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Poly(silaethylene): A Novel Analog of Polyethylene

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Despite the considerable attention that has been devoted over the past half-century to the study of polyethylene, $[CH_2CH_2]_n$ (PE),[1] and the equally well-developed state of organosilicon chemistry, efforts to investigate analogs of PE in which one or both of the carbon atoms have been replaced by silicon have received little attention. The all-Si analog of PE, polysilane, $[SiH_2]_n$ (PS), has been the subject of at least two theoretical studies.[2,3] However, the initial reports of its synthesis as an air-sensitive orange solid in 1983[4] have not been followed by details of its structure and properties. Among the predictions of the theoretical studies was an unusually high torsional mobility for the PS chains, owing to the relatively long Si−Si bonds and, consequently, low barriers for rotation. A similarly high degree of chain flexibility predicted[5] for the monosilicon analog of polyisobutylene, poly(silabutylene), is supported by the results of physical property measurements on this polymer in solution; however, this polymer is apparently amorphous, with a T_g of about −100 °C.[6]

The recent synthesis of poly(1-silaethylene), $[SiH_2CH_2]_n$ (PSE), has now enabled the detailed characterization of the unsubstituted "parent" member of the polycarbosilane family and the monosilicon analog of polyethylene. This polymer was prepared by ring-opening polymerization of 1,1,3,3-tetrachloro-1,3-disilacyclobutane, followed by reduction with $LiAlH_4$.[7] The resulting polymer is apparently air-stable under ambient conditions and is soluble in hydrocarbon solvents. It has been characterized by elemental analysis, gel permeation chromatography, NMR (^1H, ^{13}C, and ^{29}Si), and IR spectroscopy as a high molecular weight, linear polymer with little chain branching or extraneous components.[7] It converts to stoichiometric silicon carbide in high yield on pyrolysis to 1000 °C and is currently under investigation in our laboratories as a precursor to this important ceramic material.

In contrast to its all-carbon analog PE, which is a relatively high-melting solid even when it has a significant amount of chain branching,[1] PSE was obtained as a viscous liquid at room temperature upon isolation from hydrocarbon solvents. On cooling to just below room temperature, however, it forms a translucent white solid. Observations in a light microscope equipped with a cooling stage revealed a highly birefringent spherulitic pattern typical of a crystalline polymeric solid. Differential scanning calorimetry (DSC) showed distinct melting and crystallization transitions in the range −22 to 25 °C, depending on the heating/cooling rate and the average molecular weight of the polymer fraction employed.[8] A plot of the melting temperature vs the number average molecular weight indicated a limiting value of *ca.* 25 °C above about 11 000 amu. This is to be compared with the T_m value of 138 °C which has been reported for PE.[1] Low-temperature XRD of solid PSE gave a distinct crystalline diffraction pattern, which showed no obvious similarity to those previously reported for any of the known forms of PE.[1,10]

The glass transition temperatures for the uncrystallized portion of the PSE samples were also examined by using DSC. A change in slope of the DSC base line was observed at *ca.* −140 to −135 °C, depending on the molecular weight fraction employed. This unusually low value for T_g[11] suggests that the uncrystallized portion of PSE remains mobile down to extremely low temperatures.

In pursuit of an explanation for the unusually low T_m and T_g observed for PSE, *ab initio* Hartree−Fock (6-31g*)[12] calculations were performed on the model system, $H_3SiCH_2SiH_2CH_2SiH_3$, to determine the torsional surface for the two dihedral angles containing the heavier atoms of the system. A relatively flat torsional surface was obtained with the all-trans (*t,t*) form as the global minimum and the corresponding g^+,g^+ form (with dihedral angles = 62°, 62°) only 1.26 kJ/mol higher in energy.[13] A general similarity to the torsional surface for the corresponding *n*-pentane[14] was observed, but with a considerably flatter surface overall for the carbosilane. The barrier for rotation about the internal Si−C bonds (converting the *t,t* to the t,g^+ form) was found to be 4.5 kJ/mol. The low torsional barrier in this carbosilane compared to that calculated for *n*-pentane (14.6 kJ/mol)[14] is due to the greater length of the Si−C (1.89 Å) and Si−H (1.49 Å) bonds compared to the C−C (1.53 Å) and C−H (1.10 Å) bonds. This significantly reduces the repulsive interactions between the substituents. Similar conclusions were reached in prior theoretical studies of poly(silabutylene)[5] and of polysilane,[2,3] where the even longer Si−Si bonds lead to yet lower torsional barriers.

