

SYNTHESIS AND MESOMORPHIC PROPERTIES OF FISHBONE-LIKE LIQUID CRYSTALLINE POLYSILSESQUIOXANES

I. FISHBONE-LIKE, β -DIKETONE-BASED LIQUID CRYSTALLINE POLYSILSESQUIOXANES AND THEIR COPPER COMPLEXES*

ZHANG Rongben** (张榕本) XIE Zushou (谢祖琚) WAN Youzhi (万有志)
JIN Sunzhi (金顺子) and HOU Jianan (侯建安)

(Institute of Chemistry, Academia Sinica, Beijing, 100080)

ABSTRACT

Two kinds of fishbone-like, β -diketone-based liquid crystalline polysilsesquioxanes (FBDKLCP'S), homopolymeric (H-FBDKLCP) and copolymeric (C-FBDKLCP) have been first synthesized via the hydrosilylation reaction of a vinyl-terminated β -diketone with the homopolymeric ladderlike polyhydrosilsesquioxane (LPHSQ) and random copolymethylhydrosilsesquioxane (LRPMHSQ) respectively. These new kinds of FBDKLCP with M_n of 10^4 is thermotropic liquid crystalline polymer and its clearing temperatures T_i 's and mesophase range ΔT 's are much higher than those of the corresponding comb-like β -diketone liquid crystalline polysiloxane (DKLCP) by about 200 °C. Similar results have been observed with the comparison of the two different structure Cu-coordinating compounds. The significant increases in T_{cl} 's and ΔT 's of the FBDKLCP and Cu-FBDKLCP are mainly attributed to the great rigidity of the ladderlike polysilsesquioxane backbone.

INTRODUCTION

Since Jackson^[1], Shibaev^[2] and Blumstein^[3] et al.^[4-9] reported the synthesis and properties of comb-like liquid crystal polymer (CLCP) this new field has attracted polymer scientists' attention to its theoretical significance and potential application. So far, the CLCP has not been commercially used because of the low concentration of functional groups in the polymer molecule and poor mechanical property such as the film-forming ability and tensile strength. In the first part of this paper a new kind of Fishbone-like LCP was reported. Its main chain is a ladderlike, double chain polysilsesquioxane to which the β -diketone-based mesogenic moieties are attached via the Si-C bonds. The structure and properties of ladderlike polysilsesquioxanes were comprehensively studied^[10-11]. In comparison with the corresponding comb-like DKLCP, the FBDKLCP possesses much higher T_i and wider ΔT as well as an improved film-forming ability. In the second part of this paper copper-coordinating fishbone-like β -diketone-based liquid crystalline polysilsesquioxane Cu-FBDKLCP was reported. It is well known that as a new frontier of LCP, the metal-coordinating LCP (MCLCP) is receiving a growing attention because it combines the coordination chemistry with polymer science so that it is of prospective property for the functional polymer materials^[12-16]. Recently, three novel metal-coordinating MCLCP's;

Received March 19, 1992

(*) A part of this paper was presented at "International Symposium on Fine Chemistry and Functional Polymers", Sept 11-16, 1992, Hangzhou, China

(**) for correspondence

β -diketone, imine and azo-based liquid crystalline polysiloxanes were synthesized in our laboratory^[17-22]. The results indicated that the incorporation of metal ions into the LCP's can play a positive effect on the mesomorphic properties. It was pointed out that the clearing temperatures T_{cl} 's and mesophase range ΔT of Cu-FBDKLCP were higher than the corresponding Cu-coordinating comb-like LCP (Cu-DKLCP) by about 100 °C although its T_{cl} 's and ΔT 's were lower than those of the parent ligands FBDKLCP because it was decomposed prior to T_{cl} . Owing to the higher density of functional groups and an improved mechanical property, especially the metal-coordinating units of various electric or magnetic behaviors can lead the MFBLCP to be promising material for the use in electric, magnetic and nonlinear optical fields.

EXPERIMENTAL

The schematic reaction route is shown in Fig. 1.

