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Synthesis and characterization of side-chain liquid crystalline polycarbosilanes with siloxane spacer

Katsuhiko Komuro, Yusuke Kawakami*

Graduate School of Materials Science, Japan Advanced Institute of Science & Technology,
Asahidai 1-1, Tatsunokuchi, Ishikawa 923-1292, Japan

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Summary

Synthesis and polymerization of silacyclobutanes with mesogenic groups were studied. Polymers (PSB-Meso, Meso = mesogenic group) obtained by platinum complex, such as Pt(COD)Cl_2, had head-tail regular structure, and showed low glass transition and clearing temperatures. PSB-B (Meso = cyanobiphenyl) and PSB-C (Meso = 4-[4-cyanophenyloxycarbonyl]phenyl) exhibited focal-conic fan textures at room temperature under observation by optical polarization micrograph.

Introduction

Since the first report on side-chain liquid crystalline polymer (SLCP) by Finkelmann in 1978(1), much attention has been paid to SLCP as electronic devices and display materials(2). Until now, extensive discussions on the relationship between the chemical structure of main chain and liquid crystallinity have been made. Polysiloxane, polyacrylate and polymethacrylate are frequently used as main chain(3). Recently, SLCP with polyether(4-6), poly(ethylene imine)(7), polydiene(8, 9), poly(vinyl ether)(10), polystyrene(11) and polysulphone(12) as main chain were reported by several research groups. There are some reports, in which siloxane linkage is introduced in the spacer(8, 9, 13, 14).

In previous paper, we reported on head-tail regular polymers by ring-opening polymerization of silacyclobutane derivatives with disiloxane side chain(15). We, herein, report on the synthesis and polymerization of silacyclobutanes with mesogenic groups connected through siloxane spacer by platinum complex, and thermal behavior of the formed polymers.

Experimental

General

300 MHz ^{1}H and 79.5 MHz ^{29}Si NMR spectra were recorded on Varian NMR spectrometers model Gemini 2000 and UNITY INOVA 400, respectively. The chemical shifts are given in ppm relative to $CHCl_3$ (7.26 ppm for ^{1}H) and tetramethylsilane (0.00 ppm for ^{29}Si) as internal standards in $CDCl_3$. IR spectra were measured on KBr disk samples on a JASCO VALOR-III spectrometer, and characteristic absorptions are given in cm^{-1}. Molecular weights of the polymers were estimated by a JASCO HPLC model 980 at 40 °C equipped with Shodex KF-800P (precolumn), KF-801 (exclusion molecular weight, polystyrene M_n = 1.5 X 10^3), and KF-804 (exclusion molecular weight, polystyrene M_n = 4.0 X 10^5) columns. Mass spectra (MS) were obtained on a SHIMADZU QP-5000 spectrometer. DSC analyses were carried out on a SEIKO thermal analysis system Model SSC 5200 equipped with DSC 120 at a cooling rate of 10°C min^{-1}. Optical polarization micrographs were taken on a Nikon optical polarization microscope Model OPTIPHOTO-2 equipped with a Mettler FP82 hot stage.

Synthesis

Silanol derivatives with mesogen were synthesized similarly to the reported methods(8, 9, 14), and monomers were synthesized as shown in Scheme 1. Indication of atoms for NMR analysis is also shown in the scheme.

