Macromolecules 1995, 28, 5160−5161

Alkoxy-Substituted Poly(silylenemethylenes). A New Class of Alkoxy-Substituted Polymers

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Received March 20, 1995
Revised Manuscript Received May 3, 1995

The poly(silylenemethylenes), $[SiRR'CH_2]_n$, constitute a relatively undeveloped class of inorganic polymers that are of potential interest as relatives of both the carbon-based polyolefins[1] and such inorganic polymers as the polysilanes, polysiloxanes, and polyphosphazenes. Until quite recently, the only route that has been available for the preparation of high molecular weight, linear polymers of this type has involved the Pt-complex-catalyzed ring-opening polymerization of the corresponding substituted 1,3-disilacyclobutane monomers. This route works best for R and R′ = Me and Me, Ph substituents on Si.[2] Of the polymers prepared by this route, only poly[(dimethylsilylene)methylene] has been well characterized,[3] and this is apparently an amorphous material with a relatively low T_g. Earlier attempts to introduce other functionality on Si by polymerization of the corresponding substituted disilacyclobutanes as well as by methyl-cleavage reactions on poly[(dimethylsilylene)methylene] resulted in low molecular weight materials.[2a,4] The discovery made in our laboratory that polymerization and subsequent reduction of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane[5] and tetrachlorodisilacyclobutane[6] gives high molecular weight poly(silapropylene) and poly(silaethylene), respectively, effectively opened up a new route to the preparation of substituted poly(silylenemethylenes).

Among the possible substituted poly(silylenemethylenes) that would be of particular interest to prepare are the alkoxy-substituted polymers, since these would apparently represent the first well-characterized linear polymers with alkoxy substituents on a backbone silicon atom. Such polymers may also have potential for use as sol−gel precursors to inorganic/organic network polymers and as functional polymers with novel physical properties. Moreover, to our knowledge, the only polymers known that have two alkoxy groups on the same backbone atom are the polyphosphazenes, some of which show such interesting properties as mesophase formation[7] as well as ionic conductivity when various Li salts are added.[8]

We report here our investigations of synthetic routes for the preparation of alkoxy-substituted poly(silylenemethylenes) as well as the preliminary characterization of some new members of this class of polymers, namely, $[Si(OR)_2CH_2]_n$ and $[Si(CH_3)(OR)CH_2]_n$ where R = CH_2CF_3 and CH_2CH_3.

Generally speaking, there are two possible ways to synthesize alkoxy-substituted poly(silylenemethylenes). The first is the polymerization of the corresponding substituted monomers, and the second is the functionalization of a preformed polymer which has suitably reactive groups on the Si atoms.

Based on our previous observation that the polymerization and subsequent reduction of tetrachlorodisilacyclobutane gives poly(silaethylene) with a degree of polymerization (DP) of 200,[1] functionalizing poly[(dichlorosilylene)methylene] to obtain poly[(dialkoxysilylene)methylene] was tried first. Unfortunately, all attempts to introduce ethoxy groups through reactions of the chloropolymer with sodium ethoxide or an ethanol/triethylamine mixture led to incompletely substituted and generally intractable materials. Therefore, the polymerization of tetraethoxydisilacyclobutane[9] was attempted.

It was found that the polymerization of neat tetraethoxydisilacyclobutane with H_2PtCl_6 at 100 °C or $(C_6H_8)_2Pt_2Cl_4$ at room temperature, followed by reprecipitation from hexane at −60 °C, gives poly[(diethoxysilylene)methylene][10] of reasonably high molecular weight. This polymer is a moisture-sensitive solid which is quite soluble in most organic solvents, including alcohols, and insoluble in acetonitrile. Due to its sensitivity to moisture, molecular weight determination by GPC[11] was attempted only after reduction with $LiAlH_4$ to give poly(silaethylene). The resultant polymer was obtained with $\bar{M}_n$ = 5800 and polydispersity (PD) = 3.8. This corresponds to a DP = 130. The large polydispersity is due to a small shoulder of high molecular weight polymer in the size-exclusion chromatogram. Thermal analysis by DSC[11] shows no noticeable T_g and T_m = 31 °C. The corresponding poly(diethoxyphosphazene) is an amorphous material with T_g = −84 °C.[12]

Polymerization of tetrakis(trifluoroethoxy)disilacyclobutane[13] by H_2PtCl_6 at 100 °C gave a solid material which, after washing with toluene, was extracted with THF. The THF-soluble fraction accounted for around 50% of the polymer.[14] Both fractions showed no T_g and T_m = 132−138 °C and a similar enthalpy of fusion (ΔH = 13.5−15 J/g). No mesophase formation, as has been observed for poly[bis(trifluoroethoxy)phosphazene],[15] was detected by DSC or by optical microscopy; however, a spherulitic pattern typical of a crystalline polymer was observed below T_m. In contrast to the diethoxy derivative, this polymer is stable toward hydrolysis and only slightly soluble in polar organic solvents. Due to its insolubility, molecular weight determination by GPC was not attempted.

