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The efficient synthesis of poly(silapropynylenes) via condensation of NaC≡CNa with $R^1R^2SiCl_2$ activated by pyridine

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Summary

To efficiently prepare poly(silapropynylenes), the condensation of NaC≡CNa with $R_1R_2SiCl_2$ activated by pyridine were investigated. The condensation produced tactable polymers(Mw ca. 2100-9000) with significantly higher yields of 80-97% than those from $R_1R_2SiCl_2$ itself and also gave rise to much more improvement in the yields and molecular weight than with acetylenic "di Grignard" or "di lithium salts". The activation of $R_1R_2SiCl_2$ by pyridine accelerated the condensation reaction, which resulted in production of macrocyclic polymers as well as linear polymers.

Introduction

The poly(silapropynylenes) having acetylene group in main chain are expected to be used as impregnating agents for strengthing ceramics, precursors for β-SiC fibers because of its high ceramic char yields due to resistance to oxidation and thermal stability of Si-ethynyl bond to high temperature(1), and its potent photo-curing.

These polymers are currently produced by condensation of dihalosilanes with acetylenic "di Grignard" or "di lithium salts"(from metallation of HC≡CH by Grignard or n-BuLi), but only low molecular weight materials(Mw ca. 1000-3000) are obtained with low yields(2). This has been ascribed to the inevitable presence of monoacetylide, which is contained in dianion, acting as a chain terminator. More recently, high molecular weight polymers were prepared by using pure di lithium salts, which prepared from trichloroethylene and n-BuLi(3). On the other hand, sodium carbide(NaC≡CNa) has been known to be the cheapest acetylenic dianion with high purity(from metallation of HC≡CH by sodium metal), and sodium acetylide(NaC≡CH) has also been known not to act as a chain terminator(4), but it has not been applied in preparation of poly(silapropynylenes) because of its low reactivity with dichlorosilanes(5,6).

However, from condensation of activated dihalosilanes with NaC≡CNa we developed tactable polymers of high molecular weight with high yield. In this article we describe the synthesis of poly(silapropynylenes) using NaC≡CNa.

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Experimental

^{1}H NMR spectra were determined with a Jeol model JNM-PMX60Si NMR spectrophotometer in deuteriochloroform or benzene-d_6 with TMS(1%) used as an internal standard. ^{13}C NMR spectra and ^{29}Si NMR were obtained on Varian Cemini-300 and Bruker AM-200, respectively, in deuteriochloroform as a solvent without internal standard. IR spectra were determined with Mattson Instruments model 6030 Galaxy series FT-IR using KBr disk or thin film coated on NaCl cell. UV spectra were obtained with Simadzu UV-Visible Recording spectrophotoimeter (model UV-240) using thin films spin-coated on qurtz plate.

Gel permiation chromatography(GPC) was carried out on a Waters associates model 150-C ALC/GPC instrument equipped with differential refractive index dector : Seperation was effected by four Tosoh TSK-GEL column in series with pore sizes 10^3, 10^4, 10^5, and 10^6 Å and with THF as the eluent at flow rate of 1mL/min(35°C). All molecular weight were reported versus polystyrene standards.

1. Sodium Carbide($NaC{\equiv}CNa$) Preparation(7)

Sodium acetylide($NaC{\equiv}CH$) was prepared by reaction of acetylene gas with dissolved sodium metal in liquid ammonia and the sodium carbide($NaC{\equiv}CNa$) was prepared as pale yellow powder by thermal decomposition of the sodium acetylide in vacuo, the evolved acetylene being removed at 170-180°C/10^{-3} mmHg for 4 hrs.

2. Synthesis of Polymer 1 as a General Example of Polymer Preparation

A 500mL, three-necked, round-bottomed flask was equipped with a magnetic stirrer, a pressure-equalizing addition funnel, and a reflux condenser with a gas outlet tube and one neck was sealed with a septum. The inner of the reaction flask was thoroughly dried and purged with dry argon. About 29.4g of sodium carbide(0.21 mole) and 80mL of dry pyridine were added to the flask in inert atmosphere and 51.6g of dichlorodimethylsilane(0.40 mole) was added in a dropwise manner to the sodium carbide/pyridine slurry. After the addition was done, the reaction mixture was heated to reflux for 6 hrs with stirring and then cooled to room temperature. About 50mL of tetrahydrofuran was added to the reaction mixture while stirring and quenched with 250mL of 50% aqueous methanol. The product after filteration of the precipitated polymeric powder was washed a number of times with aqueous methanol and methanol, and dried in vaccum oven at 60°C/1 torr for 5 hrs to give Polymer 1.