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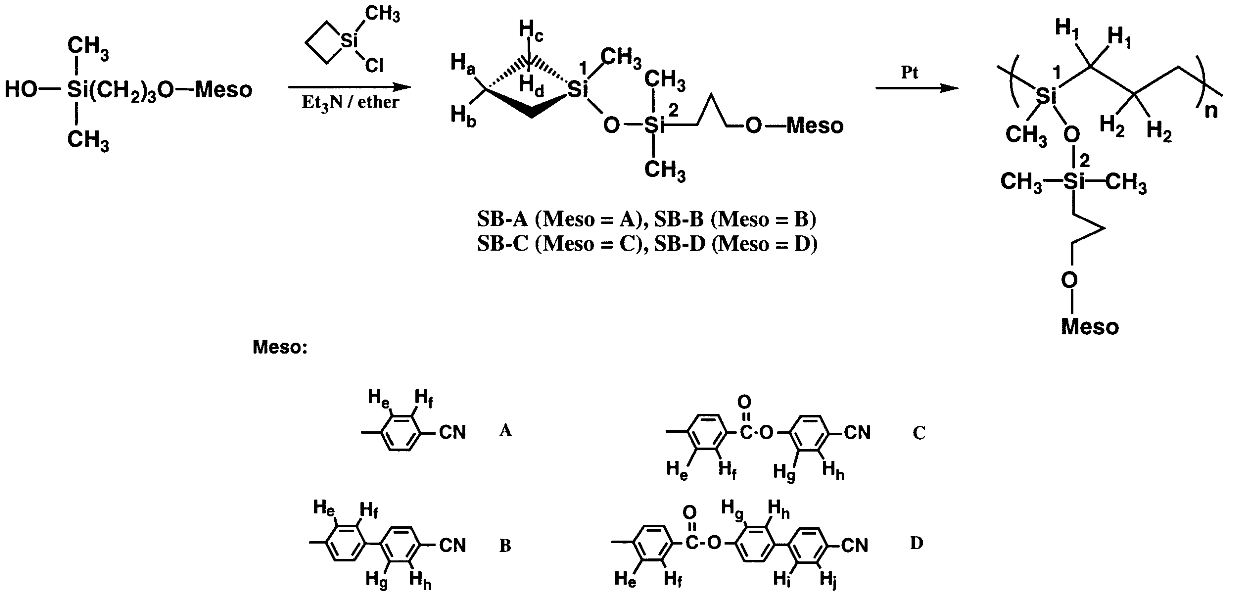
[*] Corresponding author



Scheme 1. Synthetic route to monomers and indication of atoms.

1-Methyl-1-{[3-{1(4-cyanobiphenyl-4'-yl)oxy}propyl]dimethylsiloxy}silacyclobutane (SB-B)

To a solution of 1-chloro-1-methylsilacyclobutane (0.57 g, 4.74 mmol) and triethylamine (0.60 g, 5.93 mmol) in THF (5 mL) was added a solution of [3-{(4-cyanobiphenyl-4'-yl)oxy}propyl]dimethylsilanol (1.12 g, 3.60 mmol) in THF (5 mL). After completion of the addition, the reaction mixture was stirred for 3h at room temperature, the solvent was removed, and the product was purified by column chromatography (hexane : CH_2Cl_2 = 1:1, R_f = 0.35). Viscous liquid (0.67 g, 47 %).

^{1}H NMR: 0.16 (s, 6H, Si^{2}CH_3), 0.24 (s, 3H, Si1CH_3), 0.70 (m, 2H, SiCH_2), 1.14 (m, 4H, H_c, H_d), 1.43-1.60 (m, 1H, H_a or H_b), 1.76-2.00 (m, 3H, SiCH$_2$CH_2, H_a or H_b), 4.00 (t, 2H, J = 6.6 Hz, CH_2O), 6.99 (d with fine coupling, 2H, J = 9.0 Hz, H_e), 7.53 (d with fine coupling, 2H, J = 9.0 Hz, H_f), 7.64, 7.69 (two d with fine coupling, 2H each, J = 8.7 Hz, H_g, H_h). ^{29}Si NMR: 5.39 (Si^2), 9.72 (Si^1). IR: 2227 (CN), 1251 (Si-C), 1050 (Si-O-Si). MS (m/z): 395 (M$^+$).

1-Methyl-1-[{13-(4-cyanophenyloxy)propyl}dimethylsiloxy]silacyclobutane (SB-A)

[Viscous liquid, 55 %, R_f = 0.56 (hexane: CH_2Cl_2 = 1 : 1)].

^{1}H NNM: 6.93 (d with fine coupling, 2H, J = 9.0 Hz, H_e), 7.57 (d with fine coupling, 2H, J = 9.0 Hz, H_f). ^{29}Si NMR: 5.24 (Si^2), 9.59 (Si^1).

