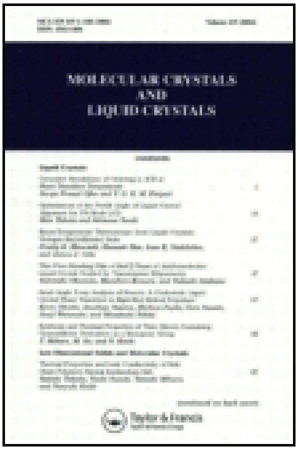

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Synthesis and Characterization of the β-Diketone Based Side Chain Liquid Crystalline Random Copolyphenylsilsesquioxane and Its Metal Complex

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The attachment of low molecular weight β-diketone compound to random copolyphenylhydrosilsesquioxane (abbr. as Ph-T) backbone gave rise to the formation of β-diketone based side chain liquid crystalline copolyphenylsilsesquioxane (abbr. as Ph-DK). Its copper complexes (abbr. as Ph-DK-Cu) were prepared following a heterogeneous reaction procedure. The structures of the Ph-DK and their copper complexes were well characterized by IR, NMR and GPC. The DSC heating curves of the Ph-DK-Cu show three endothermic transitions. The first transitions are from crystalline state to liquid crystalline state (I), the second transitions are from liquid crystalline state (I) to liquid crystalline state (II), and the third transitions are from liquid crystalline state to the isotropic liquid. The Ph-DK-Cu are thermotropic liquid crystalline polymers. Their clearing temperature and mesophase range ΔT are lower than those of the corresponding Cu-coordinated β-diketone based copolymethylsilsesquioxane liquid crystalline polymers. The influence of the content of the Cu^{2+} on the Ph-DK-Cu has been discussed. The chemical incorporation of metal ion into polysilsesquioxane molecule can change the liquid crystal molecular arrangement and the transition temperature.

Keywords: β-diketone; side chain liquid crystalline polymers; copper(II) complex; copolyphenylsilsesquioxane

INTRODUCTION

Since Jackson[1], Shibaev[2] and Blumstein et al[3,4,5] first reported the synthesis and properties of comb-like liquid crystalline polymers (abbr. as C-LCP), this new

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field has attracted the interest of polymer scientists from the standpoint of their theoretical and potentially applicable significance. By contrast with lyotropic liquid crystalline polymers mainly used as engineering materials with good mechanical properties, the comb-like liquid crystalline polymers are potentially functional polymer materials with special properties. However, they have not been commercially used mainly because of their poor mechanical properties such as the film-forming ability, tensile strength, toughness and comparatively slow response behavior to external fields. In order to improve these properties, in 1993, Zhang et al[6] reported a new type of LCP whose main chain was double chain polysilsesquioxane and the mesogen moieties were attached via the Si-C bonds. This LCP possesses an improved film-forming ability. At the same time, the metal ions were introduced into the LCP by the complexing.

The presence of metal ions, especially transition metal ions, in liquid crystals is interesting from an academic points of view because of the rich diversity of coordination numbers and geometries available, which opens up new possibilities on the design of liquid crystals. Meanwhile, this metal-coordinating LCP (abbr. as MCLCP) also can offer the possibility of accessing materials with unusual physical properties such as color, magnetic, electrical and optical properties.[7]

The study of metallomesogenic polymers is an emerging area in the research of liquid crystalline polymers.[8] A combination of the chemistry of liquid crystalline polymers with that of coordination chemistry is of prospective property for the functional polymer materials and will lead to a surge of new metallomesomorphic chemistry.[9,10] In 1981, Takahashi first described the synthesis of liquid crystalline transition metal-poly(yne)organometallics.[11] Later L. Oriol et al. reported a new type of Cu(II)-chelated polymers derived from hydroxy functionalized homo- and copolyazomethines and reviewed new development on metallomesogenic polymers.[12,13] The incorporation of metal ions into liquid crystal chemistry not only can enrich liquid crystal chemistry, but also can pave a way to explore a new family of advanced materials largely used in high techniques. In order to describe the influence on mesomorphic properties of liquid crystalline polymers through metal content and the main chain structure, recently, a new type of β-diketone based liquid crystalline random copolyphenylsilsesquioxane Cu(II)-complexes (Ph-DK-Cu) were synthesized and their liquid crystalline properties were characterized in our laboratory. The results indicated that the incorporation of metal ions into the LCP could play a major effect on the mesomorphic properties. In comparison with the corresponding metallomesogenic polymer with a single main chain, this metallomesogenic polymer with a double chain has wider mesophase range and higher clearing temperature. But, in comparison with the corresponding metallomesogenic polymer – copolymethylsilsesquioxane and its copper complex, the title polymer has lower clearing temperature and the narrower mesomorphic temperature range. This paper describes the synthesis and characterization of copper coordinated β-diketone based liquid crystalline random copolyphenylhydrosilsesquioxane.

