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# Preliminary Communication

## Comb-like polycarbosilanes-routes to a new group of liquid crystal polymers

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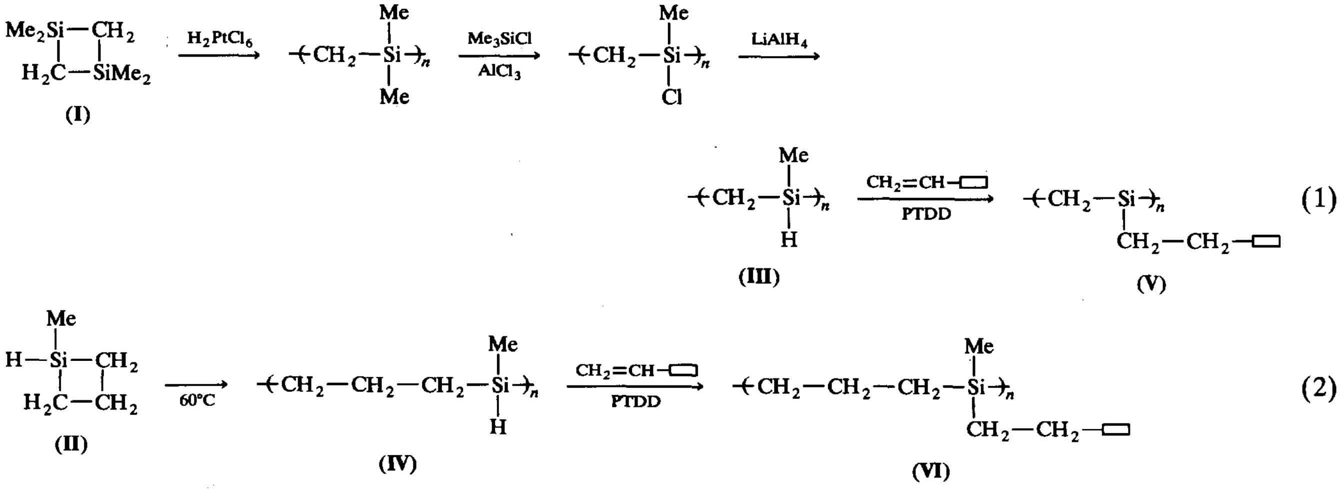
### Abstract

Routes to two novel types of liquid crystal polycarbosilanes are described and preliminary studies of their properties are reported.

Three groups of organosilicon polymers are currently known to be able to exist in a mesomorphic state: side chain liquid crystal (SCLC) polysiloxanes [1], linear and cyclolinear poly(diethyl)- and poly(dipropyl) siloxanes [2], and polysilanes having long-chain (n-pentyl, n-hexyl) alkyl substituents on the silicon atom [3]. The last two types of polymers belong to a specific group having no typical mesogens in either the main or the side chain (often referred to as "condis" crystals). However, the most commonly studied of these polymers are the SCLC polysiloxanes. The significant flexibility of the siloxane backbone gives polysiloxanes lower glass transition and mesophase transition temperatures than those of hydrocarbon polymers. The $t_g$ values are often below room temperature, leading to liquid crystalline state in the 0–20°C range [4].

We report here the synthesis of liquid crystal polycarbosilanes that were expected from their chain structure, to have properties intermediate between those of SCLC acrylates and methacrylates on the one hand and SCLC polysiloxanes on the other. The first step in the preparation of these polymers (Scheme 1) involves ring opening polymerisation of the strained silacyclobutanes — 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) and 1-methyl-1-silacyclobutane (II) [5]. The poly[(dimethylsilylene)methylene] obtained from I is then chlorinated (with $Me_3SiCl$ $AlCl_3$) and reduced (with $LiAlH_4$) to give poly(silapropylene) (III) [6].

In the case of reaction (1) however, there is a significant decrease in molecular weight on chlorination, from $M_n = 5000$ for poly[(dimethylsilylene)methylene] to $M_n = 500$ (as measured by GPC) for the



PTDD = platinum tetramethyldivinyldisiloxane

—▭ = mesogenic unit

Scheme 1.

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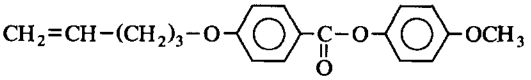
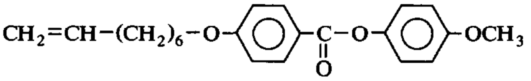
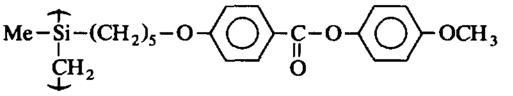
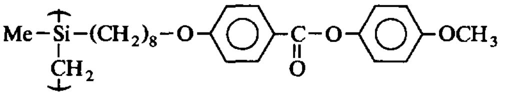
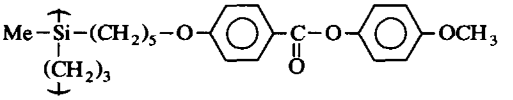
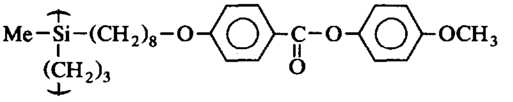
TABLE 1. Transition temperatures for mesogenic precursors and polycarbosilanes (K = crystal, S = smectic, I = isotropic liquid, $T_g$ = glass transition temperatures)

| Mesogenic precursor polymer | Transition temperatures (°C) |
|---|---|
|  | K, 90.0, I |
|  | K, 56.2, S, 64.8, I |
|  | $T_g$, 19.3, S, 47.2, I |
|  | K, 48.0, S, 91.3, I |
|  | $T_g$, 7.0, K, 61.2, I |
|  | K, 50.6, S, 82.7, I |

poly(silapropylene) (**III**), the value of $M_n$ for **IV** was 40000.

The alkene mesogenic side chain precursors used in the hydrosilylation reactions were prepared by standard methods [7]. The polycarbosilanes **V** and **VI** were made by a typical hydrosilylation procedure [8] involving use of a catalytic amount of platinum tetramethyldivinylsiloxane (PTDD). Although hydrosilylation was also achieved with other platinum complexes (*e.g.* $(CH_2{=}CH_2)Pt(PPh_3)_2$, $Cp_2PtCl_2$, or $H_2PtCl_6$) PTDD was found to be the most effective. The progress of the reaction was usually monitored by IR spectroscopy (by observing the decrease of the Si–H absorption at 2100 $cm^{-1}$). The changes in the $^1H$ spectrum in the Si–H regions at 3.6 ppm (**III**) and 4.1 ppm (**IV**) were also used to assess the extent of reaction.

The structure of the SCLC polycarbosilanes (**V**, **VI**) were confirmed by $^1H$, $^{13}C$ and $^{29}Si$ NMR spectroscopy. The SCLC polycarbosilanes were also examined by use of a hot-stage polarizing microscope and by differential scanning calorimetry (DSC) (DuPont Instruments 910).

Both of the polymers obtained from **III** exhibited liquid crystalline phases, whereas that with the short spacer [–$(CH_2)_5$–] made from **IV** did not exhibit any mesomorphic properties (like its alkene precursor) (Table 1).

The results confirm the importance of the "density" of the mesogenic units in a polymer chain, especially when the spacer group is short and decoupling of the mesogenic unit from the polymer motions is weaker. A detailed X-ray structural study of the novel polycarbosilanes will be published separately.

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