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# Liquid Crystals

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# Synthesis and mesomorphic properties of Cu-coordinating liquid crystalline polysilsesquioxanes with heptyl side groups

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In order to study the influence of the concentration of a flexible group on the liquid crystal behaviour of copper-containing complexes, series of Cu-coordinated, β-diketone-based liquid crystalline polysilsesquioxanes (abbr. H-DK-Cu) and random copolymethylsilsesquioxanes (abbr. Me-DK-Cu), have been synthesized by the hydrosilylation reaction of a vinyl-terminated β-diketone and 1-heptene with the polyhydrosilsesquioxane (H-T) and with the random copolymethylhydrosilsesquioxane (Me-T), followed by reaction with $Cu(NH_3)_4Cl_2$. Their mesomorphic properties were investigated by differential scanning calorimetry and optical polarizing microscopy. The H-DK-Cu and Me-DK-Cu complexes with $M_w$ of $\approx 1 \times 10^4$ are thermotropic liquid crystalline polymers and their clearing temperature and mesophase ranges are lower than those of the corresponding Cu-coordinated, β-diketone-based liquid crystalline polymethylsilsesquioxanes (Cu-FBDKLCP) without the *n*-heptyl flexible group. However, their liquidity within the temperature range of the liquid crystal state is better. The results are mainly attributed to the heptyl, flexible side group.

## 1. Introduction

Recently, much attention has been paid to liquid crystalline polymers, and numerous papers and books have been published on the subject, especially since the development of metal-coordinating liquid crystals based on fishbone-like polymethylhydrosilsesquioxanes [1, 2] which have special mechanical properties. Polysiloxanes [3, 4] have of course been employed for the preparation of liquid crystalline materials but generally using organic mesogenic units as side group substituents [5, 6]. The number of metallic elements incorporated into liquid crystalline structures has increased during the last few years as a consequence of the development of metallomesogens, a new and emerging area of research [7, 8] in the field of liquid crystals. The presence of metal atoms, especially transition metals, in liquid crystals is interesting from an academic point of view because of the rich diversity of coordination numbers and geometries available, and their magnetic, electrical, and optical properties. Early in 1981, Takahashi *et al.* [9] reported the synthesis of liquid crystal transition metal-poly(-yne) organometallic compounds, and later Carfagna *et al.* [10] and Moore and Stupp [11] synthesized thermotropic metal-containing liquid crystalline polymers by incorporation of metal-complexing units into the polymer backbone. Serrano *et al.* [12] also described a type of Cu(II)-chelated polymer derived from hydroxy functionalized liquid crystalline homo- and co-polyazomethines.

Different from the complexes mentioned above are the type of Cu-coordinating β-diketone-based, fishbone-like liquid crystalline polymethylsilsesquioxanes (Cu-FBDKLCP) with a double main chain of high rigidity and other excellent properties. However, the liquidity is poor in the liquid crystal phase state. In order to improve the liquidity, a certain content of heptyl chains has been introduced into the system giving the Cu-coordinated β-diketone-based, fishbone-like liquid crystalline polysilsesquioxanes (H-DK-Cu or Me-DK-Cu). In comparison with the corresponding polymer without the *n*-heptyl group, the clearing temperatures ($T_{cl}$) and mesophase ranges ($\Delta T$) are lower. However, the liquidity is good within the temperature range of liquid crystal state. The results are mainly attributed to the flexible *n*-heptyl side groups.