EXPERIMENTAL

1. Materials and techniques

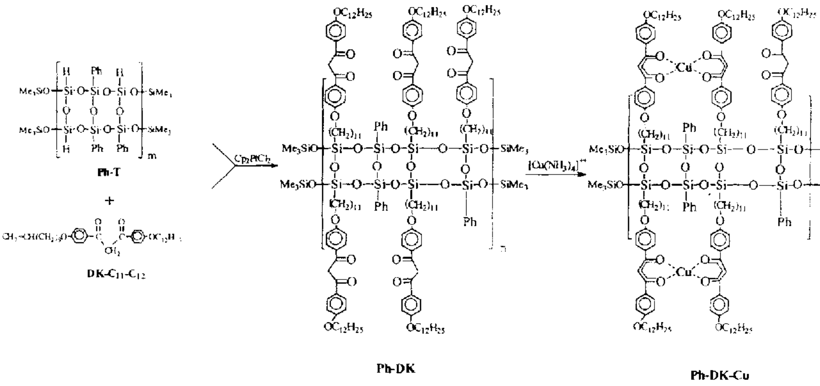
All the reagents and solvents were commercially available and of analytical purity. The toluene used was purified with sulphuric acid to remove methylthiophene (which can inactivate the hydrosilylation catalyst Cp_2PtCl_2), and then distilled from sodium sand. The vinylterminated β-diketone mesogen compound, 1-[4-(dodecyloxy) phenyl]-3-[4-(10-undecenyloxy) phenyl]-1,3-propanedione (abbr. as DK-C_{11}-C_{12}), m.p. 87.5 °C, was prepared following the reference[14]. The random copolyphenylhydrosilsesquioxane (Ph-T) was prepared following to Zhang work[15]. The catalyst for the hydrosilylation reaction, Cp_2PtCl_2, was prepared referring to Apfel's work[16]. The IR and H-NMR measurements were run in routine manner. The IR spectra were recorded on FT-IR spectrophotometer, PE-80. The NMR spectra were recorded on Pulse Fourier Transform Nuclear Magnetic Resonance Soectrometer, AC-80 (SPECTRON). The GPC measurement was made on LC-10 instrument versus polystyrene standard (Japan Analytical Industry Co.). The determination of cupric content was run on UV-Visible spectrophotometer 730 (Shanghai Analytical Factory). The DSC thermographs were obtained with Perkin-Elmer DSC-4 instrument. The mesophase textures were examined on XPIA-XINTAIN optical polarizing microscope with the heating stage.

The structural characterizing data were listed in Tab. I. The mesomorphic properties were shown in Tab. II, Fig. 1 and Fig. 2.

2. Synthesis

a. Random copolyphenylhydrosilsesquioxane (Ph-T)[6,17,18]

In one container, 1.7 g (0.0125 mol) of trichlorosilane was added rapidly into 25 ml of toluene under stirring at −10~-15°C. In another container, 25 ml of freshly purified toluene and 2.64 g (0.0125 mol) of $PhSiCl_3$ were added under the same condition. A solution of 25 ml of acetone dissolved with 1.35 g (0.0125 mol) of 1,4-phenylenediamine (PDA) was added dropwise respectively, and kept stirring for 30~60 minutes. Then an additional solution of 5 ml of acetone containing 0.5 ml of water was added at low temperature and was stirred for 30 min-



SCHEME 1 Reaction route for the synthesis of Ph-DK-Cu

utes at R.T. The mixed solution of the two containers was stirred continuously. A solution of 5 ml of acetone containing 0.25 ml of water was added below 0°C and the solution was stirred for 30 minutes at RT. and then stirred for 2 hrs at 40~50°C. 0.55 g of $(CH_3)_3SiCl$ was added and reacted at 40~50°C under stirring for 30 minutes. After that filtered and the filtrated solution was washed with saturated salt solution to neutral, and washed with distilled water for two times. The solution was dried with sodium sulfate and became transparent and colorless after filtration. Its concentration was 27.7 mg/ml and the yield was 69.0%.