The same polymerization procedure was tried for 1,2-dimethyl-1,2-diethoxy-1,2-disilacyclobutane.[9] In accord with prior observations,[2a] the product obtained was a low molecular weight polymer/oligomer mixture with $\bar{M}_n$ = $(0.7-1.5) \times 10^3$ and PD = 1.8−2. In this case, a higher molecular weight polymer was prepared by the reaction between poly[(chloromethylsilylene)methylene] (prepared by the ring-opening polymerization of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane[5]) and an ethanol/triethylamine mixture in diethyl ether (2-fold excess). After three reprecipitations from a diethyl ether/methanol mixture (30/70), the polymer was obtained as a viscous melt which was soluble in most organic solvents and insoluble in alcohols and acetonitrile;[16] its $\bar{M}_n$ = 40×10^3 and PD = 4.5. This polymer showed no T_m and T_g = −79 °C by DSC.

Poly[[(trifluoroethoxy)methylsilylene]methylene] obtained by the same procedure showed a T_g of −50 °C and no T_m. This polymer is insoluble in nonpolar organic solvents and moderately soluble in THF.[17]

The linear, high molecular weight structure of all of these polymers was confirmed by NMR spectroscopy.[10,14,16,17] In the case of the poly[(alkoxymethylsilylene)methylenes], the NMR spectra, in general, resembled those of poly[(chloromethylsilylene)methylene], including the stereochemical effects arising from the various possible $-SiRR'CH_2-$ stereoisomers.[4] The methylene group of both polymers shows the four lines of the expected AB pattern for the isotactic (mesomeric)

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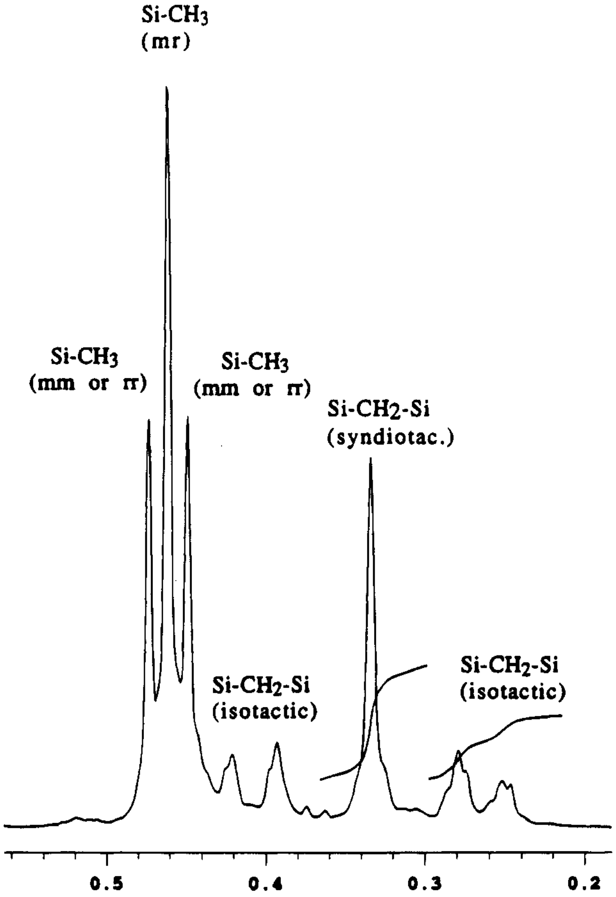

Figure 1. ^1H NMR spectrum of poly[(ethoxymethylsilylene)methylene] in C_6D_6.

diads and the single line for the syndiotactic (racemic) diad sequences (Figure 1). Integration of the intensity of the mesomeric pseudoquartet to that of the racemic singlet gives the tacticity of the polymer which was found to be atactic in this case. The ^{13}C peak of the methylene carbon is a broad, unresolved line. The methyl group of the poly[(alkoxymethylsilylene)methylenes] generally shows up as a broad line in the proton NMR spectrum in most solvents. In benzene, however, the methyl group of poly[(ethoxymethylsilylene)methylene] resolves into three lines. This corresponds to the three lines observed in the ^{13}C NMR spectrum for the methyl group of both alkoxy polymers. Integration of these lines in the ^1H, as well as in the ^{13}C, NMR spectrum gives a 1:2:1 ratio. Since the polymer is atactic, the central peak in both the proton and carbon NMR spectra can be assigned to the heterotactic (mr) sequence, which is statistically twice as probable as the syndiotactic (rr) and isotactic (mm) triads which give rise to the two side peaks. The amorphous nature of these alkoxymethyl polymers, as is evidenced by their thermal properties, is presumably a consequence of their lack of structural stereoregularity.