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## 2. Experimental

### 2.1. *Materials and techniques*

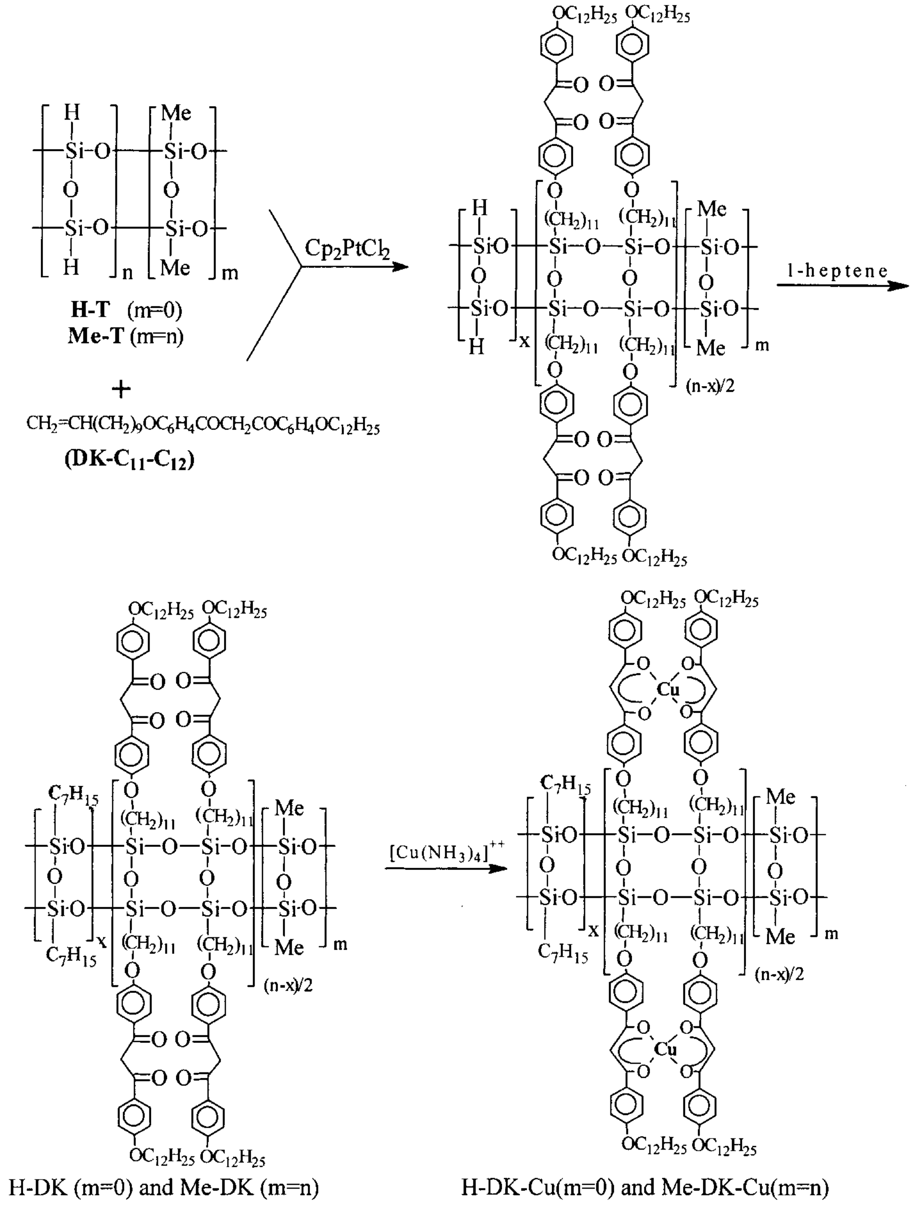
All the reagents and solvents were commercially available and of analytical purity. The vinyl-terminated diketone mesogen, 1-(*p*-*n*-dodecyloxyphenyl)-3-(*p*-*n*-ω-undecenyloxylphenyl)propan-1,3-dione (abbr. DK-$C_{11}$-$C_{12}$), m.p. 87.5°C, was prepared according to ref. [13]. The polyhydrosilsesquioxane (H-T) and its copolymer, copolymethylhydrosilsesquioxane (Me-T), were prepared as described by Zhang *et al.* [14]. The catalyst for the hydrosilylation reaction, $Cp_2PtCl_2$, was prepared according to Apfel *et al.* [15]. The toluene used was purified by completely removing methylthiophene with sulfuric acid and distilling from sodium sand. The GPC measurements were made on an LC-10 instrument (Japan Analytical Industry Co.) with polystyrene as standard. DSC thermographs were obtained with a Perkin-Elmer DSC-4 instrument. The mesophase textures were examined using an XPIA-XINTAIN optical polarizing microscope equipped with heating stage.

### 2.2. *Synthesis*

#### 2.2.1. *Synthesis of the homopolymeric H-DK-Cu*

**a-1**. The hydrosilylation reaction was carried out in a similar manner to that described for the synthesis of the fishbone-like liquid crystal, diketone-based polymers Cu-FBDKLCP [1].

As shown in the scheme, 23 ml of toluene containing 74.6 mg of H-T (1 mmol of Si–H group) was introduced into a solution of 50 ml of toluene containing 460.8 mg



Scheme. Reaction route for the synthesis of H-DK-Cu and Me-DK-Cu.

