Preparation

All reactions were conducted under an atmosphere of purified nitrogen or argon and were protected from light at all times. The polymers (1)-(4) shown in Table 1 were all prepared using the same general procedure as described here for the preparation of polymer(1).

A four-necked round bottom flask was eqipped with a gas inlet, a reflux condenser, a drop funnel and a mechanical stirrer. 24mL of dry toluene, 5mL of dry dioxane and 5mL of dry diglyme were transferred with a syringe to the reaction flask, and then heated to reflux. Freshly cut sodium(2.53g,0.11mol) was added and then the stirrer was turned on at high speed to create a sodium dispersion. Monomer(5) (1.84g,0.006mol) in 8mL toluene was added dropwise to the flask during 0.5h at a rate which maintained vigorous refluxing. The pale purple reaction mixture was refluxed for 1h, and then dichlorodimethylsilane(5.7g,0.044 mol) in 8mL toluene was added dropwise to the mixture according to method described previously[16]. After the addition of the monomers, the mixture was stirred at about 105°C for 5h and then allowed to cool to room temperature and stirred overnight. At this point, the mixture was quickly filtered under nitrogen. The filtrate was separated and the solvents were removed at 50°C under reduced pressure protected by nitrogen. After most of the solvents were removed, 50mL THF was added. To precipitate this polymer, a mixture of 50mL isopropanol and 10mL methanol was slowly added dropwise with stirring to the THF solution. The precipitate was collected and dried in a vacuum oven(about 0.5 Torr) at 25°C for 4h. 2.3g(58%) polymer(1) was obtained as a pale yellow solid. ^{1}H-NMR($CDCl_3$) δ -0.1-0.41(vbr m, 30H,-$SiCH_3$); IR(film) 2978(m), 1023(m), 880(w), 783(m), 430(w)cm^{-1}; UV(THF) λ_{max} 296nm(ϵ_{Si-Si} 5200).

Polymer(2): Yield 48%; ^{1}H-NMR($CDCl_3$) δ -0.1-0.42(br m, 24H, -$SiCH_3$), 6.80-7.36(br m, 10H, aromatics); IR(film) 3070(m), 3062 (w), 2976(m), 1490(w), 1026(m), 884(w), 780(m)cm^{-1}; UV(THF) λ_{max} 304nm(ϵ_{Si-Si} 6400).

Polymer(3): Yield 53%; ^{1}H-NMR($CDCl_3$) δ 0.10-0.40(br m, 27H, -$SiCH_3$), 6.94-7.20(br m, 5H, aromatics); IR(film) 3070(m), 3062 (m), 1958(w), 1486(w), 1026(m), 882(m), 437(w)cm^{-1}; UV(THF) λ_{max} 301nm(ϵ_{Si-Si} 6200).

Polymer(4): Yield 49%; ^{1}H-NMR($CDCl_3$) δ -0.12-0.35(br m, 27H, -$SiCH_3$), 4.0(br s, 1H, -SiH); IR(film) 2970(s), 2092(s), 1249(s) 1027(m), 880(m), 520(w)cm^{-1}; UV(THF) λ_{max} 291nm(ϵ_{Si-Si} 4800).

RESULTS AND DISCUSSION

Syntheses

Polysilanes(1)-(4) were prepared by cocondensation of monomer(5) with other organodichlorosilanes(Me_2SiCl_2, Ph_2SiCl_2, $PhMeSiCl_2$, or $MeHSiCl_2$) in the mixture of toluene and other solvent additives(dioxane and diglyme). Since the activity of (5) is lower than those of other organodichlorosilanes, the yields of formable copolymers were very low (<5%) when (5) and other organodichlorosilanes were directly refluxed with sodium dispersion in solvents for 10h. In this case, we have used the method of step polymerization to replace coupling method which has been used for preparation of commom copolysilanes[1,2]. At first, the toluene solution of (5) was added to the sodium dispersion in the mixture of solvents. After the mixture was refluxed for 1h, the other dichlorosilane was added dropwise to the mixture. Copolymerization was carried out for another 5h, and copolymers(1)-(4) containing cyclodisilazane units in the backbone were obtained with good yields. A small amount of insoluble material(2-5%) was formed when polymer(1) and polymer(2) were synthesized.

The yields, molecular weights, compositions, nitrogen contents, and appearances of polymers (1)-(4) were listed in Table 1.

Table 1 Yields, Molecular weights, Compositions, Nitrogen contents, and Appearances of Polymers(1)-(4)[a]

Polymer	Yield (%)	$\bar{M}w \times 10^{-3}$ [b]	m[c]	N (%)[d]	Appearances
1	58	360(3.8)	8	3.84(3.87)	pale yellow sol.
2	48	186(2.7)	12	1.11(1.15)	pale yellow sol.
3	53	200(3.5)	9.5	1.95(2.01)	yellow sol.
4	49	160	6	5.30(5.34)	pale yellow sol.