1. Materials and techniques

All the reagents and solvents are commercially available and of analytical pure. The vinylterminated diketone mesogen compound, 1,3-di(p-n-dodecyloxy-phenyl-p-n-undecenyl-oxyphenyl) propane -1, 3-dione (abbr. as β -DK-C₁₁-C₁₂), mp 87.5 °C, was prepared following the reference [23]. The catalyst for the hydrosilylation reaction, Cp₂PtCl₂, was prepared referring to Apfel's work^[24]. The used toluene was purified by completely removing methylthiophene with sulfuric acid and distilled out on sodium sand. The GPC measurement was made on LC-10 instrument (Japan Analytical Industry Co.) with polystyrene as the standard. The DSC thermographs were obtained with Perkin-Elmer DSC-4 instrument. The IR spectra were recorded on FT-IR spectrophotometer, PE-80. The temperature-variable X-ray diffraction was carried out on Rigaku DMAX/38 diffractometer with a temperature-variable attachment and the Cu-K α radiation with wavelength of 0.154 nm was utilized. The mesophase textures were examined on XPIA-XINTAIN optical polarizing microscope with a heating stage. The determination of cupric content was run on UV-Visible spectrophotometer 730 (Shanghai Analytical Factory).

2. Synthesis

(1) Ladderlike polyhydrosilsesquioxane (LPHSQ) and random copolymethyl hydrosilsesquioxane (LR-PMHSQ)

The detailed synthetic procedures of LPHSQ and LR-PMHSQ were described in our previous paper^[25]. The typical examples were given as follows:

(a) Preparation of LPHSQ

A solution of 25 ml of acetone containing 2.9 g (0.025 mol) of 1,4-phenyldiamine (PDA) was added dropwise into a solution of 15 ml of toluene dissolved with 3.4g (0.025 mol) of trichlorosilane (TCS) upon vigorously stirring at -15—-6 °C and then the system was kept stirring for 30 minutes. A solution of 15 ml of acetone, 1.5 ml of water and 20 ml of toluene was introduced into the system which was, in turn, stirred for additional four hours at room temperature (R.T.). After being filtered and dried with anhydrous sodium sulfate, the filtrate solution was washed with distilled water to neutral and stripped off water under reduced pressure to give 1.2 g of a white solid polymer with

