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Polymeric organosilicon systems

XIII *. Thermal polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes

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Abstract

Treatment of 1,2,5,6-tetrasilacycloocta-3,7-diynes in a degassed sealed tube at 230 °C afforded ring-opened polymers, poly[(disilanylene)ethynylenes] in high yields.

Recently, we have demonstrated that the reaction of 1,2,5,6-tetrasilacycloocta-3,7-diynes with a catalytic amount of butyllithium in THF at room temperature gives with ring-opening polymerization poly[(disilanylene)ethynylenes] with high molecular weights [1,2]. Later, however, we found that there are some limitations to this method. For example, the polymerization of 1,2,5,6-tetramethyltetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**1a**) gives poly[(1,2-dimethyldiphenyldisilanylene)ethynylene] (**2a**) only in low yield [1], and gel permeation chromatography (GPC) of the polymers obtained by this method shows broad molecular weight distribution, owing to the redistribution reaction involved in this system [2–4].

We have now discovered a more convenient route to the poly[(disilanylene)ethynylenes] [5]; the thermal polymerization of the 1,2,5,6-tetrasilacycloocta-3,7-diynes affords ring-opened polymers with high molecular weights in high yields. When **1a** was heated in a degassed sealed tube at 230 °C for 24 h, and the resulting polymer was reprecipitated from ethanol–chloroform, polymer **2a** was obtained in 87% yield. Its molecular weight was determined as 220,000 ($M_w/M_n = 3.99$), relative to polystyrene standards (Scheme 1). All spectral data obtained from the polymer **2a** corresponded with those of the previously reported polymer prepared by the anionic ring-opening polymerization of **1a** [1,2].

The thermal ring-opening polymerization is remarkably general for 1,2,5,6-tetrasilacycloocta-3,7-diynes and readily affords poly[(disilanylene)ethynylenes]. Thus,

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* For Part XII see ref. 2.

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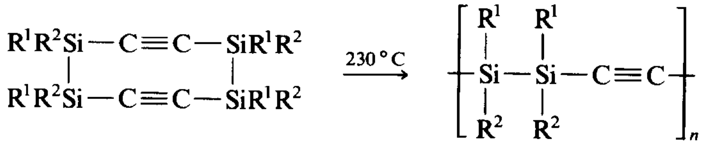

(**1a**: R^1 = Me, R^2 = Ph;
1b: R^1 = Me, R^2 = Hexyl;
1c: R^1 = R^2 = Et)

(**2a**: R^1 = Me, R^2 = Ph;
2b: R^1 = Me, R^2 = Hexyl;
2c: R^1 = R^2 = Et)

Scheme 1

treatment of 1,2,5,6-tetrahexyltetramethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**1b**) gave poly[(1,2-dihexyldimethyldisilanylene)ethynylene] (**2b**) under the same conditions in 41% yield. Other products such as oligomers were not detected by GPC, although 45% of the starting compound **1b** was recovered unchanged. Similarly, heating 1,1,2,2,5,5,6,6-octaethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**1c**) at 230 ° C for 24 h gave poly[(tetraethyldisilanylene)ethynylene] (**2c**) in 34% yield, along with 46% of the starting compound **1c**. Prolonged heating (48 h) of **1c** under the same conditions gave the polymer **2c** in higher yield (52%). GLC analysis of the solvents used for reprecipitation of **2c** showed that 48% of **1c** was recovered unchanged. It seems likely that the rate of thermal polymerization would be slower for the tetrasilacycloocta-3,7-diynes **1b** and **1c**, as they have large alkyl groups on silicon atoms in the eight-membered cyclic ring. Molecular weights determined by GPC after 48 h reaction were 32,700 ($M_w/M_n = 3.76$) and 384,000 ($M_w/M_n = 4.29$) for **2b** and **2c** respectively.

The polymer **2b** is viscous liquid, but **2c** is solid and melts at 143–149 ° C without decomposition. The polymers **2b** and **2c** are soluble in common organic solvents such as THF, benzene and halocarbons.

All spectral data obtained for **2b** and **2c** were consistent with the proposed structures. The ^{13}C NMR spectrum of **2b** revealed two resonances at δ -4.54 and -4.36 (methylsilyl carbons), and a singlet resonance at 114.52 ppm (*sp*-carbons), as well as six resonances at 14.14, 22.66 (two carbons), 24.55, 31.63 and 33.12 ppm (hexyl group), while the polymer **2c** showed two resonances at 4.84 and 8.29 (ethyl carbons), and a singlet resonance at 113.87 (ethynylic carbons).

The presently studied thermal polymerization involved no radical mechanism because treatment of tetrasilacycloocta-3,7-diynes with radical initiators gave no ring-opened polymers. Thus, heating **1a** or **1c** with a catalytic amount of benzoylperoxide at 100 ° C for 4 h gave no polymeric products, and the starting cyclic compounds are recovered unchanged. Similarly, treatment of **1a** or **1c** in the presence of a catalytic amount of AIBN in refluxing toluene gave no polymeric products, and again **1a** or **1c** were recovered unchanged, respectively. We are now continuing our research on this system.

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