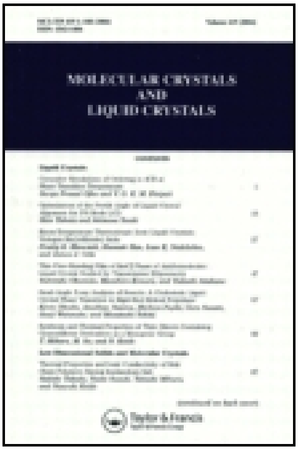

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Synthesis and Mesomorphic Properties of Fishbone-Like Liquid Crystalline Polysilsesquioxanes 2. Imine-Based Side Chain Mesogenic Polysilsesquioxanes

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Synthesis and Mesomorphic Properties of Fishbone-Like Liquid Crystalline Polysilsesquioxanes
2. Imine-Based Side Chain Mesogenic Polysilsesquioxanes[†]

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Fishbone-like, imine-based liquid crystalline polysilsesquioxanes (FP) including homopolymeric H-FP and copolymeric (C-FP) have been first synthesized by hydrosilylation reaction of a vinyl-terminated imine mesogen compound with highly ordered ladderlike polyhydrosilsesquioxane [H-T] and random copolymethylhydrosilsesquioxane [MH-T] in the presence of Cp_2PtCl_2 used as the catalyst. This novel thermotropic side-chain liquid ctystalline polymer with Mw of 10^{5-6} can form a transparent uniform film on melting. Their clearing temperature Tcl and mesophase range ΔH are much higher than those of the corresponding comb-like, imine-based liquid crystalline polysiloxane (single main chain) by about 200°C.

Keywords: Fishbone-like liquid crystalline polymer; imine-based mesogen

It is over twenty years now since Shibaev, Blumstein and Ringsdorf reported the synthesis and characterization of comb-like liquid crystalline polymers (C-LCP) [1–3]. In contrast to main chain liquid crystalline polymers: lyotropic aromatic polyamide and thermotropic copolyesters mainly used as high performance engineering material with good machanic properties, the thermotropic C-LCP is a potentially functional polymeric material with special electric, optical or magnetic properties. However, it has not

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[†] The project was supported by NSFC.

been commercially available so far partly due to poor mechanical properties such as film-forming ability, strength and toughness. To improve the film-forming ability, a fishbone-like, β-diketone-based liquid crystalline polysilsesquioxane (FBDKLCP) was first prepared in our laboratory [4], recently, and another type of fishbone-like, azo-based liquid crystalline polysilsesquioxane (FBAZLCP) was also reported [5]. Their unique physicochemical properties such as peculiar optical texture, much wider mesophase range (ΔH) than corresponding comb like polysiloxane (single chain) and good film-forming ability should be attributed to the high regularity and semirigidity of ladderlike polysililsesquioxane as a macromolecular backbone. This paper describes another sort of fishbone-like imine-based liquid crystalline polysiloxane, which could be used as a skeleton material of polymer network liquid crystal (PNLC) in electro-optical display testing [6].

EXPERIMENTAL

The schematic reaction route is shown in Figure 1.

Materials and Techniques

All the reagents and solvents are commercially available and are of analytical purities. The vinyl-terminated imine mesogen compound, p-unde-