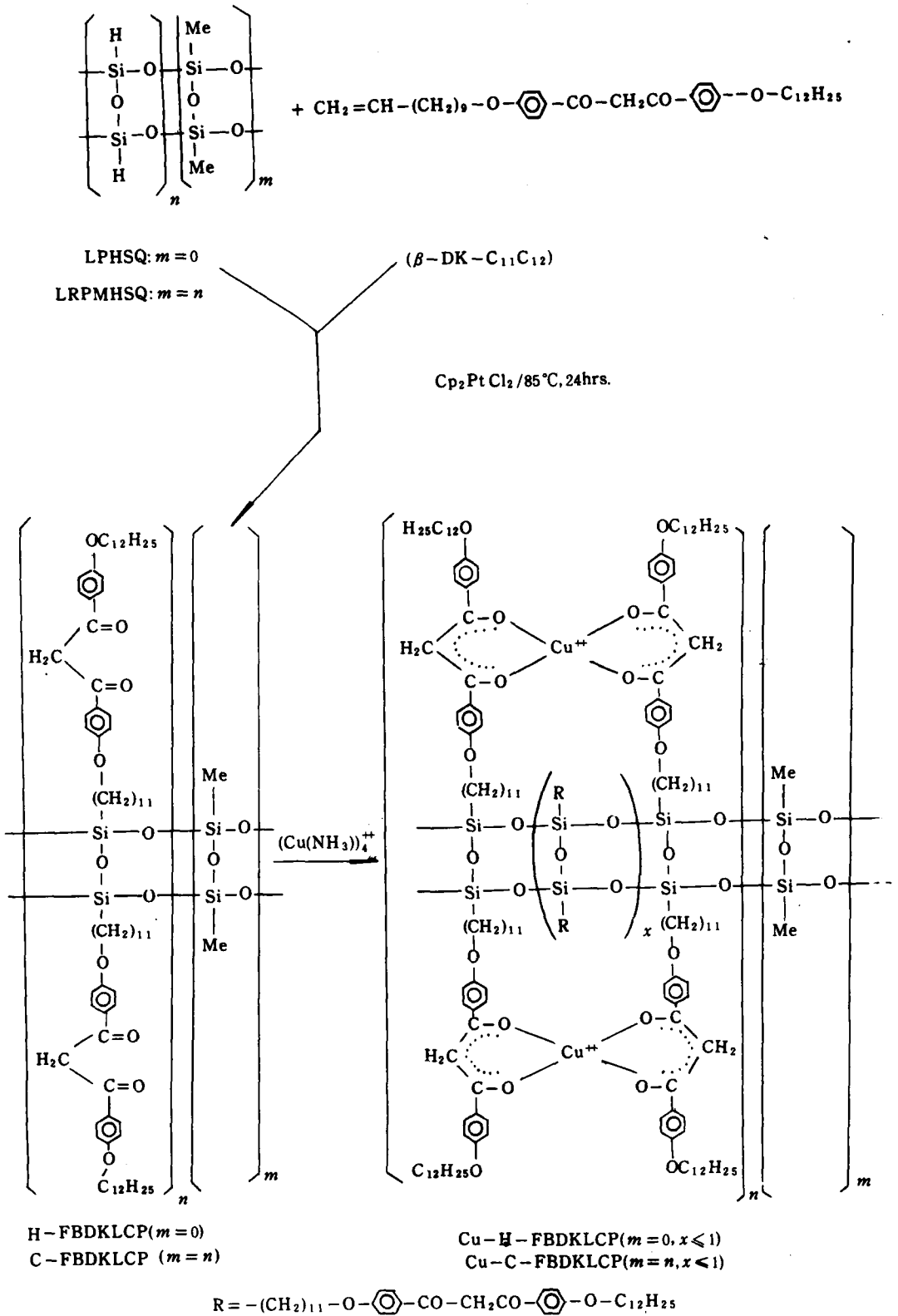


Fig. 1 Schematic reaction route for the synthesis of FBDKLCP and its copper complexes

a yield of 90%. The molecular weight M_w measured by GPC with polystyrene as standard was 4×10^3 .

(b) Preparation of LR-PMHSQ

A solution of 10 ml of toluene containing 3.8 g (0.025 mol) of methyltrichlorosilane (MTCS) was added dropwise to a solution of 25 ml of acetone containing 2.7 g (0.025 mol) of PDA on stirring at -15 — -6°C for 30 minutes to obtain an intermediate solution 1. As described above in (1-A), the reaction of 3.4 g (0.025 mol) of TCS with 2.7 g (0.025 mol) of PDA to give an intermediate solution 2. The mixed solution of 1 and 2 was cohydrolyzed with 3 ml of water dissolved in 20 ml of acetone at R. T. for four hours. Then the system was filtered and the filtrate solution was washed with water to neutral and dried in vacuum-oven to give 2.8 g of white or yellowish solid polymer with a yield of 92% and M_w of 3×10^3 .

(2) The homopolymeric FBDKLCP (H-FBDKLCP)

The hydrosilylation reaction was carried out in the similar manner described in the synthesis of comb-like liquid crystalline, β -diketone-based-polysiloxane (DKLCP)^[2]. 3.5 ml of toluene containing 0.02 g of LPHSQ was introduced into a solution of 50 ml of toluene containing 0.2 g (0.35 mmol) of β -DK- C_{11} - C_{12} under protection of argon at 70°C . Then 0.45 mg of Cp_2PtCl_2 dissolved in 0.45 ml of dichloromethane (DCM) and the system was stirred at 80°C for 24 hours. In turn, 100 ml of methanol was added and the precipitate was filtered out. The crude product was redissolved in toluene and reprecipitated with methanol again and stripped in vacuum-oven at R.T overnight to give 1.3 g of yellow title polymer with M_w of 2×10^4 (yield: 62%).

(3) The random copolymeric FBDKLCP (C-FBDKLCP)

The procedure was the same as above-mentioned homopolymeric H-FBDKLCP except that the random LR-PMHSQ with M_w 3×10^3 was used instead of homopolymeric LPHSQ to produce a yellow solid polymer C-FBDKLCP with M_w of 8×10^3 and a yield of 70%.

(4) Copper-coordinating homopolymeric FBDKLCP, Cu-H-FBDKLCP:

As shown in Fig. 1, the title polymer was prepared by the chelation reaction of liquid crystalline polymeric ligand H-FBDKLCP with cuprammonia complexing ion at weak basic condition. The synthesis of Cu-H-FBDKLCP with a molar ratio of 1/2 of Cu/ β -DK was taken as an example: Solution 1 containing 0.126 g (0.1 mmol) of H-FBDKLCP dissolved in 20 ml of DCM was mixed with solution 2 containing 1 ml of cupric chloride aqueous solution (0.1 mol) and the pH of the mixed solution was adjusted with ammonia water to 9 and stirred at R. T. for 4 hours. Afterwards, the organic layer was separated out and precipitated with methanol. Finally, the precipitate was stripped off the solvent in vacuum-oven overnight to give a slightly green solid with a yield of 97%. Similarly, the Cu-H-FBDKLCP's with different contents of Cu/ β -DK were obtained by using different proportion of Cu/ β -DK of the starting materials.