Results and discussion

Attempts to condense dichlorodimethylsilane with $LiC{\equiv}CLi$ or $MgClC{\equiv}CMgCl$ to obtain tactable poly(dimethylsilapropynylene) with high molecular weight so far led only to low molecular weight polymer(Mw 2300 and 1500, respectively) with low yields of 60% and 65%, respectively.

$$\begin{array}{ll} & LiC{\equiv}CLi \xrightarrow{THF} -[-Me_2SiC{\equiv}C-]_n- \text{ Mw : } 2300(\sigma=1.6) \\ Me_2SiCl_2 + & \text{or} \\ & MgClC{\equiv}CMgCl \xrightarrow{THF} -[-Me_2SiC{\equiv}C-]_n- \text{ Mw : } 1500(\sigma=1.9) \end{array}$$

$$R_1R_2SiCl_2/\text{pyridine} + NaC{\equiv}CNa \xrightarrow{PYRIDINE} -[-R_1R_2SiC{\equiv}C-]_n- \qquad \text{(eq.1)}$$

Polymer 1: $R_1= R_2= CH_3$ Polymer 2: $R_1= CH_3$, $R_2=$ phenyl
Polymer 3: $R_1= R_2=$ phenyl Polymer 4: $R_1= CH_3$, $R_2=$ vinyl
Polymer 5: $Me_2SiCl_2/MePhSiCl_2(1{:}1)$

$$R_1R_2SiCl_2 + NaC{\equiv}CNa \xrightarrow{THF} -[-R_1R_2SiC{\equiv}C-]_n- \qquad \text{(eq.2)}$$

Polymer 6: $R_1= R_2= CH_3$ Polymer 7: $R_1= CH_3$, $R_2=$ phenyl

However, in condensation of dihalosilanes with NaC≡CNa all monomers were almost converted to polymeric materials and the yields and molecular weight were unchanged when reaction were carried out for longer than 6 hrs. The oily or waxy oligomers were removed by pouring methanol into THF solution of reaction product. All Polymer 1-7 obtained after removal of oligomer were completely melted without decomposition and soluble in THF but only Polymer 4 contained infusible fraction of 9.7% which perhaps reflects the cross-linked polymers at vinyl group. The physical appearance of Polymer 1, 4, and 6 was of powder and that of Polymer 2, 3, 5, and 7 was of brittle, hard glassy solid which can be molded, cast into films or drawn into fibers with fine denier (<10μm). Results for the condensation polymerizations using NaC≡CNa are listed in Table 1. The spectral properties of ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR and FT-IR for the above polymers correspond to the recently reported data(3,8) and are summarized in Table 2.

Polymers with Mw 2000-9700 from the polymerization using NaC≡CNa were always obtained, whose molecular weight are greater than those by using of

Table 1. Results of the condensation of $R_1R_2SiCl_2$ and NaC≡CNa.

Polymer[a]	yield (%)	mp (°C)	molecular weight	Mw/Mn (σ)	color
1	84	165.5	8,950	1.4	yellowish brown
2	95	—	3,980	2.6	redish brown
3	97	—	2,100	1.5	brown
4	89(9.7)[b]	—	6,790	1.5	dark brown
5	80	—	6,490	1.7	redish brown
6	55	171.5	9,740	1.7	off-white
7	65	—	5,500	3.8	red

a : Fusible and soluble fractions in THF obtained after removal of oligomer.
b : Infusible and insoluble fraction in THF.

Table 2. Characterization data for polymers obtained from the condensation of $NaC\equiv CNa$ and $R_1R_2SiCl_2$ activated by pyridine.

Polym.	UV(film) λ_{max}(nm)	FT-IR (KBr or Film) (cm^{-1})
1	<200	3275,2961,2908,2043,1406,1260
2	220	3272,3077,3025,2967,2903,2039,1429,1408,1256,1117,1028,999,799,737
3	225	3270,3077,3025,2039,1429,1117,1026,1003,747
4	223	3275,3057,3019,2967,2905,2041,1404,1256,799,747
5	213	3272,3077,3025,2965,2903,2039,1429,1408,1256,1117,1028,999,799,747

	^{1}H NMR(ppm)	^{29}Si(ppm)	^{13}C(ppm) ($SiCH_3$, $C\equiv C$, Phenyl)
1	0.285[0.33]	-41.22(s)	0.09;110.95[1.5,112]
2	0.50[0.55];7.35(m),7.68(m)	-45.23(s)	-0.20;111.1[1.0,111.5];128.2,130.3,132.8,134.3
3	7.18(m),7.57(m)	-49.66(s)	111.1[111.3];128.1,13.5,131.7,134.9
4	0.37;5.99	-48.05(s)	-1.19;110.17;132.21,135,98
5	0.28;0.50;7.35(m),7.65(m)	-40.88(t) -45.50(t)	-0.11(m);112.9(m),110.9(m),109.1(m); 128.2,130.4,133.7,134.3

