

SYNTHESIS AND PROPERTIES OF METAL COMPLEXES OF β -DIKETONE BASED SIDE CHAIN LIQUID CRYSTAL POLYSILOXANE

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ABSTRACT

A new type of metal coordinated liquid crystalline polymers has been synthesized by complexation of metal ions with β -diketone based side chain liquid crystal polysiloxane (DKLCP). The complexation of copper ions with DKLCP greatly increases the phase transition temperature T_k from crystalline state to liquid crystalline state and T_{cl} from LC to isotropic state and makes the range of phase transition ΔT ($\Delta T = T_{cl} - T_k$) widened. These complexes are soluble in common organic solvents. However, the incorporation of europium ions into DKLCP molecules gives rise to reduction in liquid crystallinity and crosslinking in some cases. The DKLCP coordinated with suitable amount of Eu ions can show good liquid crystallinity and fluorescent property.

INTRODUCTION

The combination of the unique properties of liquid crystal polymers with the interesting electric and magnetic properties of metal complexes has attracted much interest in the synthesis of metal-containing liquid crystal polymers^[1-5]. Takahashi et al. reported that metal-containing lyotropic poly(-yne) polymers can be oriented either perpendicular or parallel to the external applied field depending on the embedded metal atoms^[1]. The photo- and electric properties of poly(γ -benzyl-L-glutamate) covalently bound metal phthalocyanines (as dye components) are currently under investigation^[2]. Thermotropic liquid crystalline polyesters containing transition metals were synthesized either through the complexation of metal ions with mesogenic bipyridinediyl units by Hanabusa^[3], or through the ester exchange reaction of paramagnetic metal complex units with polyester by Moore^[4] in an attempt to prepare highly paramagnetic liquid crystal polymers. Unfortunately, these metal ions showed adverse effect on the liquid crystallinity of these polymers.

Although several kinds of metal-containing liquid crystals have been synthesized^[5,6], little has been done to use liquid crystal complexes as mesogens of liquid crystal polymers^[7]. We have already synthesized a novel type of β -diketone based side chain liquid crystal polysiloxanes (DKLCP as shown in Fig. 1) by hydrosilylation reaction^[8]. This paper deals with the synthesis and properties of the metal-coordinating DKLCP. Due to the mesogenic property of the square-planar bis(β -diketonato-) copper complexes^[9], the complexation of the

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copper ions into DKLCP does not give an adverse effect on this liquid crystallinity. On the contrary, the copper-coordinating DKLCP with much higher T_{cl} and good solubility in common organic solvents was obtained. The introduction of Eu ions into DKLCP causes decrease in liquid crystallinity and crosslinking usually occurred upon complexation because the coordination number of lanthanide ions is variable and higher than six, often.

EXPERIMENTAL

Preparation of β -diketone based side chain liquid crystalline polysiloxane

A detailed description of the synthesis and characterization of DKLCP were reported in our previous paper^[8]. The conventional hydrosilylation catalyst, hexachloroplatinic acid, is not applicable in this case and the utilization of dicyclopentadienyldichloroplatinum (II) catalyst could avoid some side reactions.

Preparation of copper complexes of DKLCP

20 ml dichloromethane solution containing 0.43 g of DKLCP-2 (7×10^{-4} mol β -diketone units) was mixed with 10 ml of water solution containing 3.5×10^{-4} mol of $(\text{Cu}(\text{NH}_3)_4)^{2+}$ and was stirred at room temperature for 3—4 hours. The organic layer was separated and precipitated with methanol. Then, the precipitate was collected and dried and the final product Cu-DKLCP-2(1) was obtained in approximately 100% yield.

Other complexes of Cu-DKLCP containing different proportions of copper ions were prepared in a similar way by varying the molar ratio of Cu^{+2}/β -diketone.

Preparation of Eu complexes of DKLCP

An accurately weighed amount of EuCl_3 was dissolved in a mixed solvent of methanol and tetrahydrofuran (1/1, v/v, 5.6g/ml). The following procedure was used in the experiments: to a THF solution of DKLCP calculated amount of EuCl_3 in solution was added and the pH was adjusted to 9 with piperidine and was finally precipitated with methanol.

Analysis of the metal contents

Copper-containing samples were treated with nitric acid and perchloric acid. The Cu contents were then determined by polarometric titration on the treated samples. The Eu contents were assumed to be as added.