The Hartree−Fock surface was input as a reference function for the dihedral energetics, and the single chain conformational statistics were explored using Monte Carlo methods.[15] The

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(8) A typical preparation has a monomodal MW distribution by GPC (M_n = 12 300, M_w = 33 000; refractive index detector; relative to PS standards), but with a tailing toward lower molecular weight suggestive of the presence of low molecular weight oligomers. Fractionation was achieved by reprecipitation from benzene with methanol. Successively lower molecular weight fractions were isolated from the solution by addition of increasing amounts of methanol. In this manner, fractions having the following average M_n values were obtained, each with polydispersities of about 3: 13 000, 11 000, 9000, 7000, and 3000.

(9) This determination of the "limiting" T_g by DSC should be considered as only approximate, as the second-order transition in the DSC base line became increasingly more difficult to discern for the higher molecular weight fractions. It should be noted that poly(dimethylsilicone) is generally credited with having the lowest T_g value of any polymer (−123 °C) (cf.: Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992; p 150).

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(11) In the case of linear polyethylene, the T_g of the uncrystallized portion is controversial, with values from −130 °C to 60 °C having been quoted in the literature; cf.: Beatty, C. L.; Karasz, F. E. *J. Macromol. Chem.* **1979**, *C17*, 37. Brydson, J. A. *Plastics Materials* 4th ed.; Butterworth: London, 1982; p 193.

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(13) The *t,t*, t,g^+, and g^+,g^+ forms were shown to be stable minima as determined by their calculated vibrational spectra which consisted of real, positive values.

(14) Results of calculations carried out on *n*-pentane at the HF 6-31g* level in the same manner as those on the model system.

(15) The Monte Carlo calculations were performed using Polygraf software, which is a licensed product of Molecular Simulation Inc.

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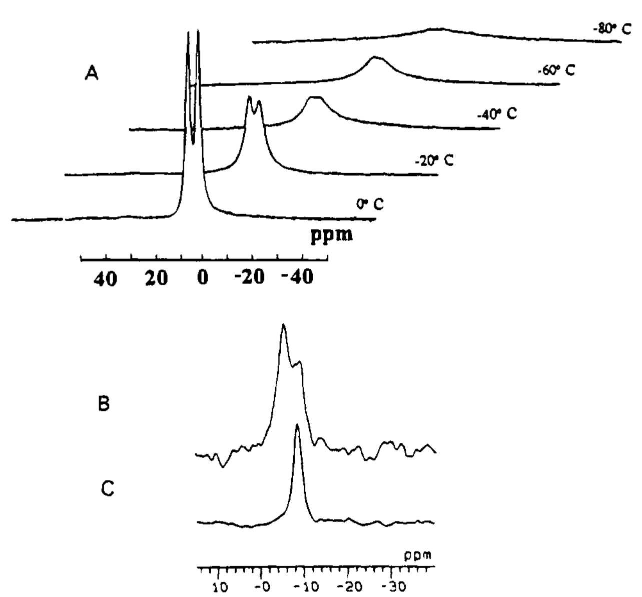

Figure 1. (A) Single-pulse ^{1}H NMR spectra as a function of temperature for a high molecular weight fraction of PSE (M_n = 13 000 amu). (B) ^{13}C NMR spectrum of this sample of PSE at −130 °C. (C) ^{13}C NMR spectrum of this sample at 40 °C.

relatively more coiled form found for PSE vs PE, as is indicated by its smaller characteristic ratio (5.26 vs 6.75[16]), suggests a higher entropy of fusion for PSE, consistent with its lower melting point.