[ ] : ref.(3)

$ClMgC\equiv CMgCl$ or $LiC\equiv CLi$(from metallation of $HC\equiv CH$ by MeMgCl or n-BuLi). The yields of tactable fractions by using of pyridine as a solvent (eq.1), which ranged from 80 to 90%, were significantly greater than the yields of corresponding fractions by using of THF(eq.2), which ranged from 50 to 65%, but showed somewhat lower molecular weights and more narrow molecular weight distribution. Though the dissociation of $NaC\equiv CNa$ is more in pyridine than THF, above results could not be explained by only polar effect of solvents because substitutions of chlorosilane with $NaC\equiv CH$ resulted in ethynylsilanes with low yields of 10-50% even in aprotic polar solvent such as N-methylmorpholine, nitrobenzene, $(Me_3N)_3PO$ etc.(5).

Hydrido-halosilanes and pyridine have been generally known to form the ionic adducts of various structure versus stoicheiometry of pyridine(9), and the amminolysis of these adducts were reported to lead polysilazanes with higher molecular weight than amminolysis of hydrido-halosilane itself(10). And also in the case of halosilanes in which hydrogens at silicon atom are substituted to methyl group, Me_2SiCl_2-pyridine adduct is known not to be precipited at room temperature because of weakened acceptor power of silicon atom. However, as soon as substituted dichlorosilanes are contacted with pyridine, the white fume is generated and soon disappeared. This strongly suggests that the unstable adducts are formed due to weak election donor-acceptor power between pyridine and the silicon atom of substitutied dichlorosilane. Therefore, the activation of disubstituted dihalosilanes due to formation of the above unstable adducts probablely are thought to accelerate the reaction of dihalosilanes with $NaC\equiv CNa$.

On the other hand, as discribed by Table 2, all polymers 1-7 were shown to be linear polymer because their IR spectra show sharp band in the region of 3270-3275cm^{-1} attributed to stretching vibration of terminal ≡C-H. As shown Fig.1, however, the relative ratios of transmittance % height of terminal ≡C-H bond versus internal C≡C bond stretching vibration (T_2/T_1) for Polymer 1 and 2 with the lower molecular weight (using pyridine) are less than those for Polymer 6 and 7(using THF), respectively. Therefore, the polymerization in pyridine were assumed to produce cyclic polymer as well as open chain polymer. Recently, Bortolin, Brown, and Parbhoo(8,11) have reported that polymers composed of an alternating silyl group and diethynyl unit undergo a redistribution reaction occurring nucleophilic substitution at the silicon atom in the presence of a catalytic amount of the silylethynyl-lithium species.(eq.3) This redistribution reaction in cyclic polymers resulted in ring-opening polymerization, but open chain

$$-[-\mathrm{SiC}\equiv\mathrm{C}-]_m-\mathrm{Li} + \begin{array}{l} [-\mathrm{SiC}\equiv\mathrm{C}-]_n- \longrightarrow -[-\mathrm{SiC}\equiv\mathrm{C}-]_{m+n}-\mathrm{Li} \\ \text{ring structure} \\ -[-\mathrm{SiC}\equiv\mathrm{C}-]_n- \longrightarrow -[-\mathrm{SiC}\equiv\mathrm{C}-]_{m+x}- + \mathrm{Li}-[-\mathrm{SiC}\equiv\mathrm{C}-]_y- \\ \text{open chain} \end{array} \qquad \text{(eq.3)}$$

polymers completely transformed into oligomer owing to depolymerization(phenyl-substituted polymers) or lower molecular weight polymers with much broader molecular weight distribution (alkyl-substituted polymers).(12)

So, we next carried out the above redistribution reaction to investigate the presence of cyclic polymer in Polymer 1, 2, 6 and 7. A mixture of the polymer and a catalytic amount of n-butyllithium in THF was stirred at room temperature for 18 hrs, followed the removal of oligomer by methanol precipitation. As described by Table 3, the soluble fractions in THF which obtained from redistribution reaction for Polymer 1 and 2 were much greater than those for Polymer 6 and 7, and especially in the case of Polymer 1, the insoluble fraction in