b. β-diketone based copolyphenylsilsesquioxane (abbr. as Ph-DK)

6.8 ml of Ph-T (0.1887g, 1.04×10^{-3} mol of Si-H group) was added into a solution of 60 ml of freshly purified toluene dissolved with 0.6g (1.04×10^{-3} mol) of β-diketone ($DK-C_{11}-C_{12}$) and stirred vigorously. The solution was degassed using N_2 and heated at 80°C. 0.7 mmol catalyst (1 mg Cp_2PtCl_2 dissolved in 1 ml of dichloromethane) was added and the reaction mixture was stirred for 24 hrs at 80°C. After that 30 ml methanol was added slowly into the container, and stirred vigorously. When got rid of solvents and dried naturally, it could give yellowish solid. The crude product was redissolved into toluene and reprecipitated with methanol again and stripped in vacuum-oven at RT. overnight to give 0.051 g of light yellowish solid with a yield of 64.8%.

c. Copper coordinated β-diketone based copolyphenylsilsesquioxane (abbr. as Ph-DK-Cu)

As shown in scheme 1, the title polymer Ph-DK-Cu was prepared by the chelation reaction of the Ph-DK with cuprammonia complex ion at weak basic condition.

c-1 Cu^{2+}: β-diketone unit= 0.5:1

Firstly dissolved 0.0735 g (9.67×10^{-5} mol of β-diketone unit) of Ph-DK in 30 ml of CH_2Cl_2, 4.84 ml (4.84×10^{-5} mol) of $CuCl_2$ solution (0.01 M) was diluted with distilled water to 15 ml, and added dropwise ammonia water until PH=9. Mixed the above two solutions and stirred for 4 hrs. The organic phase was separated out and dried naturally to give 0.039 g of dark green solid with a yield of 50.4%. (Product label: c-1)

c-2 Cu^{2+} : β-diketone unit = 0.25:1

The reaction conditions were similar as mentioned above for c-1. The reactants used were as follows.

Ph-DK : 0.07622 g (1.003×10^{-4} mol of β-diketone unit)

$CuCl_2$ solution: 2.51 ml (2.51×10^{-5} mol)

Which is to give 0.040 g of green solid with a yield of 51.8%. (Product label: c-2)

c-3 Cu^{2+} : β-diketone unit= 0.125:1

The reaction conditions were similar as mentioned above for c-1. The reactants used were as follows.

Ph-DK : 0.07410 g (9.75×10^{-5} mol of β-diketone unit)

$CuCl_2$ solution: 1.22 ml (1.22×10^{-5} mol)

Which is to give 0.055 g of green solid with a yield of 72.5%. (Product label: c-3)

3. Determination of the content of cupric ions

The determination of cupric ions was carried out following the procedure reported in reference.[6,19]

3 ml of sulfuric acid was cautiously added into a flask containing 0.02 – 0.04 g of Ph-DK-Cu (c-1, c-2 or c-3), 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.

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 following 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 volumetric flask 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 actual molar ratio of Cu^{2+} to β-diketone unit was found from the standard working curve. The analytical results were listed in Tab. I.

TABLE I Characterization data for Ph-DK-Cu and Ph-DK

Sample	*Mw (by GPC)*	*Molar ratio of Cu^{2+}/DK-C_{11}-C_{12}*		*^{1}H-NMR (δ in ppm)*	*IR wavenumber (in cm^{-1})*
		applied	*found*		
Ph-DK-Cu(c-1)	5.3×10^3	0.5	0.47	$-CH_2-CH_2-$:0.86	
				$-CH_2-O-$:4.03	Si-O-Si:1248&1133
				$-COCH_2CO-$:2.7 & 6.8	$Si-CH_2-$:782&1259
Ph-DK-Cu(c-2)	5.3×10^3	0.25	0.24	$-CH_2-CH_2-$:0.87	C=O:1606
				$-CH_2-O-$:4.03	CH(enol):782
Ph-DK-Cu(c-3)	5.1×10^3	0.125	0.12	$-COCH_2CO-$:2.7 & 6.6	C=O(Cu^{2+}):1591
				-C(OH)=C-CO-:17.1	
Ph-DK	5.2×10^3	0	\	$-CH_2-CH_2-$:0.87	Si-O-Si:1248&1130
				$-CH_2-O-$:4.03	$Si-CH_2-$:780&1257
				$-COCH_2CO-$:2.7 & 6.6	C=O:1606
				-C(OH)=C-CO-:17.1	CH(enol):784

