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Synthesis of A New Kind of Acetylenic Polysilazane

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Abstract: A new kind of conjugated polymer, acetylenic polysilazane was prepared by ammonolysis of acetylenic dimethylchlorosilane. The polymer was characterized by ^{29}Si、^{13}C NMR and elemental analysis.

Keywords: Synthesis, acetylenic, polysilazane, conjugated polymer.

Conjugated polymers have attracted much attention because of their academic interests and a wide variety of potential applications, such as large area flat-panel displays and light-emitting diodes[1]. The properties of conjugated polymers would be improved and the electron delocalization will be affected if organosilicon unit is incorporated into the polymer backbone. Research of silicon-containing acetylenic polymers has been focused on those containing the Si-C or Si-O polymers before[2,3], but the acetylenic polymers containing Si-N bonds have not been reported to the best of our knowledge. We reported the synthesis of acetylenic polysilazane in this paper. The introduction of nitrogen atom with a lone pair of electrons may result in the variation of a few properties. In addition, this acetylenic polysilazane has possibility of application in the field of ceramic[4,5].

Materials and instruments

n-Butyllithium was purchased from Acros Co. Trichloroethylene (TCE), Me_2SiCl_2 were distilled before use. Diethylether and THF were distilled from deep purple solutions of sodium benzophenone. ^{13}C NMR and ^{29}Si NMR spectra were recorded in $CDCl_3$ solution with a Bruker WM 300 spectrometer, tetramethylsilane (TMS) as an external standard in ^{13}C NMR and hexamethyldisiloxane (δ 6.9 ppm) as an external standard in ^{29}Si NMR. Elemental analysis was determined with a Carlo Erba 1106 analyzer.

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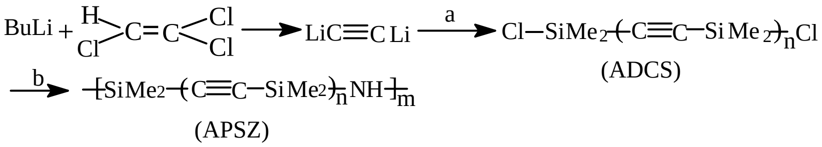
General procedure for the reactions

Scheme 1



a) Me_2SiCl_2 ;

b) NH_3

The acetylenic polysilazane (APSZ) was synthesized as described in **Scheme 1**.

Preparation of dilithioacetylene (*$LiC\equiv CLi$*)

Into a 250 mL three-necked flask (equipped with a reflux condenser, a dropping funnel and flushed with nitrogen) was added 100 mL of a 1:1 mixture of freshly distilled ethyl ether and tetrahydrofuran (THF) and 0.12 mol of BuLi. After cooling the solution to -78℃, 0.04 mol of trichloroethylene in 30 mL of Et_2O was added dropwise over 20 min. to the stirred solution. Then the -78℃ bath was removed. After 12 h of stirring at room temperature, the mixture was full of white solid (LiCl).

Preparation of acetylenic dimethylchlorosilane (ADCS)

Into a 500 mL three-necked flask equipped with a reflux condenser and an adding funnel, was added 30 mL of Et_2O and 0.16 mol of Me_2SiCl_2 under N_2. The as-prepared $LiC\equiv CLi$ was added dropwise while stirring under 0°C. After completion of addition, the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was filtered, and 100 mL Et_2O was added to wash the slurry 2-3 times, and then the Me_2SiCl_2 and the solvent was distilled off at room temperature under reduced pressure. Oligomers ADCS was obtained as yellow viscous liquid (yield: 95%). ^{29}Si-NMR (δ ppm): -0.6 (Cl-Si-C≡C), -40.0 (C≡C-Si- C≡C); ^{13}C-NMR (δ ppm): 1.0, (Si-CH_3), 112(Si-C≡C-Si).

Preparation of acetylenic polysilazane (APSZ)

APSZ was synthesized from ammonolysis of ADCS. Into a 250 mL three-necked flask equipped with a reflux condenser, under N_2 were added 100 mL toluene and 2 g ADCS. Ammonolysis was carried out at room temperature under high speed stirring till the reaction mixture did not absorb NH_3 any more. Precipitated NH_4Cl was removed by filtration and transparent solution was obtained. The resulting solution was concentrated to give APSZ as a yellow solid. ^{29}Si-NMR (δ ppm): -16.7, -18.4 (Si-NH) , -40.5, (C≡C-Si- C≡C); Elemental analysis. Found: C, 52.53; H, 7.93; N, 3.10; Cl,<0.3. Calcd.: C, 54.66; H, 7.66; N, 2.90; Cl, 0.

Results and Discussion

The structure of the ADCS was identified by ^{29}Si- NMR and ^{13}C-NMR. **Figure 1** shows ^{29}Si- NMR spectrum of ADCS. The peak at 0.6 ppm is assigned to Si-Cl[7], and the peak at –40.0 is assigned to C≡C-Si- C≡C[6]. **Figure 2** shows the ^{29}Si-NMR of APSZ. As the Si-N introduced, the Si-Cl peak of the ADCS at 0.6 ppm disappeared and new Si-N peaks appeared at –16.7 and –18.4 ppm. The signal migration from δ 0.6 to –16.7, -18.4 ppm after forming Si-N bond APSZ is probably due to a lone pair electrons of nitrogen atom.

Figure 1 ^{29}Si- NMR spectrum of ADCS

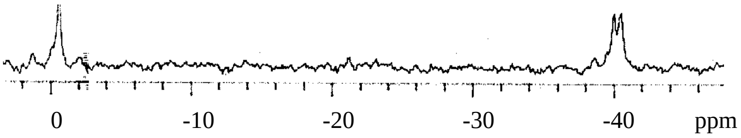
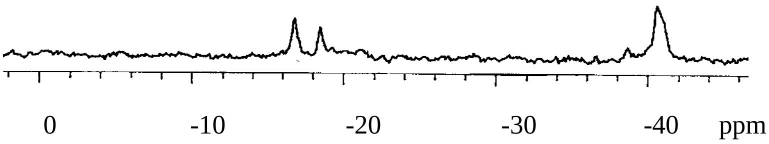


Figure 2 ^{29}Si-NMR spectrum of APSZ



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