Synthesis and polymerization of *Si*-substituted silacyclobutanes

N. V. Ushakov, G. K. Fedorova, and E. Sh. Finkel'shtein*

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

The synthesis and polymerization of silacyclobutane derivatives with ferrocenyl, 9-carbazolyl, and pentafluorophenyl fragments in substituents have been carried out. The effect of the replacement of H atoms by F in pendant groups of the polysiltrimethylene main chain on the glass transition temperature has been studied.

Key words: silacyclobutanes, ferrocenyl-, 9-carbazolyl-, fluoro-derivatives, synthesis, polymerization.

Ferrocene[1] and its alkyl and aryl[2,3] as well as organosilicon[4] derivatives form charge transfer complexes (CTC) with CBr_4, giving light-sensitive systems. The use of ferrocenyl substituents in polymers as electron-donating components in CTC makes it possible to obtain light-sensitive compositions for recording information and images based on such polymers and CBr_4.

The introduction of a substituent containing a ferrocenyl group in a silacyclobutane molecule followed by thermally induced polymerization of the resulting 1-{*p*-[(dimethyl)(ferrocenyl)silyl]phenyl}-1-methylsilacyclobutane (**1**) are presented in Scheme 1.

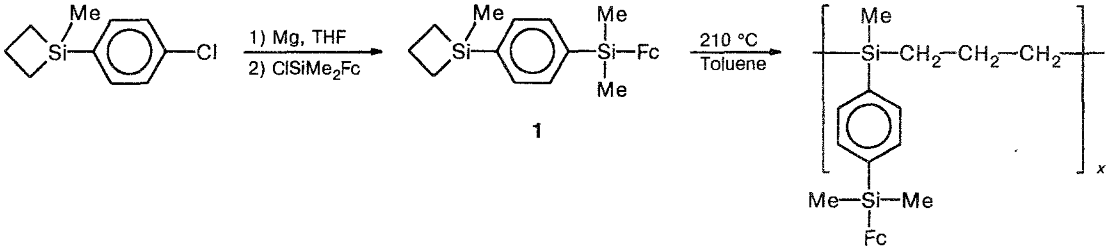
The silacyclobutane **1** synthesized in this work is a red-brown oil with a high refraction index. The main peak in its mass spectrum is a molecular ion peak (*m/z* 404). The structure of compound **1** was also confirmed by IR, ^1H, and ^{13}C NMR spectroscopic data. The IR spectrum of ferrocenyl-containing polymer **2** obtained by thermally induced polymerization (molecular weight $2.8 \cdot 10^4$) does not contain absorption bands of the silacyclobutane ring (925, 1120, and 1185 cm^{-1}). In addition to the absorption bands of the Si—Me bond and the ferrocenyl moiety, the spectrum of compound **2** contains bands characterizing the trimethylene chain between the silicon atoms (898, 943, 990, 1025, 1080, and 1142 cm^{-1}).

The method proposed by us for the introduction of a substituent containing the ferrocenyl moiety into a silacyclobutane molecule is rather simple. The presence of this moiety does not hinder thermally induced polymerization of the substituted silacyclobutane.

The γ-9-carbazolylpropyl substituents in the pendant groups of the polysiltrimethylene chain form CTC with trinitrofluorenone, which provides good parameters (sensitivity, diffraction efficiency) when these polymers are used as recording layers for photothermoplastic recording (PTR) of information and images.[5,6] To improve the effectiveness of CTC formation and to increase the softening temperature and sensitivity of PTR, we have obtained polysiltrimethylene (**4**) (mol. weight 8200) with two γ-9-carbazolylpropyl substituents according to Scheme 2.