(0.8 mmol) of DK-$C_{11}$-$C_{12}$ in a protecting atmosphere of argon at 80°C. Then 0.5 mg of $Cp_2PtCl_2$ dissolved in 0.5 ml of dichloromethane (DMC) was syringed into the system, which was then stirred at 100°C for 18 h. Next, 19.6 mg of 1-heptene were syringed into the system, and the reaction was completed after stirring at 100°C for 6 h. At room temperature, 300 ml of methanol was now added to dissolve the unreacted mesogen DK-$C_{11}$-$C_{12}$ and 1-heptene and to precipitate the target polymer. The crude product was redissolved in toluene, reprecipitated with petroleum, collected and dried in a vacuum-oven at r.t. overnight to give 480 mg of yellow polymer H-DK in a yield of *c.* 86.5%.

The title polymer (H-DK-Cu) was prepared by the chelation reaction of the liquid crystalline polymer ligand H-DK with cuprammonium ion in weakly basic conditions. The synthesis of H-DK-Cu with a molar ratio of 1/4 of Cu/DK-$C_{11}$-$C_{12}$ was carried out as follows: Solution **1** was obtained by dissolving 480 mg (0.7 mmol of DK-$C_{11}$-$C_{12}$ group) of H-DK in 20 ml of DCM. Solution **2** contained 23.6 mg of cupric chloride (0.175 mmol) which was dissolved in 10.5 ml of water and the pH adjusted to 9 with aqueous ammonia. Solutions **1** and **2** were mixed and stirred at r.t. for 4 h. The organic layer was separated and precipitation brought about with 30 ml of methanol. The precipitate was collected and freed from solvent overnight to give 472 mg of light green solid H-DK-Cu in a yield of 96.1% (product label: **a-1**).

**a-2**. The procedure is similar to that for **a-1**, but with a larger mol ratio of heptene. 23 ml of toluene containing 74.6 mg of H-T (1 mmol of Si–H group) was introduced into a solution of 50 ml of toluene containing 345.6 mg (0.8 mmol) of DK-$C_{11}$-$C_{12}$ under a protecting atmosphere of argon at 80°C. Then 0.5 mg of $Cp_2PtCl_2$ dissolved in 0.5 ml of dichloromethane (DMC) was syringed into the system, and the system stirred at 100°C for 18 h. Next, 39.2 mg of 1-heptene was syringed into the system; the reaction was complete after further stirring and heating at 100°C for 6 h. At room temperature, 300 ml of methanol was added to dissolve the unreacted mesogen DK-$C_{11}$-$C_{12}$ and 1-heptene and to precipitate the target polymer. The crude product was redissolved in toluene, reprecipitated with petroleum filtered off and dried in a vacuum-oven at r.t. overnight to give 403 mg of yellow polymer H-DK in a yield of *c.* 87.7%.

The title polymer (H-DK-Cu) was prepared by chelation of the liquid crystalline polymer ligand H-DK with cuprammonium ion in weakly basic conditions. For a molar ratio of 1/4 of Cu/DK-$C_{11}$-$C_{12}$, solution **1** was first made by dissolving 403 mg (0.53 mmol of DK-$C_{11}$-$C_{12}$ group) of H-DK in 20 ml of DCM. Solution **2** containing 18 mg of cupric chloride (0.133 mmol) in 8 ml of water was then made and the pH adjusted to 9 with aqueous ammonia. Solutions **1** and **2** were mixed and stirred at r.t. for 4 h. The organic layer was separated and the precipitate obtained on adding 30 ml of methanol was separated and freed from solvent. This gave 378.6 mg of light green solid H-DK-Cu in a yield of 92% (product label: **a-2**).

### 2.2.2. *Synthesis of the copolymeric Me-DK-Cu*

**b-1**. Under argon, 40 ml of toluene containing 150 mg of Me-T (1 mmol of Si–H group) was introduced into a solution of 50 ml of methylthiophene-free toluene containing 460 mg (0.8 mmol) of DK-$C_{11}$-$C_{12}$ at 80°C. Then 0.4 mg of $Cp_2PtCl_2$ dissolved in 0.4 ml of dichloromethane (DMC) was syringed into the system, which was then stirred at 100°C for 18 h. Next, 19.6 mg (0.2 mmol) of 1-heptene was syringed into the system, and the reaction was completed by continuing stirring at 100°C for 6 h. When the mixture had cooled to room temperature, 300 ml of methanol was added to dissolve the unreacted mesogen DK-$C_{11}$-$C_{12}$ and 1-heptene and to precipitate the target polymer. The crude product was redissolved in toluene and reprecipitated with petroleum. After drying in a vacuum oven at r.t. overnight 560 mg of yellow polymer Me-DK were obtained in a yield of *c.* 88.9%.

