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The synthesis and characterization of a mesomorphic brush type polycarbosilane: poly[1,1-*bis*(4′-biphenyl)silabutane]

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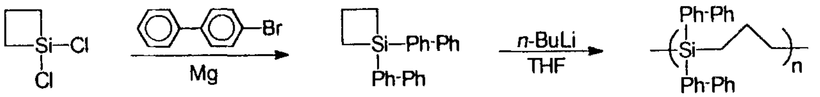
Summary

Poly[1,1-*bis*(4'-biphenyl)silabutane] (**II**) has been prepared by the anionic ring opening polymerization of 1,1-*bis*(4'-biphenyl)silacyclobutane. II shows mesomorphic behavior by DSC. The ^{13}C NMR T_1 relaxation times have been measured. These are found to be smaller than those of poly(1,1-dimethylsilabutane) by an order of magnitude. This may result from interaction of the highly rigid biphenyl side chain moieties. The thermal stability of II is higher than that for other 1,1-disubstituted polysilabutanes.



Introduction

Crystallinity in polymers often introduces desirable material properties. High T_gs, T_ms, tensile strength, toughness and solvent resistance are some of the properties linked to the degree of polymer crystallinity (1). Linear polyethylene is an example of a polymer where the extent of crystallinity in a sample determines its ultimate usefulness (2). Liquid crystalline polymers demonstrate unusual phase behavior which combines properties of the homogeneous liquid and ordered crystalline states (3). They are the subject of considerable research interest due to both practical and theoretical concerns. Polymers in which the backbone is made up of rigid biphenyl units often display liquid crystalline behavior (4). In addition, comb type polymers, which contain biphenyl units as pendant mesogens often form crystalline or liquid crystalline phases (5).

Most work on side chain liquid crystalline polymers has been done with polyacrylates, polymethacrylates and polysiloxanes (6). While there has been considerable recent interest in polycarbosilanes, polymers whose backbone is made up of regular sequences of carbon and silicon atoms, no examples of saturated polycarbosilanes containing such mesogens exists.

The low T_gs often seen for simple polysilabutanes (7) suggests that side chain substitution of rigid biphenyl mesogen units onto carbosilane backbone polymers would give interesting and useful phase behavior. If these units were directly attached to the silyl center of the polymer without a spacer unit, the thermal stability of the material may be expected to be improved (8).

In this communication, we report the synthesis and characterization of a novel

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"brush" type polycarbosilane substituted with biphenyl groups. This polymer exhibits unusual phase behavior and high thermal stability.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-360 instrument and are referenced to solvent peaks. ^{29}Si NMR spectra were recorded on a Bruker SY-270 and are externally referenced to TMS. The NMR spectra of 1,1-*bis*(4'-biphenyl)silacyclobutane were acquired in chloroform-*d* whereas those of poly[1,1-*bis*(4'-biphenyl)-silabutane] were recorded in toluene-d_8 at 80°C. ^{13}C NMR T_1 data were recorded on a Bruker AMX-500 at 80°C in toluene-d_8, using the inversion recovery method. The details of this method as applied to polycarbosilanes have been reported (9). IR spectra were recorded on an IBM FT-IR spectrometer. High resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene. Chemical ionization mass spectra were determined using methane as the ionizing gas. Elemental analysis were conducted by Oneida Research Services, Whitesboro NY. The molecular weight distribution of the polymer was determined on a Waters GPC system. Ultrastyragel columns, 10^4 Å and 10^3Å, in series with THF as an eluant (flow rate 0.7mL/min) were utilized for the analysis. The molecular weight reported is referenced to monodisperse polystyrene standards. Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGS-2 instrument. The temperature program for the analysis was 50°C for ten minutes followed by an increase of 5°C/min to 800°C. These runs were conducted under a nitrogen stream of 40cc/min. The thermal transitions in the polymer and monomer were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7. The instrument was calibrated with water (mp 0°C) and indium (mp 156°C).

1,1-Dimethylsilacyclobutane was prepared following published procedures (7). 4-Bromobiphenyl was purchased from Aldrich and was recrystallized from methanol before use. 1,1-Dichlorosilacyclobutane was obtained from Huls America and was redistilled before use. *n*-Butyllithium (2.5M in hexanes) was titrated before use (10). HMPA, used as a co-catalyst, was redistilled and stored over 4 Å molecular sieves. THF was distilled directly into the reaction glassware from dark blue solutions of sodium benzophenone ketyl. All reactions were conducted in flame dried glassware under UHP helium.