(5) Copper-coordinating copolymeric FBDKLCP, Cu-C-FBDKLCP:

The title polymer with a molar ratio of 1/2 of Cu/ β -DK was taken as an example. Solution 1 was obtained by dissolving 0.0697 g (0.1 mmol of β -DK) of C-FBDKLCP in 20 ml of DCM. Solution 2 contained 5×10^{-5} of cupric chloride dissolved in 10.5 ml of water and the pH was adjusted to 9 with ammonia water. The solution 1 and 2 were mixed and stirred at R. T. for 4 hours. The organic layer was separated out and

precipitated with 30 ml of methanol. The precipitate was stripped off the solvent overnight to give a slightly brown solid with a yield of 90.5%.

3. Analysis and characterization

(1) Determination of the content of cupric ions

The determination of cupric ions was carried out following the procedure reported in reference [26].

(a) Preparation of the sample

3 ml of sulfuric acid was cautiously added into a flask containing 0.02–0.04g of sample, Cu-H-FBDKLCP or Cu-C-FBDKLCP, and then the sample was carbonized upon heating and further carbonized after addition of 3 ml of nitric acid until no reaction occurred. After being cooled, 10 ml of hydrogen peroxide (30%) was added to obtain a sample solution.

(b) Determination by UV-Visible spectrophotometer

At first, the standard working curve ($\log T/C$) was made. T was transmittance and C was molar concentration of cupric ion. Then, in the followig order, 15 ml of citric acid (20%), 10 ml of ammonia water, 5 ml of EDTA aqueous solution (1%) and 10 ml of sodium diethyldithiocarmate (1%) were introduced into a separatory funnel containing the above prepared sample solution. After sufficiently shaken in the presence of 20 ml of carbon tetrachloride, a yellow-brown solution was obtained. The transmittance was measured at 430 nm with carbon tetrachloride as the reference solution. The molar ratio of Cu/ β -DK was 0.42/1 found from the standard working curve. The other analytical results were listed in Table 1.

Table 1 The Cu content in Cu-H-FBDKLCP and Cu-C-FBDKLCP

Sample	Wt of sample (g)	Transmittance (T)(%)	Molar ratio of Cu ⁺⁺ / β -diketone	
			applied	found
Cu-H-FBDKLCP-1	0.214	37.9	1.00	0.42
Cu-H-FBDKLCP-2	0.0117	74.9	0.50	0.24
Cu-H-FBDKLCP-3	0.0295	68.4	0.25	0.13
Cu-C-FBDKLCP-1	0.0137	63.8	0.50	0.18
Cu-C-FBDKLCP-2	0.0140	73.3	0.25	0.12
Cu-C-FBDKLCP-3	0.0160	85.1	0.13	0.06

(2) Characterization

GPC, IR and DSC measurements were run in routine manner. The temperature-variable X-ray diffraction was carried out with a 0.5 cm (in diameter) of capillary tubes made of boron-glass which possessed a low X-ray absorption.

RESULTS AND DISCUSSION

1. Synthesis

In order to carry out the hydrosilylation reaction completely, the reaction system should be anhydrous and air-free. The completeness of the reaction was confirmed by the disappearance of the peak at about 2259 cm^{-1} characterizing the vibration absorption of the

Table 2 Characterization data for FBDKLCF' s.

Sample	M_n by GPC	IR Spectra data (Cm^{-1})	NMR Spectra data (in ppm)
H-FBDKLCF	2×10^4	Si—O—Si 1018 C=O 1603 C—H(enol) 784	6.6 & 17.10 for C—H in DK.
C-FBDKLCF	8×10^3	Si—O—Si 1017 Si—Me 1257 C=O 1603 C—H(enol) 784	6.6 & 17.05 for C—H in DK.

Table 3 The structural characterization data and mesomorphic properties of Cu—H—FBDKLCF and Cu-C-FBDKLCF.