The synthesis of Me-DK-Cu with a molar ratio of 1/4 of Cu/DK-$C_{11}$-$C_{12}$ was then carried out. Solution **1** containing 500 mg (0.64 mmol of DK-$C_{11}$-$C_{12}$ group) of Me-DK in 20 ml of DCM, and solution **2** containing 21.6 mg of cupric chloride (0.16 mmol) dissolved in 9.6 ml of water and with the pH adjusted to 9 with aqueous ammonia were mixed and stirred at r.t. for 4 h. Work-up as described under **a-1** gave 491 mg of light green solid Me-DK-Cu in a yield of 96.2% (product label: **b-1**).

**b-2**. Starting with 150 mg of H-T (1 mmol of Si–H radical) and using a procedure similar to that described above in **b-1** involving the use of 345.6 mg (0.6 mmol) of DK-$C_{11}$-$C_{12}$, 0.4 mg of $Cp_2PtCl_2$, and 39.2 mg (0.4 mmol) of 1-heptene, 391 mg of yellow polymer Me-DK were obtained in a yield of *c.* 73.1%.

By similar procedures to those described, the title polymer (Cu-FBLCPH) was prepared by chelation of the polymeric ligand Me-DK-Cu with cuprammonium ion in weak base. For a molar ratio of 1/4 of Cu/DK-$C_{11}$-$C_{12}$, solution **1** containing 391 mg (0.44 mmol of DK-$C_{11}$-$C_{12}$ group) of Me-DK in 20 ml of DCM and solution **2** containing 14.9 mg of cupric chloride (0.11 mmol) in 6.6 ml of water and with pH adjusted to 9 with aqueous ammonia were mixed and stirred at r.t. for 4 h. The normal work-up method gave 352.4 mg of light green solid Me-DK-Cu in a yield of 88.5% (product label: **b-2**).

### 2.3. *Analysis and characterization*

The determination of copper in the polymers was carried out following reported procedures [1, 16]. IR and H NMR measurements were made routinely, and GPC measurements were made using an LC-10 instrument with polystyrene standards. The structural characterization data are listed in table 1. The mesomorphic properties were examined by DSC and optical polarizing microscopy (OPM). The results are shown in figures 1 and 2, and table 2.

## 3. Results and discussion

Since the Si–H bond is sensitive to oxygen and water, all reactions for the synthesis of H-DK and Me-DK were carried out under anhydrous and air-free conditions. The completeness of the reactions was confirmed by the disappearance of the IR peak at about 2259 cm$^{-1}$ for the Si–H bond.

The Si–H bonds of H-T and Me-T were easily destroyed, and the actual content of Si–H was determined by the reaction:

$$\text{–Si–H} + \text{NaOH} = \text{–SiONa} + H_2$$

Because the reaction is quantitative, the Si–H content can be calculated from the volume of $H_2$ evolved. In this study, the ratio of actual content to ideal content was 71% for H-T. This means that 29% of the Si–H was destroyed in the preparative procedure. For Me-T, the ratio of actual content to ideal content was 80%.

The data from GPC, IR and H NMR are shown in table 1. The results indicate the existence of Si–C, C=O and C–H (enol) groups in the H-DK-Cu and Me-DK-Cu macromolecules.

Phase transition temperatures and heats of transition ($\Delta H$) were determined by DSC. The data are summarized in table 2. In addition to the calculated entropies of

Table 1. Characterization data for H-DK-Cu and Me-DK-Cu obtained by IR, H NMR, GPC and polarizing microscopy.

| Sample | | Mol ratio of Cu(II)/DK-$C_{11}$-$C_{12}$ Applied | Found | $M_w$ (by GPC) | IR wavenumber/cm$^{-1}$ | | $^1$H NMR $\delta$/ppm | |
|---|---|---|---|---|---|---|---|---|
| H-DK-CU | **a-1** | 0.25 | 0.24 | $1.6 \times 10^4$ | Si–O–Si: | 1015 & 1100 | $-CH_2-CH_2-$: | 0.86 |
| | **a-2** | 0.25 | 0.25 | | Si–$CH_2$: | 766 & 1260 | $-CH_2-O-$: | 4.02 |
| | | | | | C=O: | 1608 | $-COCH_2CO-$: | 6.62 & 15.1 |
| | | | | | Ch(enol): | 786 | | |
| Me-DK-Cu | **b-1** | 0.25 | 0.21 | $1.1 \times 10^4$ | Si–O–Si: | 1015 & 1100 | $-CH_2-CH_2-$: | 0.86 |
| | **b-2** | 0.25 | 0.21 | | Si–$CH_2$: | 766 & 1260 | $-CH_2-O-$: | 4.03 |
| | | | | | Si–$CH_3$: | 1256 & 1257 | $-COCH_2CO-$: | 6.6 & 17.1 |
| | | | | | C=O: | 1603 | | |
| | | | | | CH(enol): | 786 | | |