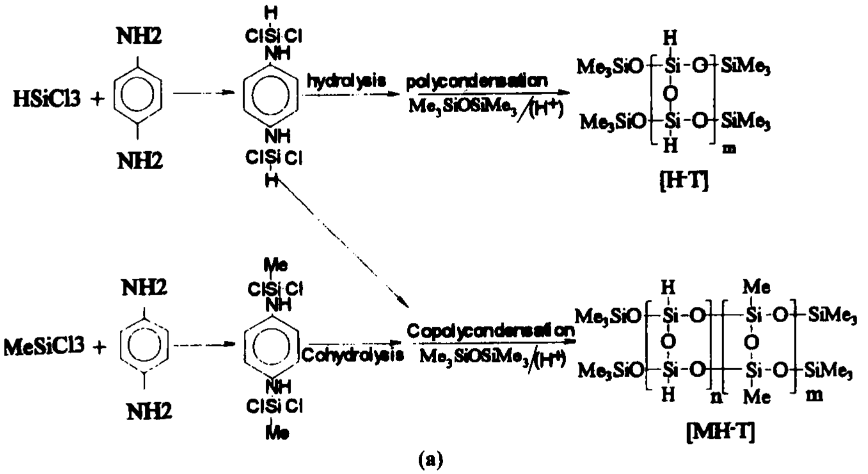
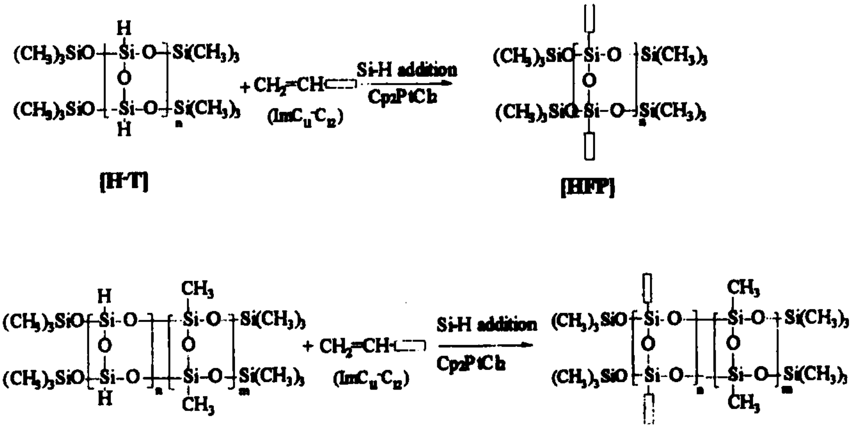


FIGURE 1 Schematic reaction route for Fp's. (a) preparation of H-T and MH-T, (b) preparation of H-FP and C-FP.



(b)

FIGURE 1 (Continued).

cenyloxybenzylidene (abbr. Im—$C_{11}C_{12}$, $CH_2{=}CH{-}(CH_2)_9{-}O{-}C_6H_4{-}O{-}C_{12}H_{25}$, mp 96.9°C) was prepared following the precedure described in reference [7]. The Si—H contents of ladderlike polyhydrosilsesquioxane H-T and MH-T were determined gas-volumetrically [8]. Toluene used was purified with sulfuric acid to completely remove methylthiophene which can inactivate the hydrosilylation catalyst Cp_2PtCL_2 and distilled over sodium sand. The catalyst was prepared according to Apfel's work [9]. The GPC measurement was run on an LC-10 instrument (Japan Analytical Company) versus polystyrene standard. The DSC study was carried out with Perkin-Elmer DSC-4. The IR spectra was made on FT-IR Spectrophotometer PE-80. The temperature-variable X-ray diffraction was performed on an improved Rigaku dmax/38 diffractometer with Cu/Kα radiation of a wavelength of 0.154 nm. The optical birefringence was examined with XPIA/XINTIAN optical polarizing microscopy equipped with a heat-plate.

Synthesis

A. Preparation of ladderlike polyhydrosilsesquioxane [H-T] and random copolymethylhydrosilsesquioxane [MH-T]

A-1. [H-T]

A solution of 25 ml of dried acetone containing 2.7 g (0.025 mol) of 1, 4-phenylenediamine (PDA) was added dropwise into a solution of 15 ml of toluene dissolved containing 3.4 g (0.025 mol) of trichlorosilane (TCS) on vigorously stirring at − 15 − 5°C and then the system was kept stirring for 30 minutes. A solution of 10 ml of acetone and 0.9 ml of water was dropwise introduced into the system and stirred for 30 minutes and the system graduauy turned from pink to slightly brown. Then an additional solution of 0.45 ml of water and 5 ml of acetone was added and stirred for one hour at 5°C. After that the mixture was filtered in vacuo to remove the solid amine salt and the filtrate solution was evaporated in vacuo to distill out acetone and then dried with anhydrous sodium sulfate overnight at below 0°C. Next, agitation was kept at 30°C for one day in the presence of 0.041 mg (0.00025 mmol) of hexamethyldisiloxane used as molecular weight-controlling agent and three drops of concentrated sulfuric acid as the catalyst of polycondensation and equilibration reaction. Finally, the solution was washed at least five times with a saturated aqua solution of sodium chloride to be neutral. The solution was dried with sodium sulfate again and became transparent and colorless after filtration. Its concentration was 15 mg/ml and the yield was 57%. The characterization data are listed in Table I.