The TGAs of all the alkoxide polymers show a slight weight loss before 300 °C and a rapid decomposition above 400 °C. At the end of the run, all polymers except poly[(ethoxymethylsilylene)methylene] show practically no residue. Poly[(ethoxymethylsilylene)methylene], on the other hand, leaves around 35% of its initial weight.

In summary, we have found that, while poly[(dialkoxysilylene)methylenes] of reasonably high molecular weight can be prepared by ring-opening polymerization of the corresponding substituted tetraalkoxydisilacyclobutanes, high molecular weight poly[(alkoxymethylsilylene)methylenes] can be prepared only by functionalizing poly[(chloromethylsilylene)methylene]. The nature of the alkoxy substituents in these polymers (i.e., trifluoroethoxy vs ethoxy) appears to have a profound effect on the thermal properties, with the trifluoroethoxy groups providing the highest T_g's and T_m's. The synthesis and investigation of other alkoxy-, aryloxy-, and acyloxy-substituted poly(silylenemethylenes) are in progress.

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(10) For $[Si(OEt)_2CH_2]_n$: 500-MHz ^1H NMR (C_6D_6) δ 3.98 (q, *J* = 8 Hz, 4H, OCH_2CH_3), 1.32 (t, *J* = 7 Hz, 6H, $OCH_2\mathbf{CH_3}$), 0.56 (s, 2H, $Si\mathbf{CH_2}Si$); 125-MHz ^{13}C NMR (C_6D_6) δ 58.05 (OCH_2CH_3), 18.7 (OCH_2CH_3), 1.42 ($SiCH_2Si$).

(11) GPC was carried out in a toluene solution, using a Waters 600 Multisolvent Delivery System with a differential refractometer detector and three Ultrastyragel columns in series, molecular weights are referenced to polystyrene standards; all DSC measurements were performed by using a heating rate of 10 °C/min on a Sieko DSC 220C instrument. T_g was determined as the inflection point, and T_m as the extremum point, in the heating portion of the DSC curve, after an initial heating/cooling cycle.

(12) Reference 7, p 87.

(13) Prepared by refluxing tetrachlorodisilacyclobutane with 6–8 equiv of trifluoroethanol: bp 74–76 °C (0.4 mmHg); 200-MHz ^1H NMR ($CDCl_3$) δ 4.1 (q, *J* = 8.4 Hz, 6H, $O\mathbf{CH_2}CF_3$), 0.84 (s, 4H, $SiCH_2Si$); 50-MHz ^{13}C NMR ($CDCl_3$) δ 123.6 (q, *J* = 278 Hz, OCH_2CF_3), 61.6 (q, *J* = 37 Hz, OCH_2CF_3), 7.8 (s, $SiCH_2Si$).

(14) For the portion of $[Si(OCH_2CF_3)_2CH_2]_n$ that was soluble in THF: 500-MHz ^1H NMR (THF-d_6) δ 4.20 (q, *J* = 8.5 Hz, 4H, OCH_2CF_3), 0.47 (s, 2H, $SiCH_2Si$); 50-MHz ^{13}C NMR (acetone-d_6) δ 125 (q, *J* = 277 Hz, OCH_2CF_3), 61 (q, *J* = 36 Hz, OCH_2CF_3), −0.58 (s, $SiCH_2Si$). For the portion that was insoluble in THF. Elem anal. Calcd: C, 25.00; H, 2.52. Found: C, 24.97; H, 2.52.

(15) Reference 7, p 126 and references therein.

(16) For $[Si(CH_3)(OEt)CH_2]_n$: 500-MHz ^1H NMR (C_6D_6) δ 3.72 (q, *J* = 7 Hz, 2H, OCH_2CH_3), 1.25 (t, *J* = 7 Hz, 3H, $OCH_2\mathbf{CH_3}$), 0.47, 0.46, 0.45 (3H, $SiCH_3$), 0.42, 0.39, 0.33, 0.28, 0.25 (2H, $Si\mathbf{CH_2}Si$); 125-MHz ^{13}C NMR (C_6D_6) δ 58.04 (OCH_2CH_3), 18.83 (OCH_2CH_3), 7.51 (br, $SiCH_2Si$), 1.83, 1.79, 1.76 ($SiCH_3$).

(17) For $[Si(CH_3)(OCH_2CF_3)CH_2]_n$: 500-MHz ^1H NMR (THF-d_6) δ 4.3 (q, *J* = 8.5 Hz, 2H, $O\mathbf{CH_2}CF_3$), 0.29 (s, $Si\mathbf{CH_3}$), 0.36, 0.34, 0.27, 0.21, 0.17 ($SiCH_2Si$); 125-MHz ^{13}C NMR (THF-d_6) δ 125.7 (q, *J* = 278 Hz, OCH_2CF_3), 61.57 (q, *J* = 36 Hz, OCH_2CF_3), 6.9 (br, $SiCH_2Si$), 0.84, 0.82, 0.81 ($SiCH_3$).

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