Sample	Mole ratio of Cu ⁺⁺ DK	IR spectra data (Cm^{-1})	Phase transition by DSC. $\frac{T(^\circ\text{C})}{\Delta H(\text{cal/g})}$	$\Delta T(^\circ\text{C})$ ($= T_{cl} - T_*$)	$d(^\circ\text{\AA})$ by X-ray Dif.	Textures
DKLCF*	0	Si—O—Si 1023—1105 C=O 1603 CH (enol) 784	58 103 K → S → I 2.8 38.6 74 125	45	39.06	Smectic
Cu-DKLCF**	0.27		K → S → I 9.3 6.3	51		Smectic
H-FBDKLCF	0		99.96 108.77 341.2 K → LC ₁ → LC ₂ → I 22.66 3.92 50.9 98.52 82.25 LC ₂ → LC ₁ → K -4.87 -23.38 152 320	241.7	4.06	bright lines
Cu-H-FBDKLCF	0.42	Si—O—Si 1000—1100 Si—CH ₂ — 765 & 1256	K → LC → dec. 8.1 74 320	168	4.25	bright lines
Cu-H-FBDKLCF	0.24	C=O 1603	K → LC → dec. 6.0 71 320	246		bright lines
Cu-H-FBDKLCF	0.13	CH (enol) 785	K → LC → dec. 11.2	249		bright lines
C-FBDKLCF	0		87.55 108.26 286.4 K → LC ₁ → LC ₂ → I 17.02 0.26 7.0 130 290	220.4	4.15	bright bunch of lines
Cu-C-FBDKLCF	0.18	Si—CH ₂ — 1256	K → LC → dec. 5.0	160	4.09	bright lines
Cu-C-FBDKLCF	0.12	C=O 1603 C—H (enol) 784 Si—O—Si 1000—1100 Si—CH ₃ 1256, 1257	71.2 290 K → LC → dec. 5.6 71.0 290	218.8		bright lines
Cu-C-FBDKLCF	0.06		K → LC → dec. 7.8	219.0		bright lines

(*) the datum was give in ref. [8]. (**) the datum was given in ref. [9] (***) X-ray diffractions were taken at the mesophase temperature, 150 °C .

Si—H bond in IR range. The characterization data by GPC, IR and H-NMR methods are shown in Table 2. and Table 3. The results indicate the existence of Si—O—Si, Si—Me, C=O and C—H groups in FBDKLCP and Cu-FBDKLCP macromolecules.

Because the β -DK group is sensitive to acidic or strong basic condition, the coordination reaction (strictly speaking, the chelation via the ligand substitution reaction) should be effected in a weak basic (pH 9) environment. In order to have good fluidity at mesophase range and demonstrate obvious thermotropic property, the ladderlike polyhydrosilsesquioxane LPHSQ and random copolymer LR-PMHSQ used for preparation of the FBDKLCP's should have about appropriate range of molecular weight (about 10^3).

2. Mesomorphic properties

The polarizing photomicrographs for FBDKLCP and Cu-FBDKLCP are shown in Fig. 2 and Fig. 3. respectively. The mesomorphic properties examined by DSC and temperature-variable X-ray diffraction are listed in Fig. 4 and Table 3. For comparison, the liquid crystalline properties of the corresponding comb-like β -DK liquid crystalline polysiloxane (DKLCP) are also listed in Table 3. In the case of FBDKLCP, the X-ray diffraction patterns exhibit a short-range order and the photomicrographs are very characteristic. The H-FBDKLCP shows some bright birefringent lines and the C-FBDKLCP gives a bunch of bright refringent lines on the black field. The DSC results indicate that two kinds of FBDKLCP, homopolymeric or copolymeric macromolecules, do not show the glass transition at the range between -50 — 350 °C and the high enthalpies from solid to liquid state. Moreover, there is a good comparison between the temperature-increasing and temperature-decreasing DSC curves for the homopolymeric H-FBDKLCP. All these results indicate that the FBDKLCP's are crystalline polymer before melting and spontaneously coalesce to fiber-like lines or bunch-like aggregate for higher rigid H-FBDKLCP or comparatively lower rigid C-FBDKLCP after melting. Their clearing points T_{cl} 's and the mesophase range ΔT 's are much higher than the corresponding comb-like DKLCP by 240 °C and 180 °C, respectively. These interesting phenomena sufficiently indicate that the FBDKLCP's with rigid ladderlike polysilsesquioxane backbone can greatly enhance the liquid crystallinity. In other words, the rigid ladderlike main chain can play a positive effect on the liquid crystallinity.