[a] Solvent mixture was toluene-dioxane-diglyme(80:10:10).

[b] From GPC analysis using polystyrene calibration standards.

c From integration of ^{1}H-NMR signals for the different group.

[d] The data in brackets were calculation values.

Since the Si-N and Si-H bonds could be hydrolyzed and alcoholyzed easily in the presence of alkali[16], it was necessary to avoid the polysilanes getting in touch with alcohol and water under the existence of base. After the reaction has been completed, filtration was quickly carried out under nitrogen in drybox. Thus, the polymers were separated from basic system and precipitated with a mixture of isopropanol and methanol in the neutral condition, Si-N and Si-H bonds were not destroyed.

Solvent Additive Effect on Polymerization

In our experimental conditions, it was found that solvent additives , such as dioxane and diglyme, greatly improved the yields of polymers(1)-(4) and apparently promoted rapid polymerization. When polymerization was carried out in toluene alone without additives, the reaction time was very long and the yields of copolymers were quite low[11,12]. The phenomena have been carefully studied in preparation of common polysilanes by R.D.Miller et.al and us[1,17]. Some representative results are shown in the Table 2. The data in Table 2 have shown that a large amount of solvent additives could improve the yields of the polymers, but the molecular weights of the polymers usually reduce. We have found that as little as 10% of dioxane and 10% of diglyme often significantly increases the yields of isolated polymers and the molecular weights of isolated polymers usually increase. Under these conditions, the mixture of dioxane and diglyme seems to be somewhat more effective than dioxane or diglyme alone, respectively.

Characterization

The identities of these polymers (1)-(4) were established by IR ^{1}H-NMR, UV spectra and elemental analyses. In IR spectra, the Si-CH_3 absorptions appear at about 2970, 1405 and 1255cm^{-1}. The band of Si_2N stretch appears at about 880cm^{-1}. The characteristic absorptions of structures containing N-silylated silicon-nitrogen ring are observed at about 1026cm^{-1}.[14] The IR absorptions of Si-N-H(about 1190cm^{-1}) and N-H(about 3500cm^{-1}) were not found[18]. This indicated that disilazane ring was not destroyed in our experimental conditions. The IR absorptions of the polymers (1)-(4) were consistent with the structure proposed.[11-17]

In ^{1}H-NMR spectra, the peaks between -0.1-0.4ppm attributed to protons of SiCH_3 . In polymers(1)-(4), because the Si-CH_3 situated in (A) was affected by the two nitrogen atoms and the tension of the ring, its chemical shift was about 0.4ppm. The

Table 2 Solvent Additives Effect on Polymerization[a]

Polymer	Additive (Vol%)	Yield (%)	$\overline{M}_w \times 10^{-3}$ [b]	m[c]	R[d]
1a	0	8	21(3.7)	10	8.2
1b	Dioxane(10)	40	320(3.0)	9	2.7
1c	Diglyme(10)	41	328(3.6)	7.5	2.3
1d	Dioxane(10) Diglyme(10)	58	360(3.8)	8	0.8
1e	Dioxane(15) Diglyme(15)	61	282	8.3	-
2a	0	5.7	62(2.5)	10	6.7
2b	Dioxane(10) Diglyme(10)	48	186(2.7)	12	0.5
3a	0	11	96(3.0)	11	6.5
3b	Dioxane(10) Diglyme(10)	53	200(3.5)	9.5	0.2
4a	0	18	146	4.4	--
4b	Dioxane(10) Diglyme(10)	49	160	6	--

[a] Solvent was toluene.

[b] From GPC analysis using polystyrene calibration standards.

[c] From integration of ^{1}H-NMR signals for different groups.

[d] Ratio of high/low molecular weights.

Si-CH$_3$ lying in (B) was influenced by only one nitrogen atom, its chemical shift was about 0.2ppm. The proton couple of the Si-CH$_3$ (A and B) would produce a very broad absorption peak.

In UV spectra, polymers(1)-(4) showed the absorptions at about 300nm. The introduction of disilazane ring shifted the absorption maxima to shorter wavelength.[11] These were attributed to non-planar of the disilazane ring. When this unit inserted into the Si-Si bond of polysilane, the electron delocalization of long Si-Si σ bond was interrupted.

Polymers(1)-(4) are readily soluble in common solvents, such as THF, toluene, benzene, and chloroform etc.. They can be cast or molded into films. Because the polymer(4) contained silicon-hydrogen group, it can be easily crosslinked by hydrosilylation with unsaturated compounds as the crosslinking agent in the presence of catalyst.[16]

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