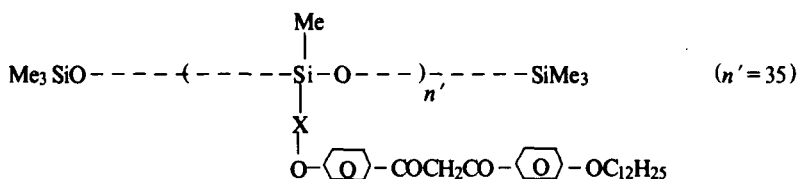
Measurement

The DSC measurements were made on a du-Pont 1090 thermal analyzer connected with DSC model 910. The polarizing microphotographs were taken on an Olympus BH-2 optical polarizer. A MPF-4 fluorescent spectrophotometer was used to measure the fluorescence spectra of Eu-DKLCP of finely powdered and dried samples. The ESCA analysis was made on a Kratos-ES 300 instrument.

RESULTS AND DISCUSSIONS

(1) The liquid crystallinity of the metal-coordinating polysiloxanes

DKLCP molecule shown in Fig.1 is capable of forming complexes of chelating



X = Flexible spacer

DKLCP - 1 : X = $\text{CH}_2\text{CH}_2\text{CH}_2$

DKLCP - 2 : X = $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$

DKLCP - 3 : X = $(\text{CH}_2)_{11}$

Fig.1 Structure of the β -diketone based side chain DKLCP

ring with almost all metal ions. To ascertain the influence of the metal ions on the liquid crystallinity of Cu-DKLCP and Eu-DKLCP, the samples of different metal content were prepared as shown in Table 1. It is very interesting that the complexation of Cu ions did not result in crosslinking, the formed Cu-DKLCP's were still soluble in solvents such as THF, CH_2Cl_2 , etc.. Thus, it is likely that the complexation occurred between the two adjacent ligands on the same polymeric backbone. The representative structure of Cu-DKLCP is illustrated in Fig.2, where m and n are the percentage of the free ligands and the complexed units in one backbone, respectively. The values of m and n were calculated from the analysis data of Cu % and are listed in Table 1. In fact, β -diketone units in DKLCP can not form complexes with Cu ions completely. A large number of free ligands existed even when the molar ratio of 1/2 of Cu/ β -diketone was applied.

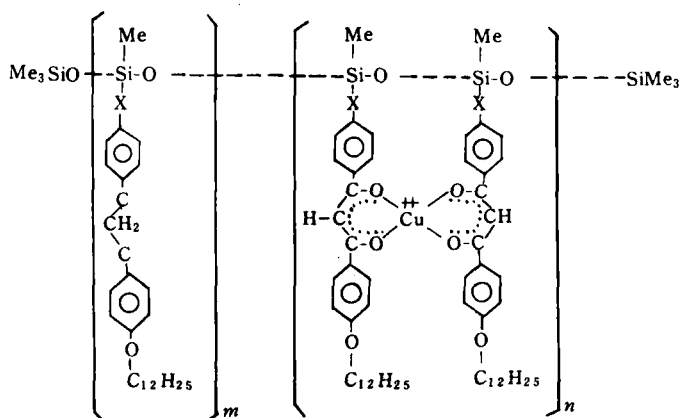


Fig.2 Representative structure of Cu-DKLCP.

Table 1 The Cu contents and values of m and n in Cu-DKLCP

Sample	Molar ratio of Cu / β -diketone applied		Cu% (Wt)	m	n
Cu-DKLCP-1 (I)	0.50	0.26	3.16	0.64	0.36
Cu-DKLCP-1 (II)	0.125	0.08	1.00	0.91	0.09
Cu-DKLCP-2 (I)	0.50	0.19	2.07	0.77	0.23
Cu-DKLCP-2 (II)	0.125	0.07	0.83	0.92	0.08
Cu-DKLCP-3 (I)	0.50	0.27	3.79	0.63	0.37
Cu-DKLCP-3 (II)	0.125	0.10	1.00	0.89	0.11

Fig. 3 shows the DSC heating curves of Cu-DKLCP complexes. Each sample gives two endothermic transitions. It is conformed by the polarizing microscopic observations that the first transition at about 60 °C is the transition from crystal state to liquid crystal state, and the second transition is one from LC state to isotropic state. It can be seen from Fig. 3 that the first transition is slightly shifted to higher temperature and the phase transition temperature T_{cl} of the second one is greatly increased with the rise of Cu content. For comparison, the DSC heating curves of metal-free DKLCP are given in Fig. 4. In addition, the changes in phase transition temperature for DKLCP and the corresponding Cu-DKLCP are listed in Table 2. These data show that the chelation of Cu ion with β -diketone group can obviously affect the mesogenic behaviour of liquid crystalline as the parent ligand. It seems that the chelation could play a role of "Fixation", namely, the ordered macromolecular arrangement at LC state would be more stably fixed, so the range (ΔT) is widened. Meanwhile the "Fixation" effect would be alleviated by the "decoupling" effect of the sufficiently long flexible spacer. Hence, the ΔT 's for DKLCP and Cu-DKLCP of No.5 and No.6 in Table 2 are similar.