The starting monomer, 1,1-bis[γ-(9-carbazolyl)propyl]silacyclobutane (**3**), was synthesized from 1,1-dichlorosilacyclobutane by the method developed previously.[6] Its structure was confirmed by IR and ^1H and ^{13}C NMR spectroscopy. The IR and ^1H NMR spectra of polysiltrimethylene **4** do not contain absorption

Scheme 1



Fc indicates ferrocenyl

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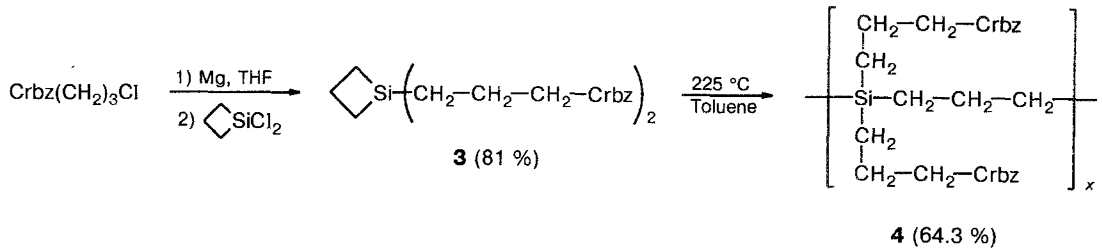
1066-5285/95/4412-2371 $12.50

Scheme 2



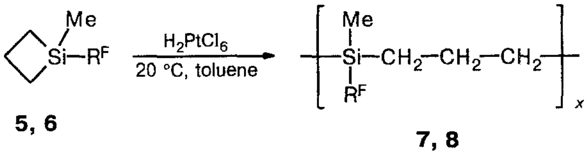
Crbz indicates 9-carbazolyl

typical of silacyclobutane, *i.e.*, bands at 928, 1116, and 1172 cm^{-1} (IR) and multiplets of α- and β-CH_2 ring groups centered at δ 0.87 and 1.94, respectively (^1H NMR).

Thus, two γ-9-carbazolylpropyl substituents can be successfully attached to the silicon atom in silacyclobutane. The thermally induced polymerization of this monomer requires elevated temperatures (no less than 220 °C).

The thermally induced polymerization of silacyclobutanes with fluorine-containing substituents is known[7] to be ineffective due to the blocking effect of the C—F polar bonds. For this reason, both the previously described[8] 1-*m*-trifluoromethylphenyl-1-methylsilacyclobutane (**5**) and 1-pentafluorophenyl-1-methylsilacyclobutane (**6**) (synthesized by treatment of pentafluorophenylmagnesium bromide with 1-chloro-1-methylsilacyclobutane) were polymerized at 20 °C in toluene using $H_2PtCl_6 \cdot 6H_2O$ as the catalyst (Scheme 3).

Scheme 3



R^F = *m*-$C_6H_4CF_3$ (**5**, **7**), C_6F_5 (**6**, **8**)

Both fluorine-containing polymers, **7** and **8**, are rubber-like compounds soluble in aromatic hydrocarbons and CCl_4. Their vibrational spectra do not contain bands typical of monomers. The molecular weights of polysiltrimethylenes **7** and **8** are 65300 and 146500, respectively. We found that the replacement of all hydrogen atoms of the methyl substituent attached to the phenyl ring for fluorine atoms and similar replacement of the hydrogen atoms of the phenyl ring differently affect the glass transition temperatures of the corresponding polysiltrimethylenes. In the former case, passing from poly(methyl-*m*-tolylsiltrimethylene) to the fluorinated polymer **7** almost does not change the glass transition temperature (T_g = −25.5 and −25 °C, respectively), while in the latter case (on going from polymethylphenylsiltrimethylene to the fluorinated polymer **8**) the glass transition temperature increases from −30 to −12 °C.

The data of elemental analyses are correct for monomeric compounds and correspond to the composition of polymers.

Experimental

^1H NMR spectra were recorded on Varian T-60 and Bruker MSL-300 spectrometers. ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer. IR spectra were obtained on UR-20 and Specord MS-82 spectrometers (in KBr pellets for solid compounds and polymers, and in films between KBr plates for liquids). Mass spectra were measured on LKB 2091, Kratos MS-25 RF, and MS-850 instruments. The glass transition temperatures of polymers were determined on a Mettler 4000 differential scanning calorimeter. Molecular weights were measured by GPC on a Waters instrument in toluene using polystyrene standards. 1-Chloro-1-methylsilacyclobutane and 1,1-dichlorosilacyclobutane were synthesized by a known procedure.[9] 1-*p*-Chlorophenyl-1-methylsilacyclobutane and 1-*m*-trifluoromethylphenyl-1-methylsilacyclobutane were obtained by the procedure reported previously.[8] 9-γ-Chloropropylcarbazole was synthesized using phase transfer catalysis.[6] Ferrocenyldimethylchlorosilane was synthesized by the method improved by us.[10]