RESULTS AND DISCUSSION

The Ph-T was prepared by preaminolysis reaction of $HSiCl_3$ and $PhSiCl_3$ with 1, 4-phenylenediamine, then by hydrolysis, polycondensation and equilibration. Brown et al have synthesized for the first time a ladder-like (double chain) polyphenylsilsesquioxane by thermal polycondensation of $PhSi(OEt)_3$ using KOH as the catalyst[17]. Because of the branching and crosslinking, its regularity was comparatively low. This can be due to the catalyst that is strong base. The highly ordered ladder-like (double chain) polysilsesquioxane has been prepared by preaminolysis reaction using 1,4-phenylenediamine as the catalyst[6,20]. Similarly, The Ph-T has been synthesized by the preaminolysis reaction with 1,4-phenylenediamine (PDA) because the phenylenediamine molecule can ensure the formation of the linear double-chain macromolecule. To avoid the cross linking reaction between terminal Si-OH on the Ph-T which maybe happen in the procedure of synthesis of Ph-DK, the terminal Si-OH was protected with the Me_3SiCl.

TABLE II Mesomorphic properties examined by DSC & polarizing microscopy

Sample		*Molar ratio of Cu/DK-C_{11}-C_{12}*	*Phase transition by DSC* $\dfrac{\text{max./onset temp.}(^\circ\text{C})}{\Delta\text{H}(\text{J/g})}$ a	*Mesophase range (ΔT in °C)*	*Texture*
Ph-DK-Cu	c-1	0.47	$\mathrm{Cr}\xrightarrow[8.03]{59/51}\mathrm{LC}_1\xrightarrow[0.59]{73/69}\mathrm{LC}_2\xrightarrow[20.4]{142/128}\mathrm{I}$	83	mosaic
	c-2	0.24	$\mathrm{Cr}\xrightarrow[6.15]{138/125}\mathrm{LC}_1\xrightarrow[3.13]{146/143}\mathrm{LC}_2\xrightarrow[0.68]{247/243}\mathrm{I}$	109	mosaic
	c-3	0.12	$\left|\mathrm{Cr}\xrightarrow[1.09]{121/109}\mathrm{LC}_1\xrightarrow[1.96]{132/126}\mathrm{LC}_2\xrightarrow[0.89]{141/138}\mathrm{I}\right|$	20	mosaic
Ph-DK		\	$\mathrm{Cr}\xrightarrow[1.4]{110/103}\mathrm{LC}_1\xrightarrow[2.1]{127/120}\mathrm{LC}_2\xrightarrow[0.9]{288/280}\mathrm{I}$	178	mosaic
^{b}Me-DK-Cu		0.18	$\mathrm{Cr}\xrightarrow[5.0]{130}\mathrm{LC}\xrightarrow{290}\mathrm{Dec.}$	160	bright lines
		0.12	$\mathrm{Cr}\xrightarrow[5.6]{71}\mathrm{LC}\xrightarrow{290}\mathrm{Dec.}$	219	bright lines
		0.06	$\mathrm{Cr}\xrightarrow[7.8]{71}\mathrm{LC}\xrightarrow{290}\mathrm{Dec.}$	219	bright lines
^{b}Me-DK		\	$\mathrm{Cr}\xrightarrow[17.0]{88}\mathrm{LC}_1\xrightarrow[0.3]{108}\mathrm{LC}_2\xrightarrow[7.0]{286}\mathrm{I}$	198	bright bunch of lines

Cr: crystal, LC: liquid crystal, I: isotropic liquid, Dec.: decomposition

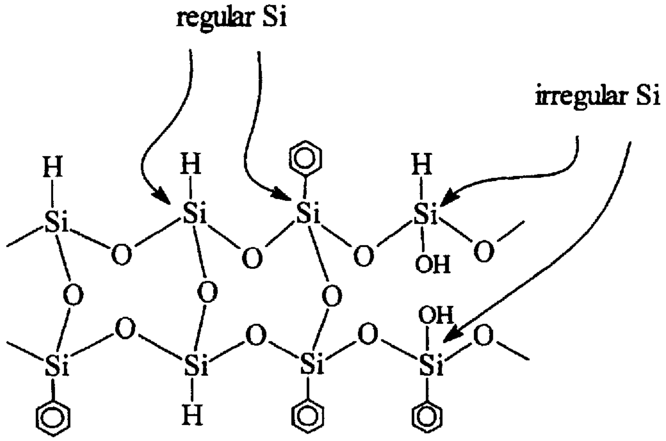
a. Data collected by DSC for first heating.
b. The data were given in ref. 6.