Other signals of this compound showed reasonable chemical shifts. **1-Methyl-1-[{3-[4-{(4-cyanophenyloxycarbonyl)phenyl}oxy]propyl}dimethylsiloxy]silacyclobutane (SB-C)** (viscous liquid, 51 %) and **1-methyl-1-{[3-{4-[{(4-cyanobiphenyl-4'-yl)oxycarbonyl}phenyl]oxy}propyl]dimethylsiloxy} silacyclobutane (SB-D)** (M.p. 56-57 °C, 56 %) similarly obtained also gave reasonable analysis data.

Polymerization by platinum complex

Polymerizations were carried out mainly with Pt(COD)Cl_2 or PtDVTMDS (1,3-divinyltetramethyldisiloxaneplatinum)(16). Formed polymers were recovered and purified by repeated precipitation from THF into methanol. The name of a polymer is abbreviated by the combination of P and the abbreviation name of the monomer.

PSB-B

^{1}H NMR: 0.03 (s, 3H, SiCH_3), 0.07 (s, 6H, Si(CH_3)$_2$), 0.40-0.62 (broad, 6H, H_1, SiCH_2), 1.24-1.41 (broad, 2H, H_2), 1.75-1.90 (broad, 2H, CH_2CH$_2$O), 3.80-3.98 (broad, 2H, CH_2O), 6.88-7.00 (broad, 2H, H_e), 7.40-7.68 (broad, 6H, H_f, H_g, H_h). ^{29}Si NMR: 6.83. IR: 2226 (CN), 1180 (Si-C), 1060 (Si-O-Si).

PSB-A, PSB-C, PSB-D also gave reasonable NMR and IR data.

Results and Discussion

Synthesis and Polymerization of the monomer

Caution was taken to avoid the liberation of HCl in monomer synthesis by the addition of excess Et_3N to 1-chloro-1-methylsilacyclobutane before the silanol was added, because silanols easily condense to give disiloxane under acidic condition. Two singlets with same intensity were observed for the monomer in ^{29}Si NMR. ^{29}Si NMR of SB-B is shown in Figure 1-A (5.39, 9.72 ppm). The higher field signal was assigned to out-ring Si atom (Si^2), and lower to in-ring atom (Si^1), by referring to the report that the signal of Si atom of silacyclobutane ring appears at lower field because of the ring strain(15, 17).

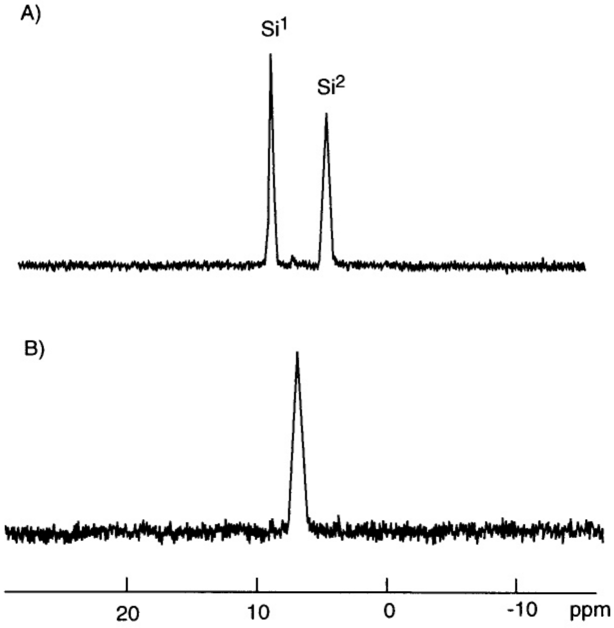


Figure 1. ^{29}Si NMR spectra, A) SB-B, B) PSB-B obtained by $Pt(COD)Cl_2$ (79.5 MHz, at room temperature in $CDCl_3$).