1-{*p*-[Dimethyl(ferrocenyl)silyl]phenyl}-1-methylsilacyclobutane (1). Ferrocenyldimethylchlorosilane (0.0354 mol) in THF (10 mL) was added under an inert atmosphere to a Grignard reagent prepared from 1-*p*-chlorophenyl-1-methylsilacyclobutane in THF (35 mL). The mixture was heated for 6 h at 55—60 °C in an inert atmosphere. The THF was removed *in vacuo*, benzene (250 mL) was added, and the solution was filtered through a porous filter. The sediment was washed with benzene, and the combined filtrates were concentrated. The target product was isolated by chromatography on a column with alumina (activity 2, elution with hexane). Yield 42.5 %; oil, $n^{20}{}_D$ 1.5985. ^1H NMR (C_6D_6), δ: 0.43 (s, 3 H, SiMe); 0.52 (s, 6 H, $SiMe_2$); 1.16 and 1.33 (m, 4 H, α-CH_2); 2.22 (m, 2 H, β-CH_2); 4.00 (s, 5 H, C_p); 4.08 (t, 2 H, α-CH Fc); 4.22 (t, 2 H, β-CH Fc); 7.57 and 7.63 (both d, 4 H, C_6H_4). ^{13}C NMR (C_6D_6), δ: 0.16 (MeSi); 1.68 ($SiMe_2$); 16.33 (α-C); 20.36 (β-C); 70.30 (C_5H_5); 71.67, 73.10, 75.41 (C_5H_4); 134.75, 135.35, 140.96, and 143.12 (C_6H_4). IR, ν/cm^{-1}: 3090 (νC—H Fc); 3050 (νC—H C_6H_4 and Fc); 2960 ($\nu_{as}CH_2$ and ν_{as}Me); 2930 (ν_sMe and ν_sCH_2); 2860, 2845 (ν_sMe and ν_sCH_2 in the ring); 1595, 1525 (νC—C C_6H_4); 1415 (Fc); (1330), (1300), 1250 (SiMe); 1185, 1120, 925 (silacyclobutane ring); 1165, 1135 (planar δFc); 1105 (sh.), 1035, 1025, 1000 (Fc); (900), 865 (δC_6H_4 and Fc, Si—Me); (815), 800 (C_6H_4, Fc); (665), 535, 495 (Fc); 450 (νFe—C). MS, *m/z* (*I*(%)): 406 (43.1), 405 (82.2), 404 $[M]^+$ (100), 389 $[M-Me]^+$ (27.5), 376 $[M-C_2H_4]^+$ (21.8), 361 $[M-C_2H_4-Me]^+$ (13.6), 339 $[M-C_5H_5]^+$ (6), 333 (7.8), 320 (8.7), 273 (9), 255 (8.3), 243 $[Me_2SiFc]^+$ (34.8), 213 (14.4), 195 (10), 189 (8), 188 (27.1), 186 $[FcH]^+$ (12.5), 182 (8.2), 148 (13.1), 121 $[C_5H_5Fe]^+$ (43.7), 107 (10), 105 (12.5), 93 (38.1), 83 (7.2), 73 (8.2), 59 (7.2), 56 $[Fe]^+$ (33.3), 53 (8.2). Found (%): C, 65.50; H, 7.13; Fe, 13.56; Si, 14.80. $C_{22}H_{28}FeSi_2$. Calculated (%): C, 65.33; H, 6.98; Fe, 13.81; Si, 13.89.

1,1-Bis[γ-(9-carbazolyl)propyl]silacyclobutane (3). One-third of a solution of dibromoethane (0.004 mol) and 9-γ-chloropropylcarbazole (0.082 mol) in THF (55 mL) was added to a mixture of magnesium (0.1 mol), 1,1-dichlorosilacyclobutane (0.035 mol), and THF (15 mL). The reaction started immediately; the remaining solution was added to the mixture over a period of 1 h in such a way that the temperature did not exceed 45 °C. Dibromoethane (0.05 mol) was added, and the mixture was stirred for 5 h at 55 °C. Benzene (200 mL) was added, and the mixture was decomposed with a solution of NH_4Cl. The usual work-up followed by chromatography on silica gel (benzene/hexane, 1 : 4, v/v) gave silacyclobutane **3** (yield 81 %), m.p. 125.5—127 °C (after recrystallization from a benzene/hexane mixture, 1 : 5, v/v).