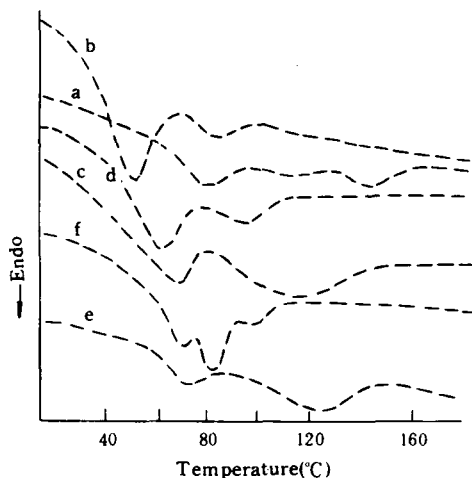


Fig. 3 DSC heating curves of Cu-DKLCP heating rate 20 °C / min

- a) Cu-DKLCP-1 (I); d) Cu-DKLCP-2 (II)
b) Cu-DKLCP-1 (II); e) Cu-DKLCP-3 (I)
c) Cu-DKLCP-2 (I); f) Cu-DKLCP-3 (II)

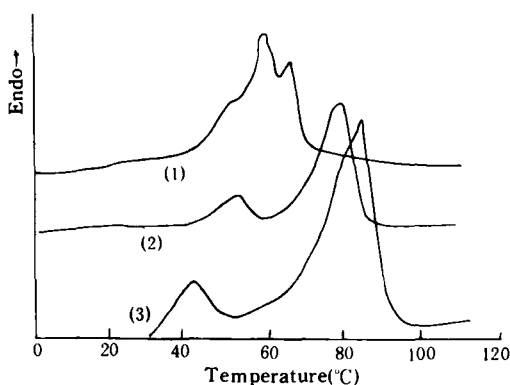


Fig. 4 DSC heating curves of DKLCP heating rate 20 °C / min

- 1) DKLCP-1; 2) DKLCP-2;
3) DKLCP-3

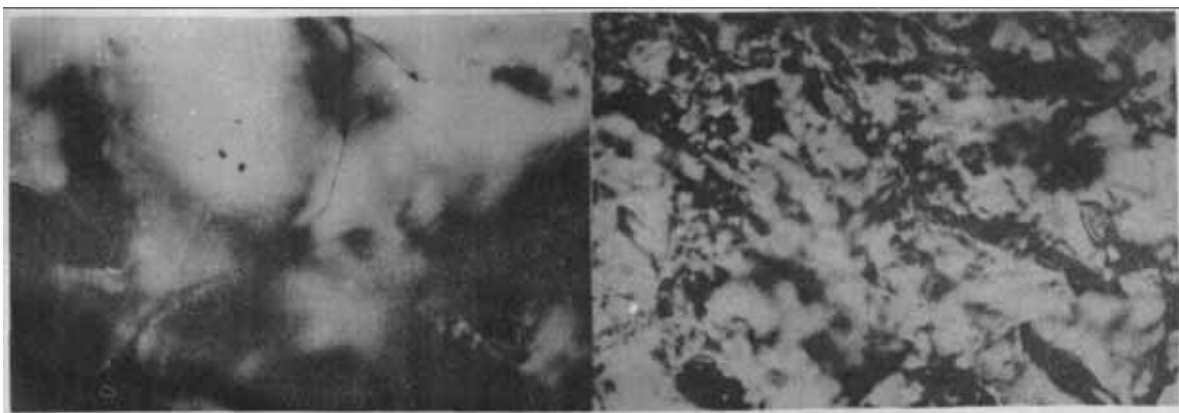
Table 2 Phase transition temperatures of Cu-DKLCP and DKLCP (*)

No.	Sample	Phase transition temp. in °C (by DSC)			ΔT (°C) ($\Delta T = T_{cl} - T_k$)
1	DKLCP-1	K52.7	LC 68.3	I	15.6
2	Cu-DKLCP-1	K80	LC 140	I	60
3	DKLCP-2	K53.7	LC 83.3	I	29.6
4	Cu-DKLCP-2	K70	LC 120	I	50
5	DKLCP-3	K43.2	LC 90	I	46.8
6	Cu-DKLCP-3	K74	LC 125	I	51

(*) K-crystalline state; LC-liquid crystalline state;
I-Isotropic state.