The Ph-DK was prepared by the hydrosilylation of Ph-T with the DK-C_{11}-C_{12}. Since the Ph-T is sensitive to oxygen and water, in which the active Si-H group can be readily hydrolyzed and in turn condensed each other to form a crosslinked gel, the whole reaction should be carried out under anhydrous and air-free for the synthesis of Ph-DK. In the preparation of Ph-DK, methanol is used to dissolve the unreacted DK-C_{11}-C_{12} on the one hand, and make the produced macromolecule deposit on the other hand. This can separate the unreacted β-diketone molecule from macromolecule to give high molecule regularity. At the same time, this procedure can purify the product by removing the low molecular weight polymers. The completeness of the hydrosilylation was confirmed by the disappearance of the peak at about 2259 cm^{-1} characterizing the vibration absorption of the Si-H bond in IR range. The data by IR and H-NMR methods are shown in Tab. I. The results indicate the existence of Si-O-Si, -CO-CH_2-CO-, Si-CH_2, -CH_2-, -CH(OH)=CH-CO- groups in this Cu-coordinated β-diketone based side chain liquid crystalline copolyphenylhydrosilsesquioxane (Ph-DK-Cu). The same phenomenon was detected in their corresponding parent polymer (Ph-DK).

Although the coordinative reaction of Cu^{2+} with β-diketone units mainly occur within two neighbouring ones in the same polymeric chain in the reason that under this condition the space obstacle is the smallest, there are still some coordination will surely occurred with β-diketone units of two different polymeric chains. These two different kinds of coordination give rise to two different polymers: normal polymer and crosslinking polymer. Normal polymer can be dissolved in common solvents like benzene and xylene while crosslinking ones can't. So by the method of filtering we can separate normal polymer from crosslinking ones. If the ratio of Cu^{2+}/DK-C_{11}-C_{12} is higher, then more crosslinking will occur. This can explain why the yield of c-1 and c-2 is so low.

The double chain structure of the copolymer Ph-T is similar to the structure of copoly(methylhydrosilsesquioxane) which has been testified by us before[21]. From scheme 2, we can see how the stereo-structure of Ph-T is formed. In general, there are two kinds of Si in the copolymer Ph-T. If the ratio of Si/O is 2/3, then it will be called regular Si, otherwise it is irregular Si.

Transition temperatures and transition enthalpies (ΔH) were determined by DSC. The data (the first heating scans) were shown in Tab. II. From those we can conclude that the curve for each sample has three transitions. Considering the results of polarizing microscope, it's sure that the first peaks of heat absorption are the transitions from crystal state to liquid crystal state (I), and the second peaks of heat absorption are transitions from liquid crystal state (I) to liquid crystal state (II) in the condition that the molar ratio of Cu^{2+} to β-diketone is 0.5:1, 0.25:1, 0.125:1. The peaks at higher temperature are transitions from liquid crystal state to isotropic liquid state.



SCHEME 2 The structure of the Ph-T

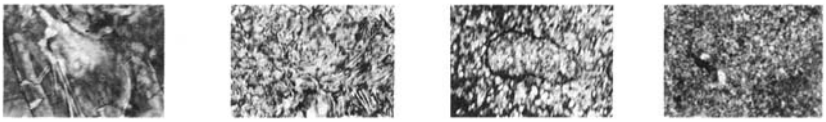

c-1 at 120°C c-2 at 138°C c-3 at 125°C Ph-DK at 140°C

FIGURE 1 The polarizing microphotographs of Ph-DK and Ph-DK-Cu

The transition enthalpy ΔH between liquid crystal state (I) and liquid crystal state (II) is not very big (0.59 ~ 3.13 J/g), which means that the order of the Ph-DK-Cu between the two mesophase is not very conspicuous. However, the c-1 has higher enthalpy content (20.4 J/g) of LC_2-I than c-2 (0.68 J/g) and c-3 (0.89 J/g). The difference of enthalpy is remarkable. This indicated that c-1 exists a different mesophase in comparison with c-2 and c-3. The reason is that almost the entire mesogen unit of c-1 is Cu-coordinated β-diketone unit whereas the mesogen unit of c-2 and c-3 is Cu-coordinated β-diketone and uncoordinated β-diketone unit.