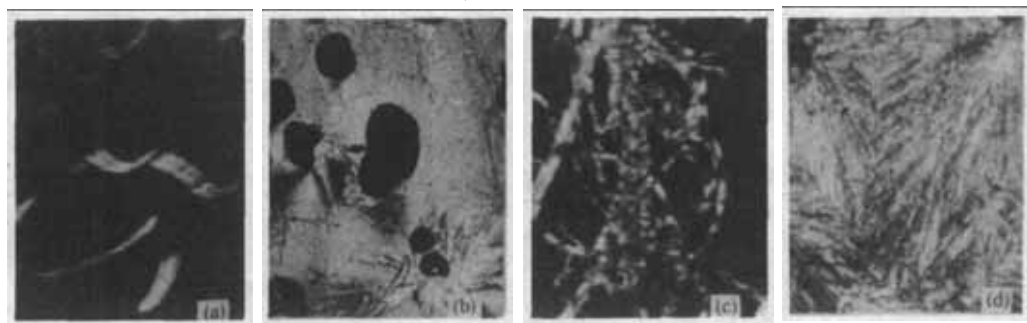


Fig. 2 The polarizing photomicrographs of FBDKLCP's

- (a) H-FBDKLCP, taken at 260 °C, (b) H-FBDKLCP, taken at R. T.,
(c) C-FBDKLCP, taken at 270 °C, (d) C-FBDKLCP, taken at R. T.

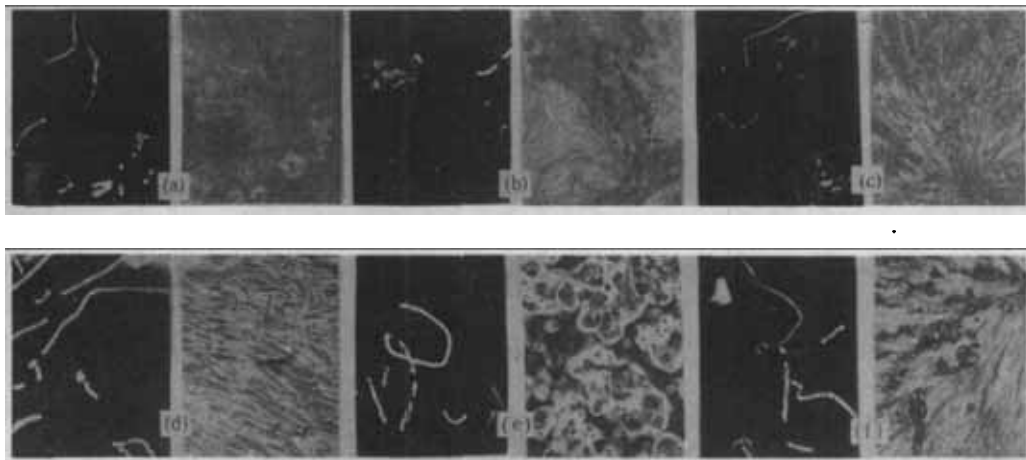


Fig. 3 The polarizing microphotographs of Cu-FBDKLCP's.

- | | | |
|---|------------------------|------------------------|
| (a) Cu-H-FBDKLCP with a 0.83:1 mol ratio of Cu/DK. | left: taken at 210 °C. | right: taken at 65 °C. |
| (b) Cu-H-FBDKLCP with a 0.48:1 mole ratio of Cu/DK. | left: taken at 190 °C. | right: taken at 65 °C. |
| (c) Cu-H-FBDKLCP with a 0.25:1 mole ratio of Cu/DK. | left: taken at 293 °C. | right: taken at 65 °C. |
| (d) Cu-C-FBDKLCP with a 0.36:1 mole ratio of Cu/DK. | left: taken at 230 °C. | right: taken at 65 °C. |
| (e) Cu-C-FBDKLCP with a 0.24:1 mole ratio of Cu/DK. | left: taken at 290 °C. | right: taken at 65 °C. |
| (f) Cu-C-FBDKLCP with a 0.12:1 mole ratio of Cu/DK. | left: taken at 294 °C. | right: taken at 65 °C. |