The results of polymerization were summarized in Table 1. Rhodium complexes did not show activity in the polymerization. $Pt(COD)Cl_2$ was the most active complex for the polymerization of SB-B, and this complex was used in the polymerization of other monomers (Run 1, 7, 8). Although the polymerization proceeded rapidly, and the monomers were consumed quantitatively, the isolated yield (26~64%) and the molecular weight of the obtained polymer (M_n~5000) were not high. ^{29}Si NMR spectrum of the purified PSB-B is shown in Figure 1-B. Other polymers also gave similar spectra. The main chain and side chain Si atoms appeared as one sharp peak (6.83 ppm) because of the relief of the ring strain of the monomer. The chemical shift is close to that of the reported poly(1-methyl-1-trimethylsiloxysilylenetrimethylene) (6.43 ppm)(15).

By a close look at the ^{1}H NMR spectrum, multiplets at 4.8~4.9 and 5.7~5.8 ppm assignable to terminal olefin protons were seen (Figure 2). These signals are assigned to allyl group at the terminal of the polymer chain by the comparison with a model allylsilane derivative.

Table 1. Polymerization of monomers in bulk

Run	Monomer[1]	Cat[1]	Time (h)	M_n[2]/10^3	M_w/M_n[2]	M_{NMR}[3]/10^3	Yield (%)
1	SB-A	$Pt(COD)Cl_2$	6	5.3	2.6	7.9	26
2	SB-B	PtDVTMDS	20	4.2	4.6	6.2	63
3		$Pt(COD)Cl_2$	6	4.1	4.9	5.9	64
4		H_2PtCl_6	12		No reaction		
5		$[RhCl(COD)]_2$	20		No reaction		
6		$Rh(Ph_3P)_3Cl$	20		No reaction		
7	SB-C	$Pt(COD)Cl_2$	20	5.0	2.6	7.9	27
8[4]	SB-D	$Pt(COD)Cl_2$	12	5.2	7.6	8.1	55

1) [M] / [Cat] = 10,000, at 80 °C. 2) Estimated by GPC, correlating to standard polystyrene in THF. 3) Estimated by ^1H NMR. 4) In toluene, [M] = 1.0 M, at 120 °C.

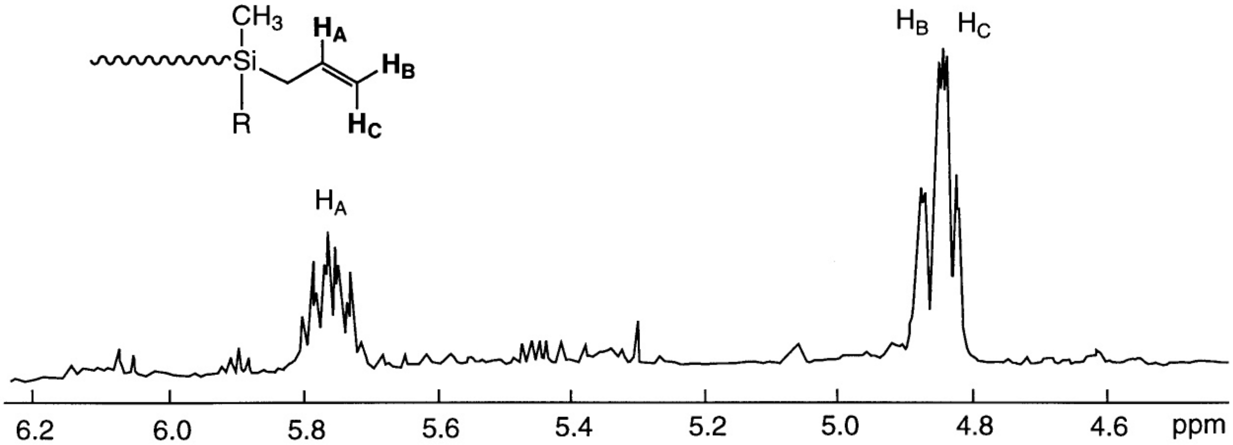
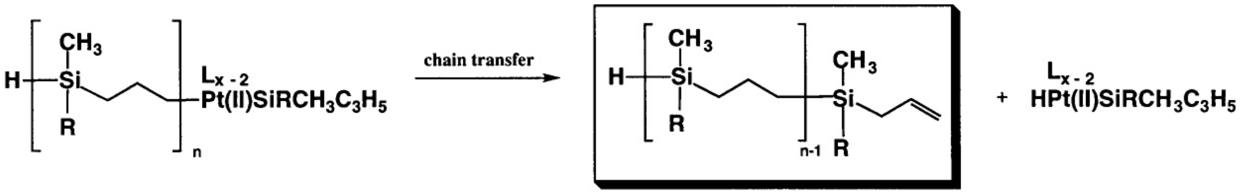