^{1}H NMR ($CDCl_3$), δ: 0.68 (t, 4 H, $SiCH_2$); 0.87 (m, 4 H, α-CH_2 of the ring); 1.85 (m, 4 H, $SiCCH_2CN$); 1.94 (m, 2 H, β-CH_2 of the ring); 4.17 (t, 4 H, CH_2N); 7.19 (t, 2 H, H-3, H-6); 7.30 (d, 4 H, H-1, H-8); 7.41 (t, 4 H, H-2, H-7); 8.06 (d, 4 H, H-4, H-5). ^{13}C NMR ($CDCl_3$), δ: 11.77 (α-C acyclic); 12.54 (α-C of the ring); 18.31 (β-C of the ring); 23.14 (β-C acyclic); 45.79 (γ-C acyclic); 108.63 (C-1, C-8); 118.81 (C-3, C-6); 120.36 (C-4, C-5); 122.87 (C-4a, C-4b); 125.63 (C-2, C-7); 140.43 (C-8a, C-9a). IR, ν/cm^{-1}: 3069 sh., 3048, 3020 (νC—H arom.); 2955, 2939, 2920, 2904, 2877, 2868, 2856 (νC—H CH_2); 1628, 1596 (νC—C arom.); 1484, 1464, 1452 (δCH_2); 1344, 1328 (Crbz); 1232 ($SiCH_2$); 1172, 1116, 928 (silacyclobutane); 1152 (δCrbz); 744 (Crbz); 720 (nonplanar deformation of the HCC angle in Crbz); (656), (616), (528), (420). Found (%): C, 81.17; H, 7.28; N, 5.62; Si, 5.57. $C_{33}H_{34}N_2Si$. Calculated (%): C, 81.43; H, 7.04; N, 5.76; Si, 5.77.

1-Pentafluorophenyl-1-methylsilacyclobutane (6). 1-Chloro-1-methylsilacyclobutane (0.05 mol) was added over a period of 0.5 h to a solution of a Grignard reagent obtained from bromopentafluorobenzene (0.05 mol) and magnesium (1.5 g) in Et_2O (35 mL). The mixture was heated for 4 h at 50 °C, cooled, and decomposed with water. The usual work-up and distillation *in vacuo* gave silacyclobutane **6** in 73.6 % yield. B.p. 108—109 °C (32 Torr), d_4^{20} 1.2730, n_D^{20} 1.4625. ^{1}H NMR (CCl_4), δ: 0.63 (s, 3 H, SiMe); 1.38 (m, 4 H, α-CH_2); 2.23 (m, 2 H, β-CH_2). IR, ν/cm^{-1}: 2960, 2940, 2880 (νCH_2 and νMe); 1640, 1520, 1475, 1465 (νC—C arom., C—F); (1380), 1285, 1255 (SiMe); 1185, 1125 (silacyclobutane); 1090, 970 (C—F); 930 (silacyclobutane); (895), 875 (SiMe); (780), (670), (655), (525), (470). Found (%): C, 47.92; H, 3.56; F, 36.12; Si, 11.54. $C_{10}H_9F_5Si$. Calculated (%): C, 47.61; H, 3.60; F, 37.66; Si, 11.13.