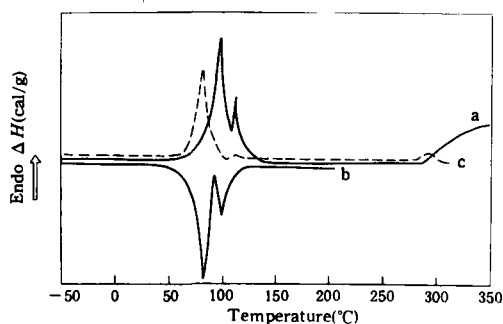


Fig. 4 The DSC curves for H-FBDKLCP and C-FBDKLCP

- (a) solid line for temperature-increasing of sample H-FBDKLCP
 (b) solid line for temperature-decreasing of sample H-FBDKLCP
 (c) dotted line for temperature-increasing of sample C-FBDKLCP

In the case of Cu-FBDKLCP's which the discotic mesogen-forming chelating unit is of square-planar configuration, the liquid crystallinities are comparatively complicated. The DSC curves are almost horizontal lines at the mesophase range. The polarizing photographs show some bright lines or bright bunch of lines. The X-ray diffraction data show a short-range order for Cu-FBDKLCP's. Compare with the comb-like Cu-DKLCP, the clearing points T_{cl} 's and the mesophase ranges ΔT 's of Cu-H-FBDKLCP are increased by 200 °C and 100 °C respectively and the T_{cl} 's and ΔT 's of Cu-C-FBDKLCP are increased by 160 °C and 110 °C respectively, too. Owing to the same reason, the significant increase could be attributed to the great stiffness of the

ladderlike polysilsesquioxane main chain which does not show a glass transition until decomposition occurs at a range between 290 °C – 320 °C. In comparison with the parent polymeric ligands, H-FBDKLCP and C-FBDKLCP, the thermal behaviors of the Cu-H-FBDKLCP and Cu-C-FBDKLCP are rather complicated. T_{cl} 's of Cu-H-FBDKLCP is lower than H-FBDKLCP by ca. 20 °C due to decomposition of the latter. Meanwhile, the melting point of Cu-H-FBDKLCP is lower than the former by ca. 25 °C when the molar ratio of Cu/ β -DK is in the range of 0.12 – 0.25. Interestingly, the T_k of Cu-H-FBDKLCP is increased to 158 °C higher than the former by 100 °C when the molar ratio is 0.42. This result is probably attributed to whether the Cu- β -DK chelating unit can play a "fixation function" or not, reported elsewhere¹⁸. A low content of the chelating unit (i.e. low molar ratio of Cu/ β -DK) could damage the highly ordered alignment of the crystalline state and consequently the T_k is decreased. Meanwhile, a comparatively high content of the chelating unit could form fairly high content of hard discogens which may enhance macromolecular rigidity and so increase the T_k of Cu-H-FBDKLCP. As the ΔT is concerned, the Cu-H-FBDKLCP with low molar ratio of Cu/ β -DK shows almost the same ΔT as H-FBDKLCP and the former with high molar ratio of Cu/ β -DK (e. g 0.42) shows lower ΔT (ca. 170 °C) than that of H-FBDKLCP (241.7 °C) because the increased T_k and lower decomposition temperature T_d ($T_d < T_{cl}$). In the case of Cu-C-FBDKLCP's, the T_{cl} 's are almost equal to those of C-DKFBLCF even though the metal contents are changed. This situation is caused by the random arrangement of the side-chains containing Cu-DK chelating units and the side chains of methyl group. But, the T_k 's is increased by 60 °C when the molar ratio is 0.18. As a result, the ΔT is shortened by ca. 60 °C in comparison with C-FBDKLCP. This complicated relation of the content of Cu/ β -DK and the mesomorphic properties is probably affected by the changes in the macromolecular structure of Cu-FBDKLCP's. The study on this aspect is under-going.

Keywords:

Fishbone-like LCP; β -diketone ligand; Ladderlike polyhydrosilsesquioxane

Acknowledgement This project was financially supported by the National Natural Science Foundation of China, and the Fund of the director of the Institute of Chemistry, and Polymer Physics Laboratory, Academia Sinica.