TABLE I Characterization data of the ladderlike polyhydrosilsesquioxanes

Items	*H-T*	*MH-T*
Solubility (in toluene)	Soluble	Soluble
Mw by GPC	10^6	10^6
Elemental Analysis		
C(%) (Cald/Found)	0.0/0.3	10.00/9.68
H(%) (Cald/Found)	1.88/2.01	3.30/3.89
N(%) (Cald/Found)	0.00/0.00	0.00/0.00
Grafting yield (%)	85	41
DSCcurve at the range between $-50° - 300°C$	Almost horizontal	Almost horizontal
IR spectra (cm^{-1})	2257 Si—H 796 & 1274 Si—Me	2250 Si—H 799 & 1274 Si—Me
^{29}Si-NMRspectra	β_1 − 92.66 H—$SiO_{3/2}$	β_1 − 92.84 H—SiO3/2 β_2 − 71.20 Me—Si—$O_{3/2}$ α_1 − 66.80 H—SiO (OH)
Content of Si—H(%) (Cald./Found)	1.88/1.46	0.83/0.82
Regularity $(A_\beta/A_\beta + A_\alpha)$ by ^{29}Si-NMR	100%	90–95%
Distance(A)/Intensity(I) by X-ray diffraction	d_1 8.733/190 d_2 4.040/210 d_3 3.843/210	8.531/60 4.168/33 2.646/17

A-2. [MH-T] (molar ratio of $MeSiO_{3/2}$: $HSiO_{3/2} = 1$)

A solution of 25 ml of acetone containing 1.35 g (0.0125 mol) of PDA was added dropwise into a solution of toluene dissoved with 0.9 g (0.0125 mol) of methyltrichlorosilane (MTCS) at $-5°C$ and stirred for 30 minutes. Then another solution of toluene dissolved with 0.8 g (0.0125 mol) of trichlorosilane (TCS) was added into the above-mentioned solution and stirred togather, to which a solution of acetone containing 1.35 g of PDA was added. After being stirred for 30 minutes at $-5°C$. The preaminolyzed chlorosilane solution was hydrolyzed with 0.9 ml of water dissolved in 10 ml of acetone upon stirring for 3 hours at 12–15°C. Same procedures adopted in A-1 were taken to obtain a clear solution, which was subjected to condensation and equilibration reaction in the presence of 0.004 mg (0.00025 mmol) of hexamethyldisiloxane and three drops of sulfuric acid upon stirring for one day at 40°C. After being washed to neutral and dried overnight, a clear colorless solution of [MH-T] was obtained with a yield of 63% and a concentration of 30 mg/ml. The chatactrization data are also listed in Table I.

B. Preparation of FP

B-1. Homopolymer [H-FP]

The hydrosilylation reaction was carried out in a manner similar to the corresponding comb-like, imine-based liquid crystalline polysiloxane (IMLCP) described in reference [7]. After being degassed with argon, the system containing 0.2 g (0.0375 mmol) of vinyl-terminated imine (IM-$C_{11}C_{12}$) and 0.019 g (0.0358 mmol of $HSiO_{3/2}$) of LPHSQ dissolved in 50 ml of methylthiophene-free toluene was heated at 70°C in the presence of Cp_2PtCl_2 (2.3□ × 10^{-7} mol) and then allowed to be stirred at 85°C for one day. Next, 150 ml of dried methanol was added to dissolve the unreacted mesogen compound IM-$C_{12}C_{12}$ and to precipitate the target product. The latter was filterd out and stripped in vacuo at below 50°C to give a yellow powderlike solid with a yield of ca. 85%. The composition and other properties are given in Table II.

B-2. Copolymer [C-FP]

Similar to above mentioned B-1, the system containing 0.2 g (0.375 mmol) of IM$C_{11}C_{12}$ and 0.04 g (0.33 mmol of $HSiO_{3/2}$) of random copolymer

TABLE II Mesomorphic Properties examined by DSC, X-ray diffraction & polarizing microscopy for FP's

Sample	*Phase transition by DSC* *T(°C)/ΔH(Cal/g)*	*ΔT* *(°C)*	**d(Å) by* *X-ray* *diffraction*	*Texture*
IMCLP**	$K \xrightarrow{88.3/11.4} S \xrightarrow{127.9/3.4} I$	39.6	$d_1 = 19.9$ $d_2 = 4.3$ $d_3 = 3.9$	Smectic
H-FP	$K \xrightarrow{98.61/17.44} LC_1 \xrightarrow{106.79/3.95} LC_2 \xrightarrow{320}$ dec. $K \xleftarrow[86.08/-19.72]{} LC_1 \xleftarrow[96.10/-2.69]{} LC_2$	221.4	37.03 4.06	bright lines
C-FP	$K \xrightarrow{98.61/-22.37} LC_1 \xrightarrow{104.6/-2.2} LC_2 \xrightarrow{300}$ dec. $K \xleftarrow[83.96/-17.36]{} LC_1 \xleftarrow[92.3/-1.72]{} LC_2$	201.4	34.47 4.15	bright lines

* The X-ray diffraction was run at the temperature (100°C) of liquid crystal state.
** The data were given in reference [5].