Polymerization of 1. A sealed tube containing monomer **1** (0.505 g) and toluene (3 mL) was prepared in a usual way and heated at 210 °C for 15 h. Polymer **2** was precipitated by methanol, yield 71 %. IR, ν/cm^{-1}: 3092 (νCH Fc); 3048 (νCH C_6H_4 and Fc); 2995, 2960 (ν_{as}CH CH_2 and Me); 2930 (ν_{as}CH Me and CH_2); 2862, 2840 (ν_sCH Me and CH_2); (2800), 1600, 1520 (νC—C arom.); 1420 (Fc); (1335), (1300), 1252 (SiMe); 1142 ($Si(CH_2)_3$); 1135, 1105 (δFc); 1080 ($Si(CH_2)_3$); 1035 (Fc); 1025 (Fc and $Si(CH_2)_3$); 1000 (Fc); 990, 943 ($CH_2CH_2CH_2$); (898), 867 (C_6H_4 and Fc); 813 (SiMe); 800 (Fc and C_6H_4); 770 (C_6H_4); 665 (SiMe); 535 (Fc); 450 (νFe—C). Found (%): C, 65.68; H, 7.27; Fe, 13.66; Si, 14.29. $C_{22}H_{28}FeSi_2$. Calculated (%): C, 65.33; H, 6.98; Fe, 13.81; Si, 13.89.

Polymerization of 3. A sealed tube containing compound **3** (1.215 g) and toluene (5 mL) prepared in a usual way was heated at 225 °C for 18 h. Polymer was precipitated by hot methanol and reprecipitated by a hot ethanol—hexane mixture. The product was washed with hot ethanol and dried to a constant mass. The yield of polymer **4** was 64.3 %. ^{1}H NMR ($CDCl_3$), δ: −0.07 to 0.54 (m, 6 H, $SiCH_2$); 1.15—1.80 (m, 6 H, CCH_2C); 3.96 (t, 4 H, CH_2N); 6.87—7.43 (m, 12 H, Crbz protons except H-4, H-5); 7.94 (m, 4 H, H-4, H-5 Crbz). IR, ν/cm^{-1}: 3069 sh., 3048, 3020 (νCH arom.); 2916, 2872 (νCH aliphatic); 1628, 1596 (νCC arom.); 1484, 1464, 1452 (δCH_2); (1380), 1344, 1328 (Crbz); 1228 (Si—CH_2); 1152 (δCrbz); 1128, 1120 (δCH_2); 748 (Crbz); 720 (nonplanar deformation of the HCC angle in Crbz); (616), (556), (528), (424). Found (%): C, 81.25; H, 6.81; N, 5.40; Si, 5.38. $C_{33}H_{34}N_2Si$. Calculated (%): C, 81.43; H, 7.04; N, 5.76; Si, 5.77.

Polymerization of 5 and 6. A solution of H_2PtCl_6 (0.005—0.1 mL, 0.1 mol L^{-1}) in isopropyl alcohol was placed into a tube preheated *in vacuo*. The solvent was completely removed by evacuating the tube at 80 °C. Monomer **5** or **6** (1 mL) and dry toluene or benzene (4 mL) were added to the catalyst prepared as described above, and the tube was sealed. After 1 h, a weak yellow coloration appeared, and the viscosity of the solution began to increase. After 20 h, the tube was opened, the contents were diluted with a threefold amount of benzene, and the mixture was poured into methanol. The yields of polymers **7** and **8** after drying were 88.5 % and 90 %, respectively. The polymers were colored due to the presence of reduced platinum. We managed to remove the residual platinum by passing dilute (~0.2 %) solutions of the polymers in benzene or toluene through a layer of alumina or silica gel. After purification, the yields of **7** and **8** decreased to ~60 and 65 %, respectively.

Polymer **7**. IR, ν/cm^{-1}: 3056, 3026 (νC—H arom.); 2960, 2920, 2870 (νC—H CH_2 and Me); 1600, 1410, 1320 (CC arom. and C—F); 1260 (SiMe); 1110, 1075, 1020 (δC—F and δCH_2); 905, 800, 705, 665 (C_6H_4); 505, 440. Found (%): C, 57.12; H, 5.38; F, 24.02; Si, 12.42. $C_{11}H_{13}F_3Si$. Calculated (%): C, 57.37; H, 5.69; F, 24.75; Si, 12.19.

Polymer **8**. IR, ν/cm^{-1}: 2965, 2940, 2863 (νCH_2 and νMe); 1600, 1520, 1470, 1400 (CC arom. and C—F); 1260 (SiMe); 1090, 1020 (C—F); 861 (Si—Me); 800, 690, 595. Found (%): C, 48.11; H, 3.38; F, 35.89; Si, 11.61. $C_{10}H_9F_5Si$. Calculated (%): C, 47.61; H, 3.60; F, 37.66; Si, 11.13.

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