Figure 2. Olefinic region of ^1H NMR spectrum of PSB-B by $Pt(COD)Cl_2$ (500 MHz, at room temperature in $CDCl_3$).

We proposed a reaction mechanism with chain transfer for the polymerization of 1, 1,2-trimethylsilacyclobutane(18). Similar transfer reaction is apparently occurring in the polymerization of these monomers (Scheme 2), resulted in rather low molecular weight and isolated yield of the polymer.



Scheme 2. Chain transfer in the polymerization.

From the ratio of terminal allyl protons (3H, CH_2=CHCH$_2$Si-) and SiCH_3OSi(CH_3)$_2$ protons (9H), the degree of polymerization was estimated (Table 1). Number average molecular weight estimated by SEC was considerably smaller (30~35 %) than that by ^{1}H NMR.

Thermal analysis of the monomers and polymers and observation by optical polarization micrograph

SB-A, SB-B and SB-C showed melting point (SB-A: -16.6, SB-B: 8.6, SB-C: -4.2 °C) in DSC. SB-D showed both melting point (6.3 °C) and phase transition temperature to isotropic phase (168.3 °C, ΔH_i = 3.7 mJ/mg), and formed a focal-conic fan texture by annealing at 160 °C for 30 min, suggesting smectic A phase.

Three kinds of polymers (PSB-B, PSB-C and PSB-D) showed glass transition (T_g), and clearing point (T_i).

Table 2. Thermal behavior of polymers

Polymer	Transition temp. (°C) [ΔH_i (mJ / mg)]$^{1)}$		Texture$^{2)}$
	T_g	T_i	
PSB-A	-45.5	-	-
PSB-B	-4.6	40.7 (4.1)	Fan
PSB-C	-19.1	27.3 (3.1)	Fan
PSB-D	10.1	170.6 (2.7)	N.d.$^{3)}$

1) Determined by DSC on 1st cooling scan of -10 °C/min. 2) By optical polarization microscope. 3) Liquid crystalline phase could not be determined.

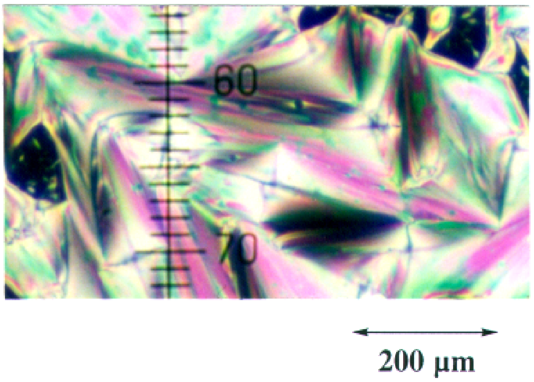


Figure 4. Focal-conic fan structure of PSB-C after annealing at room temperature for 1 week under optical polarization microscope.

Although sand type texture was observed for PSB-D, and definite texture could not be clarified, liquid crystalline phase having focal-conic fan structure [PSB-B(15), PSB-C] was formed even at room temperature because of the presence of flexible disiloxane linkage in the spacer. Batonet texture formed in 1 day grew to focal-conic fan texture by annealing for 1 week. Typical photograph is shown for PSB-C (Figure 4).

Conclusions

Silacyclobutanes with several kinds of mesogen were synthesized. The polymerization proceeded by platinum complexes to give the polymers with olefinic terminal. The polymer exhibited low glass transition and clearing temperatures due to the presence of flexible siloxane spacer. The smectic A liquid crystalline phase was suggested.

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