[MH-T] dissolved in 50 ml of toluene was heated at 70°C and then 0.4 ml (2.3×10^{-7} mol) of Cp_2PtC_{12} was added. The system was stirred for one day at 85°C and mixed with 150 ml of dried methanol to produce a viscous solid which was stripped in vacuo to give a pale-yellow powderlike solid with a yield of ca. 85%. Its composition and properties are also listed in Table II.

RESULTS AND DISCUSSION

1. Synthesis

A. Ladderlike polysilsesquioxane [H-T] and random copolysilsesquioxane [MH-T]

As early as 1960 Brown [10] first synthesized a ladderlike polyphenylsilsesquioxane [PhT] by thermal polycondensation of phenyltrichlorosilane hydrolysate using KOH as the catalyst, but its regularity was not high because of branching and crosslinking. The highlyordered ladderlike polysilsesquioxanes [H-T] and [MH-T] were first prepared by preaminolysis reaction of $HSiCl_3$ with PDA and then hydrolysis, polycondensation and equilibration reaction. The proposed reaction mechanism has been suggested in previous reports [11–13]. As shown in Table I, the high regularity of the ladderlike polysiloxane [H-T] and [MH-T] is characterized by the high ratio of $A_\beta/A_\beta+A_\alpha=$ ca. 90–100% calculated from ^{29}Si-NMR spectra, where A_β represented area of resonance absorpeion peak generated by the ordered silicon atoms in $RSiO_{3/2}$ groups (R is methyl or hydrogen) and the A_α represents that generated by the defective silicon atoms in RSiO(OH)-groups in terms of Shi's work [14]. The X-ray diffraction analysis gives the distances d_1, d_2 and d_3, which stand for the plane-to-plane distance corresponding to the distance between the double chains and the thickness of the macromolecular itself, respectively. The bigger value of the d_1 means the higher regularity ofthe ladderlike chain.

On the other hand, it is very important that the solution of the title polymer must be neutral becauce the reactive Si—H group in the ladderlike polymer chain can be easily hydrolyzed and condensed with each other to form crosslinked gel. So, it is necessary to keep the title polymer solution in a sealed and neutral bottle at lower temperature.

B. Fishbonelike imine-based FP

Because the Si-H groups in the parent polymers [H-T] and [MH-T] are very sensitive to oxygen and water the grafting hydrosilylation reaction must be carried out under air-free conditions. The completeness of the hydrosilylation reaction was confirmed by the disappearance of the absorption peak at 2260 cm^{-1} characteristic of Si—H bond in IR spectrum The grafting yield of the imine-based side chains linked to the ladderlike polysilsesqioxanes [H-T] and [MH-T] are 85% and 41%, in comparison with the calculated value: 100% and 50% respectively. The difference is mainly attributed to the steric hindrance.

2. Mesomorphic Properties

The liquid crystallinity was examined by DSC, optical polarizing microscopy(OPM) and temperature-variable X-ray diffraction. The results are shown in Figure 2, Figure 3 and Table II. As DSC curves shown in Figure 3, FP's are semi-crystalline polymers without noticeable glass transition between $-50\sim$ 350°C. The transition enthalpy ΔH (ca. 22–25 cal/g) between crystalline state to LC_1 is not very big. It means that the total changes in the order of the macromolecular alignments between the crystalline and mesophase is not very conspicuous. The FP's demonstrate a sharp peak at small angle region in X-ray diffraction patterns at melt state, which represents long-range order ($d\sim 20$ Å) or layer structure, the data were listed