Synthesis of 1,1-*bis*-(4'-Biphenyl)-silacyclobutane

Magnesium powder (1.50g, 62mmol) was placed in a 250 mL 3-neck round bottom flask, equipped with a reflux condenser and a Teflon covered magnetic stirring bar. 4-Bromobiphenyl (6.40g, 28mmol) is added and 150mL of THF is distilled into the flask. The mixture is stirred overnight at rt. 1,1-Dichlorosilacyclobutane (2.0g, 15mmol) is added in a dropwise manner via syringe to the Grignard mixture. A reaction starts upon the addition of the first few drops of 1,1-dichlorosilacyclobutane as detected by warming of the flask. The mixture is stirred overnight at rt and then refluxed for 24 h. The mixture was cooled by placing it in an ice-water bath and 50 mL of diethyl ether was added. Saturated aqueous ammonium chloride was slowly added to the mixture which results in the vigorous evolution of gas. The organic layer was separated and was extracted with saturated aqueous ammonium chloride, water and was then dried over anhydrous $CaCl_2$. The solvents were removed by evaporation under reduced pressure. A white amorphous solid was recovered (3.80g yield 73%). The monomer was purified by recrystallization from methanol. Characterization: mp 106°C (DSC); ^1H NMR δ: 1.64(t, 4H J = 8.2 Hz), 2.40(p, 2H J = 8.2 Hz), 7.39-7.83(m, 18H); ^{13}C NMR δ: 13.99, 18.41, 126.72, 127.15, 127.50, 128.78, 134.97, 135.01, 140.88, 142.44; ^{29}Si NMR δ: 6.88; IR ν: 3060, 3024, 2964, 2924, 2870, 1597, 1544, 1484, 1445, 1411, 1385, 1255, 1184, 1119, 1075, 1007, 995, 913, 897, 855, 828, 758, 726 cm^{-1}; UV λ_{nm} (ϵ): 314.3 (6425). MS CI m/e (rel intensity) 377(36), 223(100), 207(9), 155(33), 149(15), 113(13), 87(15), 61(3); High resolution MS *m/e* Calcd for $C_{27}H_{24}Si$:376.1647. Found 376.1649.

Anionic Ring Opening Polymerization (AROP)

THF (10mL) was distilled into a 25mL round bottom flask, containing a Teflon covered magnetic stir bar and 0.80g of 1,1-*bis*(4'-biphenyl)silacyclobutane. The flask was sealed with a rubber septum. The flask and its contents were purged with UHP helium. HMPA (60μL) was syringed into the flask and the vessel was immersed into a dry ice/acetone bath. After 15 minutes equilibration, 100 μL of *n*-butyllithium was syringed into the flask. The mixture was allowed to stir at low temperature for 2 h. During this time, the solution turns hazy. Methanol was added to terminate the reaction. The organic layer contained a white powder which was recovered by centrifugation. This material (0.69g 86% yield) was dried on a high vacuum line. Purification was achieved by dissolution of the polymer in hot toluene and precipitation with methanol. Characterization: GPC M_w/M_n 4220/ 3360; ^{1}H NMR δ: 1.00(br. m, 4H), 1.55(br. m, 2H), 7.23-7.47(br. m, 18H); ^{13}C NMR δ: 17.24, 18.43, 126.27, 126.96, 127.28, 128.74, 134.94, 135.33, 140.72, 141.43; ^{29}Si NMRδ : -7.05; IR ν: 3030, 2910, 2852, 1595, 1537, 1481, 1453, 1396, 1382, 1250, 1136, 1107, 1074, 1020, 995, 900, 825, 794, 756 cm^{-1}; UV λ_{nm} (ϵ): 314.7 (794). Anal. Calcd for $C_{27}H_{24}Si$: C, 85.88; H, 6.67. Found C, 82.67; H, 6.68.

Poly(1,1-dimethylsilabutane)(**III**) was prepared as above and had spectral properties identical to those reported (11) with a M_w/M_n = 8200/3400 and a T_g = -35°C.

Results and Discussion

Highly crystalline 1,1-*bis*(4'-biphenyl)silacyclobutane (**I**) was prepared via the Grignard coupling reaction of 4-biphenyl magnesium bromide and 1,1-dichlorosilacyclobutane. Polymerization of **I** at low temperature via AROP initiated by *n*-butyllithium yields poly[1,1-*bis*(4'-biphenyl)silabutane] (**II**). AROP of silacyclobutanes has been previously reported (12). The polymerization proceeds by nucleophilic attack at the silyl center to produce a hypervalent siliconate species. Opening of the strained silyl center leads to a primary carbanion which can attack another molecule of silacyclobutane. This sequence is the propagation pathway which results in polymer.