In comparison with the parent polymer Ph-DK, the mesophase range (ΔT) of Ph-DK-Cu is lower. The result is probably attributed to the Cu^{2+}, which partly restricts the tropism of the mesogen unit. This phenomenon is different from the Me-DK-Cu.

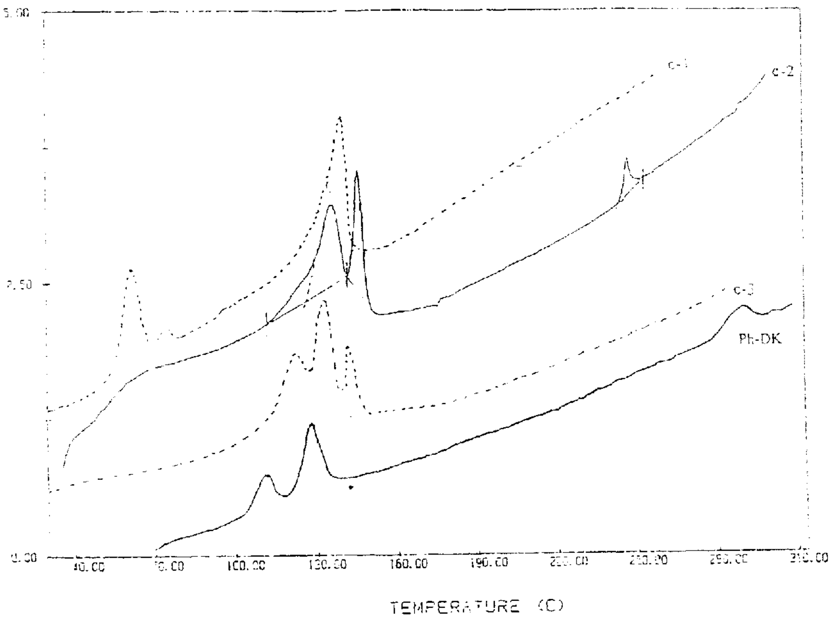


FIGURE 2 The DSC curves for the Ph-DK and Ph-DK-Cu (The first heating scan, scan rate: 10 °C/min)

Very low content of the chelating unit (i.e. molar ratio of Cu^{2+}/DK-C_{11}-C_{12}, for example, c-3) shows very low mesomorphic temperature range (ΔT=20°C). When the molar ratio of Cu^{2+}/DK-C_{11}-C_{12} is reached 0.24, it has the widest mesomorphic temperature range (ΔT=109°C) among the three cases because of the highest clearing temperature. However, the ΔT is shortened by 26°C (109 – 83) when the molar ratio of Cu^{2+}/DK-C_{11}-C_{12} is 0.47. This complicated relation of content of the molar ratio of Cu^{2+}/DK-C_{11}-C_{12} and mesomorphic properties are probably affected by the plate-like structure of mesomorphic units formed by Cu^{2+} coordinated β-diketone. If the ratio of Cu^{2+}/DK-C_{11}-C_{12} is too low (for example, c-3), the plate unites of the polymer will be scattered, and it will be difficult to obtain tropism arrangement structure. At the same time, the tropism structure is easy to be destroyed. So the mesophase region (ΔT) of c-3 is very narrow. Conversely, if the ratio is too high (for example, c-1), too many plate units will be crowded together and less freedom will be left, so the ΔT of c-1 is lower than that of c-2.

The polarizing microphotographs for Ph-DK and Ph-DK-Cu are shown in Fig. 1. As for Ph-DK-Cu, its texture patterns display mosaic. This result means that the chelating unit can play a mesogen function. Maybe it forms the discotic liquid crystalline phase.

Meanwhile, for comparison, the liquid crystalline properties of the corresponding Me-DK-Cu are also listed in Tab. II. From Tab. II, we can conclude that Ph-DK-Cu has a narrower mesomorphic phase range and lower clearing temperature. In the polarizing photographs, the Ph-DK-Cu shows mosaic texture and the Me-DK-Cu shows bright line.

These interesting phenomena result from the difference of the side groups. In the Ph-DK-Cu, the side group is Ph- on the main chain, and in the Me-DK-Cu, the side group is Me- groups.

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