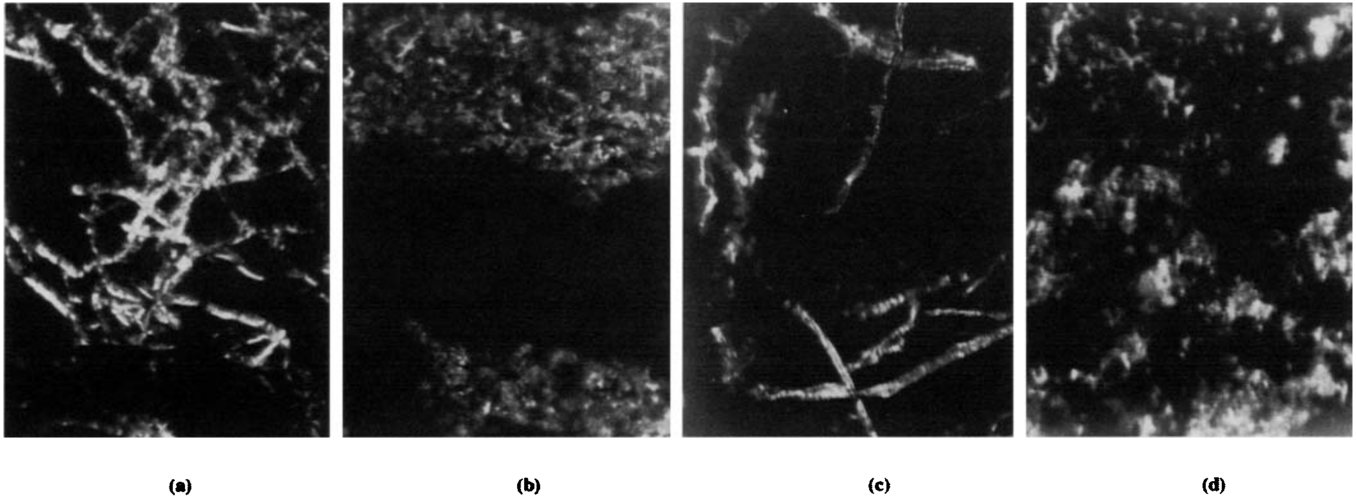


FIGURE 2 Polarizing microphotographs of FP's at elevated temperature. (a) H-FP taken at 306 °C, (b) H-FP taken at 80 °C, (c) C-FP taken at 306 °C and (d) C-FP taken at 80 °C.

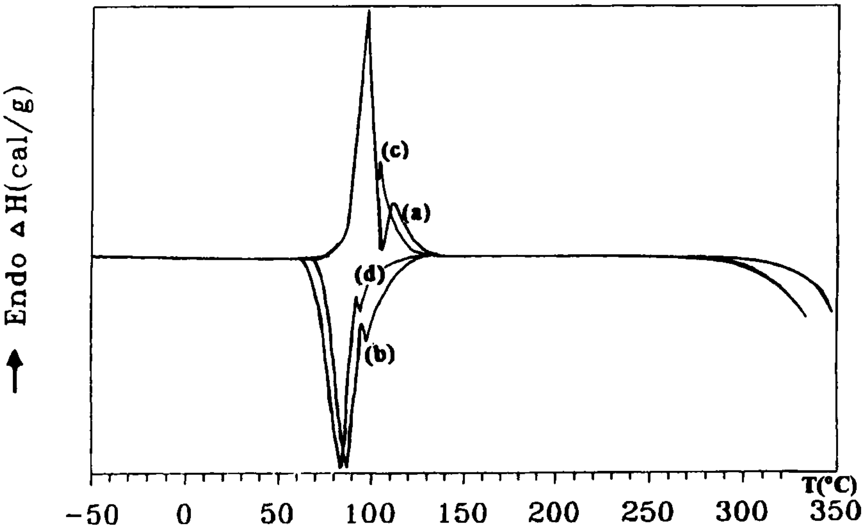


FIGURE 3 DSC curves for H-FP and C-FP. (a) is the temperature-increasing curve for H-FP, (b) is the temperature-decreasing curve for H-FP, (c) is the temperature-increasing curve for C-FP and (d) is the temperature-decreasing curve for C-FP.

in Table II. The textures are shown in Figure 2. With temperature-increasing FB's first enter a mesophase which shows normalmesomorphic texture with characteristic broad birefringent bright region. Owing to the very narrow temperature-range between LC_1 and LC_2 states the change in texture can not be distinguished on OPM. Then the broad birefringent region gradually disappear at about 130–140°C and many bright belts, lines or spots emerge on the black background until decomposition. The nature of this phenomenon has not been clearly understood, it seems that these anisotropic bright belts, lines or sports can be supposed to be a self-organized structure originated from lateral aggregation or association of ladderlike main chain via interaction between mesomorphic side chains. Meanwhile, it is very difficult dynamically to be well-aligned in a broad region or to take fully extended conformation, so it is different from the favourable alignment as in normal mesophase. The assignements for these textures are under investigation.

Acknowledgements

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