The thermal behavior of **I** is not noteworthy. **I** undergoes a melting transition at 106°C. In comparison, the thermal behavior of **II** is unusual. At 115°C **II** undergoes melting to an anisotropic liquid. On further heating it undergoes another endothermic transition at 190°C followed by a clearing at 205°C (Figure 2). On repeating this thermal cycle, only a T_g at 73°C is detected (Figure 3).

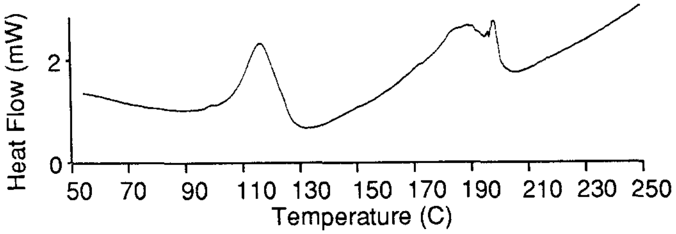

Figure 2; DSC of **II**.

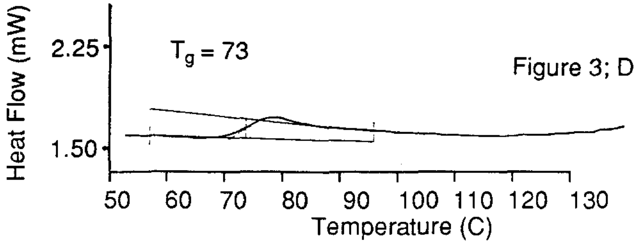

Figure 3; DSC of **I**.

The low solubility of **II** in THF and chloroform may be due to the highly rigid biphenyl side chains which inhibit motion of the central polymer chain. **II** is found to be soluble in hot toluene. ^{13}C NMR T_1 data for **II** and the relatively more flexible **III** show that this is indeed the case. As illustrated in Figure 4, the T_1 values for **II** are much smaller than that of similar molecular weight **III**. It has been established that the segmental motion of a polymer chain in solution is reflected in the ^{13}C NMR T_1 values of the central polymer backbone (13). It is known that rigid polymers have low ^{13}C NMR T_1 values for the main chain indicative of hindered motion. Apparently the segmental motion of the flexible main chain of **II** is hindered not only in the solid state (T_g = 73°C), but also in solution, by interactions between rigid pendant mesogenic biphenyl groups.

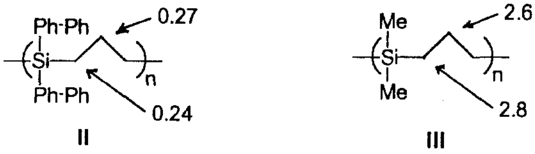

Figure 4; ^{13}C NMR T_1values in seconds for **II** and **III**.

The TGA of **II** is given in Figure 5. This material is remarkably stable for a low molecular weight carbosilane polymer. The high onset of decomposition at 454°C is most likely due to the presence of the highly stable biphenyl moieties in the polymer (8). The lack of a saturated alkyl spacer group between the biphenyl mesogens and the silyl centers improves the overall stability in this polymer. Thus, the thermal transitions seen in the DSC of **II** near 200°C cannot be due to decomposition. Therefore, **II** forms highly stable mesophases.

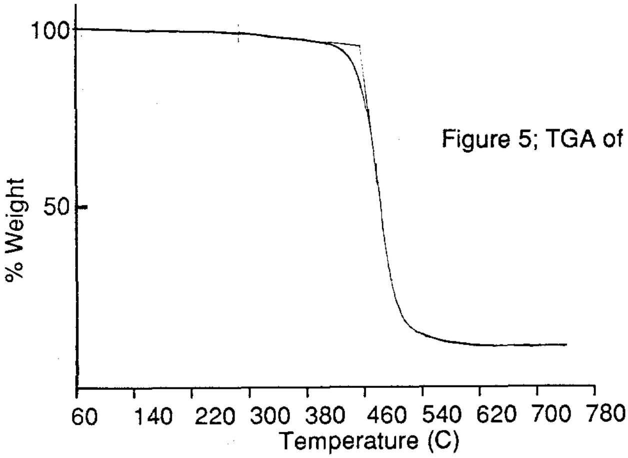

Figure 5; TGA of **II**.

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