Table 2. Mesomorphic properties examined by DSC and polarizing optical microscopy. Cr = crystal, LC = liquid crystal, I = isotropic liquid, Dec = decomposition.

| Sample | | Mol ratio of 1-heptene/DK-$C_{11}$-$C_{12}$ | Phase transition by DSC temp. $T$/°C, ($\Delta H$/J g$^{-1}$) | Mesophase range/$\Delta T$/°C | Texture |
|---|---|---|---|---|---|
| H-DK-Cu | **a-1** | 0.2 : 0.8 | $\text{Cr} \xrightarrow[(53.63)]{62.7} \text{LC} \xrightarrow[(30.72)]{149.34} \text{I}$ | 86.6 | Bright lines |
| | **a-2** | 0.4 : 0.6 | $\text{Cr} \xrightarrow[(35.94)]{59.3} \text{LC} \xrightarrow[(19.73)]{143.9} \text{I}$ | 84.6 | Bright lines |
| Cu-H-FBDKLCP[a] | | 0 | $\text{Cr} \xrightarrow[(6.0)]{74} \text{LC} \xrightarrow{320} \text{Dec.}$ | 246 | Bright lines |
| Me-DK-Cu | **b-1** | 0.2 : 0.8 | $\text{Cr} \xrightarrow[(1.09)]{120.3} \text{LC}_1 \xrightarrow[(1.96)]{132.4} \text{LC}_2 \xrightarrow[(0.76)]{141.1} \text{I}$ | 20.8 | Mosaic |
| | **b-2** | 0.4 : 0.6 | $\text{Cr} \xrightarrow[(2.54)]{63.4} \text{LC}_1 \xrightarrow[(4.17)]{142.34} \text{LC}_2 \xrightarrow[(2.3)]{148.61} \text{I}$ | 85.2 | Mosaic |
| Cu-C-FBDKLCP[a] | | 0 | $\text{Cr} \xrightarrow[(5.6)]{71.2} \text{LC} \xrightarrow{290} \text{Dec.}$ | 218.8 | Bright lines |

[a] These data were given in [1].

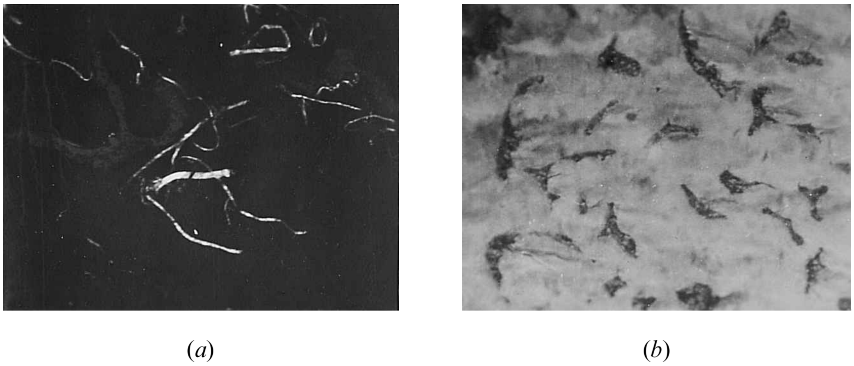


Figure 1. Polarizing photomicrographs of H-DK-Cu and Me-DK-Cu. (a) H-KD-Cu (**a-1**) at 115°C; (b) Me-DK-Cu (**b-1**) at 135°C.