The crystallization and subsequent glass transition of poly(silaethylene) was studied by solid-state NMR. Quantitative ^{1}H NMR spectra (Bloch decays) were obtained as a function of temperature.[17] Measurements were made on a high molecular weight fraction and a polydisperse sample. The spectra (Figure 1A shows the high molecular weight fraction) of both samples comprised a narrow component due to a mobile phase and a broad component from a rigid glassy or crystalline phase (the broad component is not obvious in Figure 1A because the bandwidth of these spectra have been narrowed). The narrow NMR resonances indicate that motion greater than approximately 10^5 Hz is occurring in this portion of the polymer. The mobile region exhibits two equally intense resonances, one for protons attached to silicon (4.2 ppm) and one for protons attached to carbon (−0.1 ppm). The integrated intensities of the broad and narrow regions yield the percentage of mobile and rigid regions present in the polymer sample at that temperature. At room temperature only the resonance characteristic of the mobile region is observed; however, as the temperature is lowered, a progressively greater portion of the NMR intensity is transferred into the broad resonance associated with the rigid crystalline and/or glassy phase.[18] For the high molecular weight, fractionated sample, the broadening of the NMR resonance is occurring in the same temperature region as the crystallization transition observed by DSC. A more gradual broadening is observed as the temperature is lowered below 20 °C in the case of the polydisperse sample. Below −120 °C the entire NMR signal has broadened in both samples, indicating a cessation of chain motion in the kilohertz region.

In an attempt to determine the degree of crystallinity of the polymer following the cessation of motion, ^{13}C CP MAS NMR was performed on the high molecular weight sample, cooled stepwise over 30 min to −130 °C. Two resonances are observed (Figure 1B); the main peak occurs at −5 ppm, and a prominent shoulder is centered at −8 ppm. This spectrum is reminiscent of those observed in semicrystalline PE.[19,20] By analogy to PE, the downfield peak at −5 ppm is attributable to the crystalline, all-trans component, while the upfield shoulder at −8 ppm is due to a noncrystalline component containing both trans and gauche conformations. Although a study of the relative intensities of these resonances as a function of cross-polarization contact time has not been carried out, we know from the ^{1}H NMR spectra that at this temperature all high-frequency motions have ceased. Thus, we expect the cross-polarization process to be efficient for both regions of the sample. From the relative intensities of the two peaks we estimate that about 70% of this polymer sample is crystalline and 30% is amorphous at low temperature following the stepwise cooling. When the sample is warmed to 40 °C, a single resonance line at −8 ppm is observed in the Bloch decay (Figure 1C).

Measurement of motional properties of the polymer were also performed by solid state ^{1}H NMR. A plot of T_1 for the mobile region versus $1/T$ shows a single, distinct, well-behaved minimum at −60 °C. The slopes of the T_1 curves yield the activation energy for the motion responsible for the dipolar fluctuations.[21] The low barrier of 5.4 kJ/mol for this motion is in good agreement with the barrier for rotation about the internal Si−C bond obtained from the HF calculation. The NMR results show that at room temperature the correlation time for this motion is 1.2 ns. It is perhaps notable that prior ^{1}H NMR linewidth studies[22] of the amorphous regions of linear PE have yielded a barrier for the chain torsion (25.5 kJ/mol) that is considerably higher than that observed here for PSE.

In summary, the results of the combined experimental and theoretical studies of this novel analog of PE suggest that PSE is indeed analogous to PE in some respects. In its solid form it is a highly crystalline polymer whose crystalline structure appears to contain linear chains in an all-trans conformation. The general form of the dihedral surface for rotation about the chain atoms also seems to be similar, with the all-trans form as the most stable conformation. However, in contrast to PE, solid PSE is low melting, presumably due, in part, to the large configurational entropy that results from the mobility of the PSE chains.

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