These texture pictures of Cu-DKLCP's shown in Fig.5 are not typical of any of the known mesophases. Other Cu-DKLCP's show the very similar optical textures. As far as the liquid crystal mesogen in Cu-DKLCP is concerned, the Cu- β -diketone chelating moiety does play the role of mesogen because the transition temperatures of T_k and T_{cl} are greatly increased with the increase of Cu molar percentage. As shown by Ohta^[9], the mesogen of the liquid crystalline low molar mass Cu- β -diketone complexes were the disc-like chelating moiety possessing square-planar coordination configuration which can further stack to form columnar structure. In the case of Cu-DKLCP in this paper, the main chain is very flexible Si-O backbone connecting the Cu- β -diketone chelating moiety via a sufficiently long and flexible spacer so that the Cu- β -diketone chelating discs can freely stack to form the ordered structure as free ligand β -diketone can do. The intramolecular complexation and its square-planar configuration are assumed to be responsible to the presence of liquid crystalline property of Cu-DKLCP.

Contrary to the result of chelation of Cu ion, the chelation of Eu ion with β -diketone results in decrease in liquid crystallinity of Eu-DKLCP. In Fig.6 illustrates the DSC heating curves of Eu-DKLCP-3 containing different molar ratio of



(a) (b)
Fig.5 Polarizing microphotographs of Cu-DKLCP taken at 90 °C
(a) Cu-DKLCP-3 (I); (b) Cu-DKLCP-3 (II)

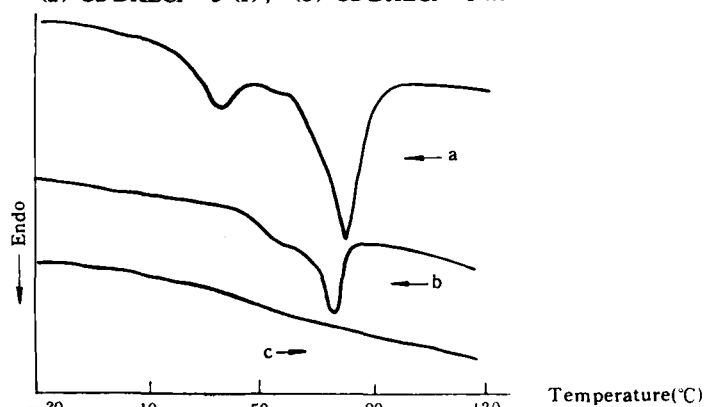


Fig.6 DSC heating curves of Eu-DKLCP-3 polymers.
heating rate: 20 °C/min
europium content: a) 0%; b) 7.6%; c) 14.8%

Eu ion. It is found that the incorporation of Eu ions into DKLCP molecules lowered the clearing temperature T_{cl} and corresponding enthalpies as well. It is understandable that Eu ion can act as a crosslinking agent because its coordination number is usually more than six and its coordination geometry is of many varieties such as cubic, octahedral, etc., but not square-planar structure. Therefore, the orientation of the side chain mesogenic units can not take place. That may be why Eu-DKLCP does not exhibit liquid crystalline property.

(2) The fluorescent properties of the Eu-complexed polysiloxane

The fluorescent properties of Eu chelate polymers containing β -diketone moiety in polymer backbones and in side chains have been studied by Okamoto et al.^[10]. The liquid crystalline polysiloxanes DKLCP, however, are composed of highly flexible spacers and comb-like arranged side chain mesogens, which means a very high density of the β -diketone moiety along the flexible main chain and lower steric hindrance for complexation. So, it would be interesting to study the fluorescent properties of metal-complexed polymers also.

The bonding energies of Eu's $3d_{5/2}$ in Eu-DKLCP containing different amount of Eu ions are listed in Table 3. The bonding energies showed slight difference, this may suggest the presence of different coordination modes in the complexed polymers. This is further supported by the fact that Eu-DKLCP-2 (IV) and Eu-DKLCP-3(IV) (in which the ratio of Eu/ β -diketone > 1) did not precipitate from the reaction solution upon complexation, indicating that the mono-coordination prevails in this condition. The crosslinked Eu-DKLCP can also be

dissolved in THF again in the presence of excess amount of EuCl_3 , the formation of the mono-coordinated polymers and the existence of the equilibrium complexation is supposed to be the reason for this phenomenon.