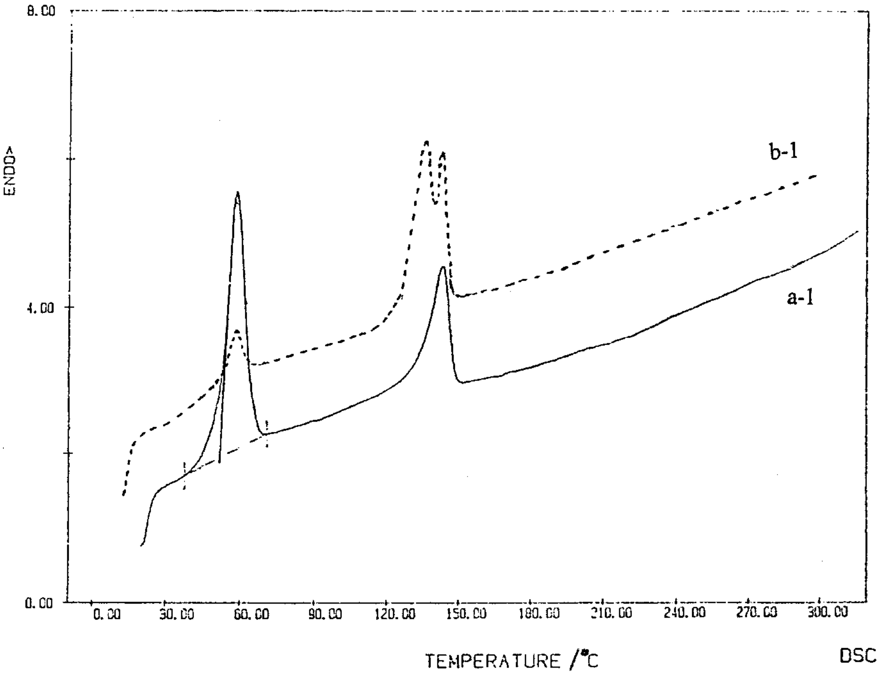


Figure 2. DSC curves or H-DK-Cu (**a-1**) and Me-DK-Cu (**b-1**).

transition, it is interesting to note that the transition temperatures can be varied by the different quantities of 1-heptene. In comparison with Cu-H-FBDKLCP and Cu-C-FBDKLCP [1] without the heptyl chains, the thermal behaviours of the H-DK-Cu and Me-DK-Cu are different. For the H-DK-Cu, the transition temperatures from crystal state to liquid crystal state are lower than for Cu-H-DBDKLCP, and the higher the content of heptyl chains, the lower the transition is. At the same time, the clearing temperatures ($T_{cl}$) are lowered respectively with increasing heptyl content. As a result, the temperature ranges of the liquid crystal phase ($\Delta T$) are decreased with increasing heptyl content. Without heptyl groups, $\Delta T$ is 246°C, but when the heptyl content is increased to 20% (mol ratio of heptyl/DK-$C_{11}$-$C_{12}$), the temperature range of the liquid crystal phase ($\Delta T$) is decreased markedly by *c.* 159.4°C. However, when the ratio of heptyl to DK-$C_{11}$-$C_{12}$ is increased from 0.2:0.8 to 0.4:0.6, the temperature range of the liquid crystal phase is only decreased by about a further 2°C. They show almost the same $\Delta T$ because the higher Cr–LC temperature and the higher clearing point effectively cancel.

In comparison with the Cu-C-FBDKLCP, the thermal behaviours of the Me-DK-Cu complex are rather complicated. They show two liquid crystal phases, but the Cu-C-FBDKLCP show only one liquid crystal phase. Compared with the Cu-C-FBDKLCP, the temperature range of the liquid crystal phase of sample **b-2** of Me-DK-Cu is obviously decreased by *c.* 132.8°C. The reason is that the $T_{cl}$ values of the Me-DK-Cu have decreased greatly. Comparing Me-DK-Cu (**b-1**) and Me-DK-Cu (**b-2**), the Cr–LC temperature of **b-1** is higher than that of **b-2**, whereas $T_{cl}$ of **b-1** is lower than that of **b-2**, with the result that the temperature range of the liquid crystal phase is extended with increasing heptyl content.

Polarizing photomicrographs for a sample of H-DK-Cu and Me-DK-Cu are shown in figure 1. In the case of H-DK-Cu, the texture pattern displays some bright lines on a black background or mosaic. By contrast, the Me-DK-Cu sample displays a bright birefringent mosaic pattern. This result shows that the methyl and heptyl groups can influence the textures of this type of liquid crystal polymer. Also of course, the chelating unit can play a mesogenic role, and possibly the formation of a columnar liquid crystalline phase explains the presence of mosaic textures.

Observations by microscopy show that, the liquidity of H-DK-Cu is better than that of the corresponding Cu-H-FBDKLCP, and examination of Me-DK-Cu shows the same result. This indicates that the heptyl chains function as a soft spacer and play an important part in decreasing the degree of crystallinity of the title polymers.

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