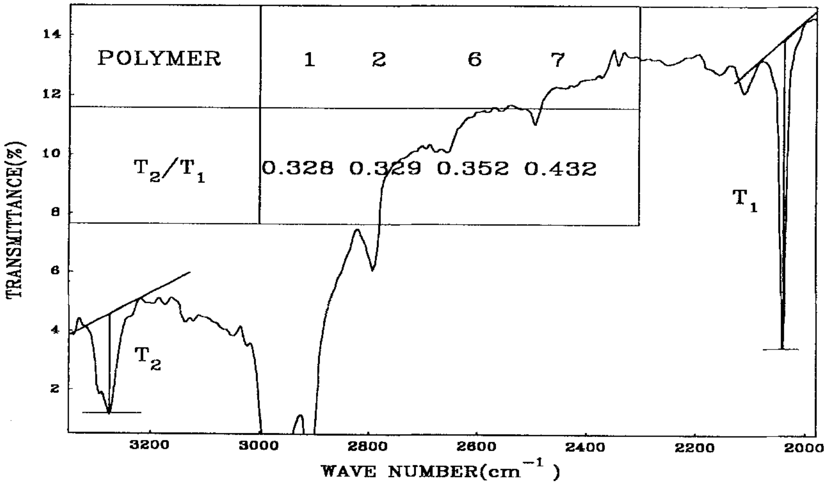

Fig.1 The relative ratios (T_2/T_1) of transmittance % height of terminal ≡C-H bond versus internal C≡C bond for Polymer 1, 2, 6, and 7.

Table 3. Results of reaction of poly(silapropynylenes) with n-BuLi[a].

Polymer	Insoluble Fraction in THF(%)	Soluble Fraction in THF(%)	Molecular Weight $(\times 10^3)^b$	Mw/Mn (σ)
1	13.8	17.7	29.5	1.9
2	——	27.9	9.1	1.1
6	——	7.3	1.0	3.9
7	——	5.5	2.2	5.7

a : the amount of n-BuLi ; 0.53 mole% per $Me_2SiC{\equiv}C$ unit, 0.38 mole% per $MePhSiC{\equiv}C$ unit.
b : Weight average molecular weights(Mw) of soluble fractions in THF were measured by GPC.

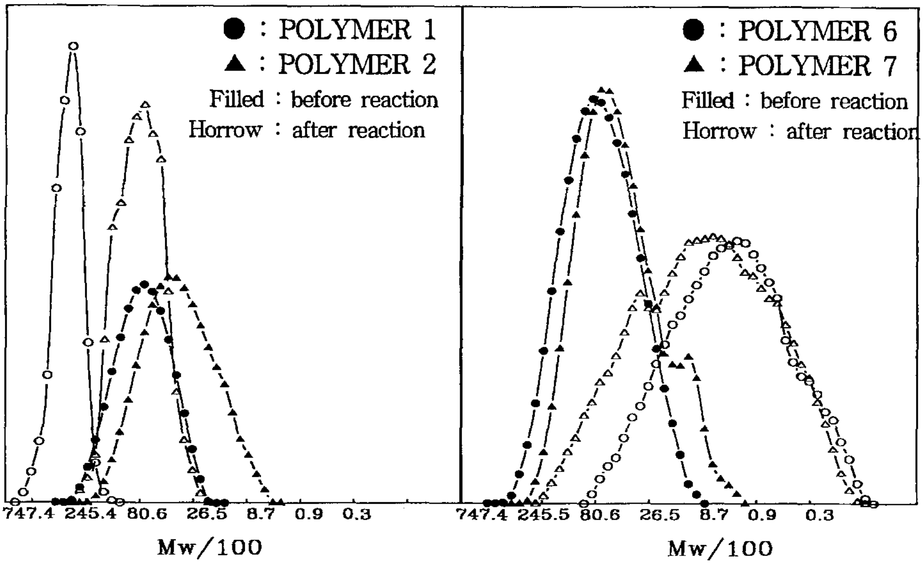

Fig.2 Normalized GPC profiles of Polymer 1, 2, 6, 7, and soluble fraction in THF which obtained after the redistribution reaction of those with n-BuLi.

THF was produced with yield of 13.8%. As can also be seen in Fig. 2. the molecular weights of the soluble fractions in THF by the treatment of Polymer 1 and 2 with n-butyllithium sharply increased, which is responsible for the presence of cyclic component occurring ring-opening polymerization by the redistribution reaction. In the case of Polymer 6 and 7 the decrease of molecular weight and much broader molecular weight distributions were observed, indicating that only the redistribution reaction of open chain systems took place.

The above results indicate that the polymerization in pyridine also produce the macrocyclic polymer which can not be removed by methanol precipitation. Therefore, we thought that the acceleration of condensation reaction due to the activation of Si-Cl bond by pyridine gave rise to increase the production of the fusible and soluble polymers, while the molecular weight was decreased more or less because of produceing the macrocyclic polymer.

The thin films of polymers under irradiattion with a 450W medium pressure-Hg lamp for 300s were infusible. The cured films have shown the high char yields of 70-80% according to TGA analysis up to 900°C. In the X-ray power differaction patterns of polymers pyrolyzed at 1200, 1300, 1400°C in Ar atmosphere, the sharp diffraction line due to β-SiC began to appear above 1300°C.

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