Fig. 7, 8, and 9 give the fluorescence excitation and emission spectra of Eu-DKLCP polymers. The peak at 615 nm in the emission spectra is due to the electron transition of $5D_0-7F_2$. The fluorescent intensities of Eu-DKLCP complexes remained almost constant in a wide range of Eu/ β -diketone ratios. The intensities are low in much low Eu/ β -diketone ratios and are quite low in much higher Eu/ β -diketone ratios, too. According to the statement of Okamoto et al.^[10], this may be explained as follows: when the ratio is quite low, the tris-coordination structure which is responsible for high intensities has not reached its maximum, so, the intensity is low; when the ratio is much higher, the monocoordination structure prevailed and the quenching effect occurred due to the increase of

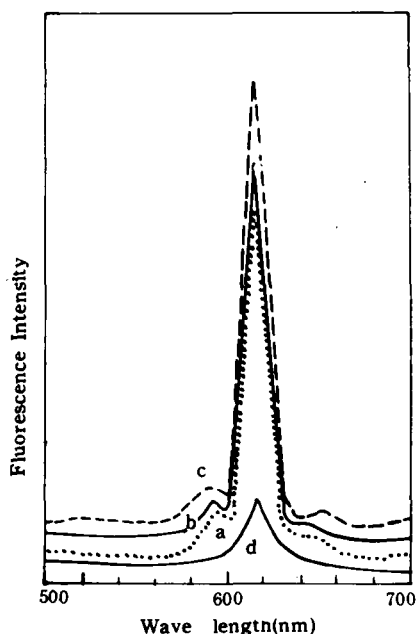


Fig. 7 Emission spectra of Eu-DKLCP-2 polymers Eu wt%: a) 7.0; b) 11.2; c) 16.0; d) 23.1; slit ex/em = 10/10, $\lambda_{ex} = 395 \text{ nm}$, sensitivity 0.1

the Eu concentration, these two will inevitably result in a sharp decrease in fluorescent intensities.

Despite that all the Eu-complexed polymers with different length of flexible spacers show good fluorescent properties, the fluorescent intensities of the Eu-DKLCP show little difference between polymers containing different length of flexible spacers and is hard to tell the genuine reason at present.

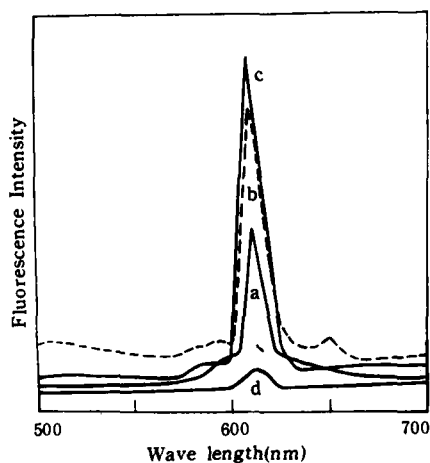


Fig.8 Emission spectra of Eu-DKLCP-3 polymers.
Eu wt%: a) 2.2; b) 7.6; c) 16.8; d) 25.0.
sensitivity 0.1, slit ex/em=10/10, λ_{ex} =395 nm.

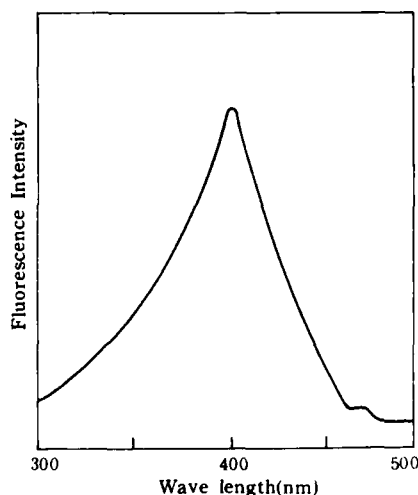


Fig.9 Excitation spectrum of Eu-DKLCP-3 polymers (Eu 16.8 wt%). λ_{em} =615 nm

Table 3 ESCA data of Eu-DKLCP polymers

Sample	C (eV)	O (eV)	Eu 3d _{5/2} (eV)	Molar ratio of Eu / β -diketone	Eu% (Wt)
Eu-DKLCP-3 (I)	283.3	530.8	1133.3	0.09	2.2
Eu-DKLCP-3 (II)	283.4	530.9	1131.0	0.33	7.6
Eu-DKLCP-3 (III)	283.6	531.1	1133.6	0.83	16.8
Eu-DKLCP-3 (IV)	283.9	531.1	1132.1	1.37	25.0
Eu-DKLCP-2 (I)	283.7	530.8	1133.8	0.28	7.0
Eu-DKLCP-2 (II)	283.6	531.3	1132.8	0.45	11.2
Eu-DKLCP-2 (III)	283.4	531.0	1133.0	0.71	16.0
Eu-DKLCP-2 (IV)	283.8	531.3	1133.3	1.11	23.1

Keywords :

β -Diketone ; Metal coordinated LCP ; Liquid Crystalline

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