REFERENCES

- [1] Estman Kodak Co. (Kuhfuss H. F. and Jackson W. J.) B. P. 1, 435, 021; Jackson W. J. and Kuhfuss H. F., *J. Polym. Sci., Chem. Ed.*, 1976, 14, 2043; *J. Appl. Polym. Sci., Polym. Lett.*, 1984, 59, 103.
- [2] Plate, N. A.; Shibaev, V. P. and Tai'roze, R. V., in "Uspekhi Khimi i fiziki, Polimerov," Khimiya, Moscow, 1973, p. 127.
- [3] Blumstein, A.; Blumstein, R.; Morphy, G. and Billard, J., in "Liquid Crystal and Ordered Fluids." Plenum Press, New York, 1974, Vol. 2, 227.
- [4] Plate, N. A. and Shibaev, V. P. *J. Polym. Sci., Macromol. Rev.*, 1974, 8, 177.
- [5] Perplies, E.; Ringsdorf, H. and Wendorff, J., *Makromol. Chem.*, 1974, 175, 553.
- [6] Brown Jr, J. F.; Voght, L. H.; Katchman, A.; Eustace, J. W. Kiser, K. M. and Krantz, K. W., *J. Am. Chem. Sci.*, 1960, 80, 6194.
- [7] Brown, Jr, J. F., *J. Polym. Sci. Part C*, 1963, 83.
- [8] Zhang, X. S.; Shi, L. H. and Huang, C. R., *Chinese J. Polym. Sci.*, 1987, 5(4), 354.
- [9] Shi, L. H.; Zhang, X. S.; Si, Y. D.; Ye, M. L. and Li, D. C., *Chinese J. Polym. Sci.*, 1987, 5 (4), 359.
- [10] Xie, Z. S.; He, Z. Q.; Dai, D. R. and Zhang, R. B., *Chinese J. Polym. Sci.*, 1989, 7(2), 183.

- [11] Xie, Z. S.; Dai, D. R. and Zhang, R. B., *Chinese J. Polym. Sci.*, **1991**, 9 (2), 266.
- [12] Hanabusa, K.; Kobayashi, C.; Koyama, T.; Masuda, E.; Shirai, H.; Kondo, Y.; Takemoto, K.; Lizuki, E. and Hojo, N., *Makromol. Chem. Rapid Commun.*, **1986**, 187, 153.
- [13] Cafagna, C.; Caruso, U.; Roviello, A. and Sirigu, A., *Makromol. Chem. Rapid Commun.*, **1987**, 8, 345.
- [14] Moore, J. S. and Stupp, S. I., *Polym. Bull.*, **1988**, 19, 251.
- [15] Hanabusa, K.; Higashi, J.; Koyama, T.; Shirai, H.; Hojo, N. and Kurose, A. *Makromol. Chem.*, **1989**, 190, 1.
- [16] Hanabusa, K.; Suzuki, T.; Koyama, T.; Shirai, H.; Hojo, N. and Kurose, A. *Makromol. Chem.*, **1990**, 191, 1.
- [17] Zhang, R. B.; Wu, F. Z.; Bi, S. W.; Zhang, S. Y.; Chen, G. and Jiang, Y. Y., Preprints on "International Symposium on Fine Chemistry and Functional Polymers", Aug. 16— 20, 1990, Lanzhou, China, p. 88.
- [18] Wu, F. Z.; Zhang, R. B. and Jiang, Y. Y., *Chinese J. Polym. Sci.*, **1991**, 9, 71.
- [19] Chen, G. and Zhang, R. B., *Chinese J. Polym. Sci.*, **1991**, 9, 283.
- [20] Zhang, S. Y.; Bi, S. W.; Xie, P. and Zhang, R. B., *Chinese J. Polym. Sci.*, **1992**, 19 (4), 281.
- [21] Chen, G.; Xie, P. and Zhang, R. B., *Mol. Cryst, Liq. Cryst.*, **1993**, 225, 373.
- [22] Zhou, Z. H.; Dai, D. R. and Zhang, R. B., *Chinese J. Polym. Sci.*, **1992**, 10, 70.
- [23] Wu, F. Z.; Zhang, R. B. and Jiang, Y. Y., *Chinese J. Polym. Sci.*, **1990**, 8 (2), 133.
- [24] Apfel, M. A.; Finkelmann, H.; Janini, G. W.; Lamb, R. J.; Luhman, B. H.; Price, A.; Roberts, W. L.; Shaw, T. J. and Smith, C. A., *Anal. Chem.*, **1985**, 57, 651.
- [25] Xie, Z. S.; Wan, Y. Z. and Zhang, R. B., *Chinese J. Polym. Sci.*, **1992**, 10(4), 361.
- [26] Martens, R. I. and Grithese, R. E., *Anal. Chem.*, **1952**, 24, 991.