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SHORT COMMUNICATIONS

# Synthesis and Properties of Thermotropic Liquid Crystalline Polymers Containing Copper Bis(β-diketonate)

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It is well known[1-5] that if a mesogenic segment is introduced into a side chain or a backbone of polymers, they show liquid crystalline behavior. Since such mesogenic segments for liquid crystalline polymers (LCP) are usually composed of C, H, N, O, and halogen, as far as we know, there is no report that a metal complex acts as a mesogen. Actually, a main chain type of thermotropic LC bipyridinyl polyester containing iron(II) or copper(II) complex[6] and a side chain type of thermotropic LC poly(acrylic ester) having platinum(II) complex[7] were synthesized and examined by us. However, in both cases metal complexes showed hindering effect on liquid crystallinity. Carfagna and his coworkers reported a metal-containing LCP by copper(II) complex formation with the bifunctional bidentate ligands,[8] but they presented neither evidence for polymer formation nor discussed the effect of copper(II) complex on LC behavior.

In this communication, we report the synthesis and thermotropic LC properties of poly(acrylic ester)-containing copper bis(β-diketonate) in the side chain. The present polymer is, to our knowlelge, the first thermotropic LCP-containing metal complex as a mesogenic segment.

## EXPERIMENTAL

A mixture of 7.5 g (0.0266 mol) of 4-(6-acryloyloxyhexyloxy)benzoic acid,[9] 4.93 g (0.0256 mol) of 4-(1,3-pentadionyl)phenol,[10] and 6.86 g (0.0333 mol) of dicyclohexylcarbodiimide in 20 ml of ethyl acetate was stirred for 24 h at room temperature. The filtrate without dicyclohexylurea was evaporated and recrystallized from chloroform-hexane. A yield of 4.53 g (38%) of monomer, 4-(1,3-pentadionyl)phenyl 4-(6-acryloyloxyhexyloxy)benzoate, was obtained. A degassed and sealed tube containing a mixture of 4.53 g (9.71 mmol) of monomer, 17 mg of AIBN, and 25 ml of toluene was heated to 80°C for 100 h. After precipitating with methanol, a yield of 4.35 g (96%) of polymer (**1**) was obtained. The molecular heterogeneity ($\bar{M}_w/\bar{M}_n$) and weight average molecular weight ($\bar{M}_w$) were 1.5 and 14000, as determined by GPC with a polystyrene standard. The monomer and polymer **1** were identified by IR, $^1$H NMR spectra and elemental analyses.

A typical reaction for copper coordination was carried out as follows. Polymer **1** (248 mg,

0.429 unit-mmol) in 7 ml of tetrahydrofuran (THF) and 23 mg (0.133 mmol) of $CuCl_2 \cdot 2H_2O$ in 1 ml of methanol were mixed and stirred for 1 h, and then 120 $\mu$l (0.429 mmol) of 3.6 M ammonia solution in methanol were added, followed by stirring for 0.5 h. The resulting precipitate (**2c**) was collected and washed with methanol. Drying, a yield of 207 mg of **2c** was obtained. The copper content of polymer **2a—d** was determined by atomic absorption spectroscopy.

**Table I.** Mole percentage of the copper chelated side chain in the polymers

| Polymer | mol% of copper-chelated side chain |
|---|---|
| | × |
| **2a** | 3.9 |
| **2b** | 7.6 |
| **2c** | 50.4 |
| **2d** | 92.4 |

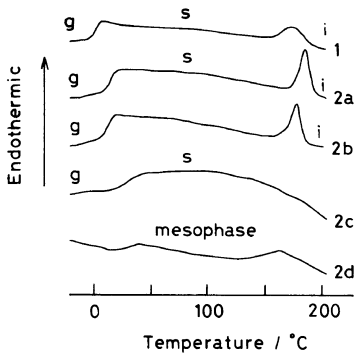
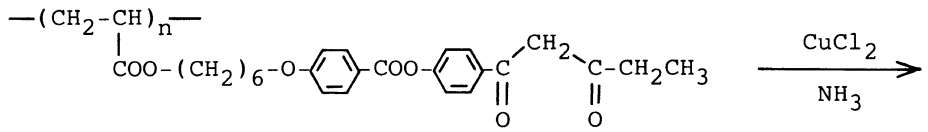
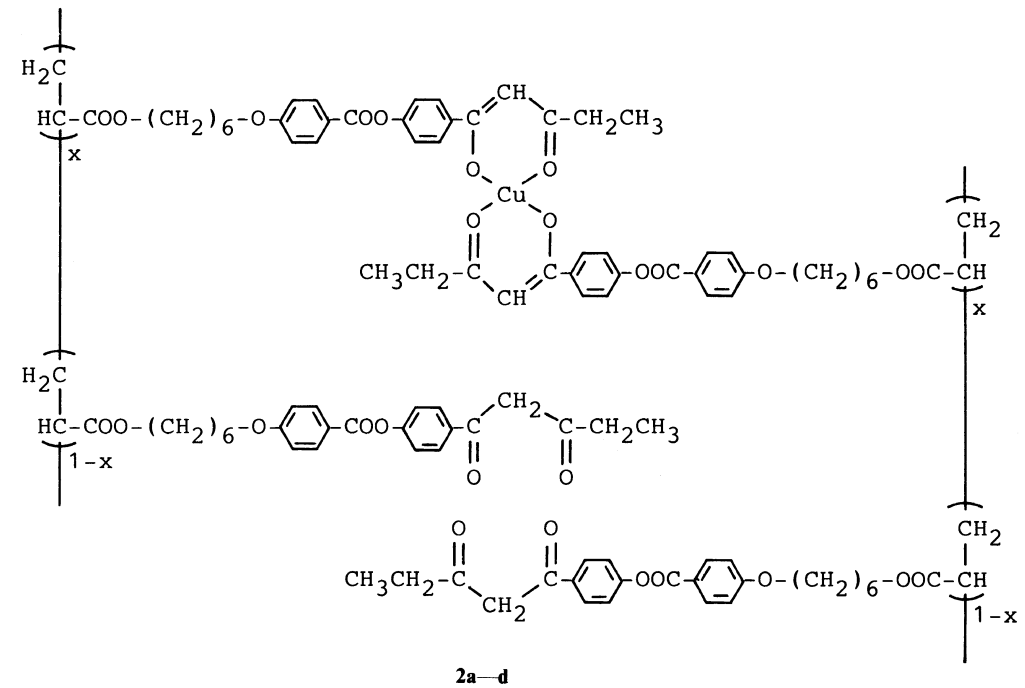



**Figure 1.** DSC heating curves of **1** and **2a—d** (heating rate, 10°C min$^{-1}$). g, glassy liquid crystal; s, smectic; i, isotropic.




**1**




**2a—d**

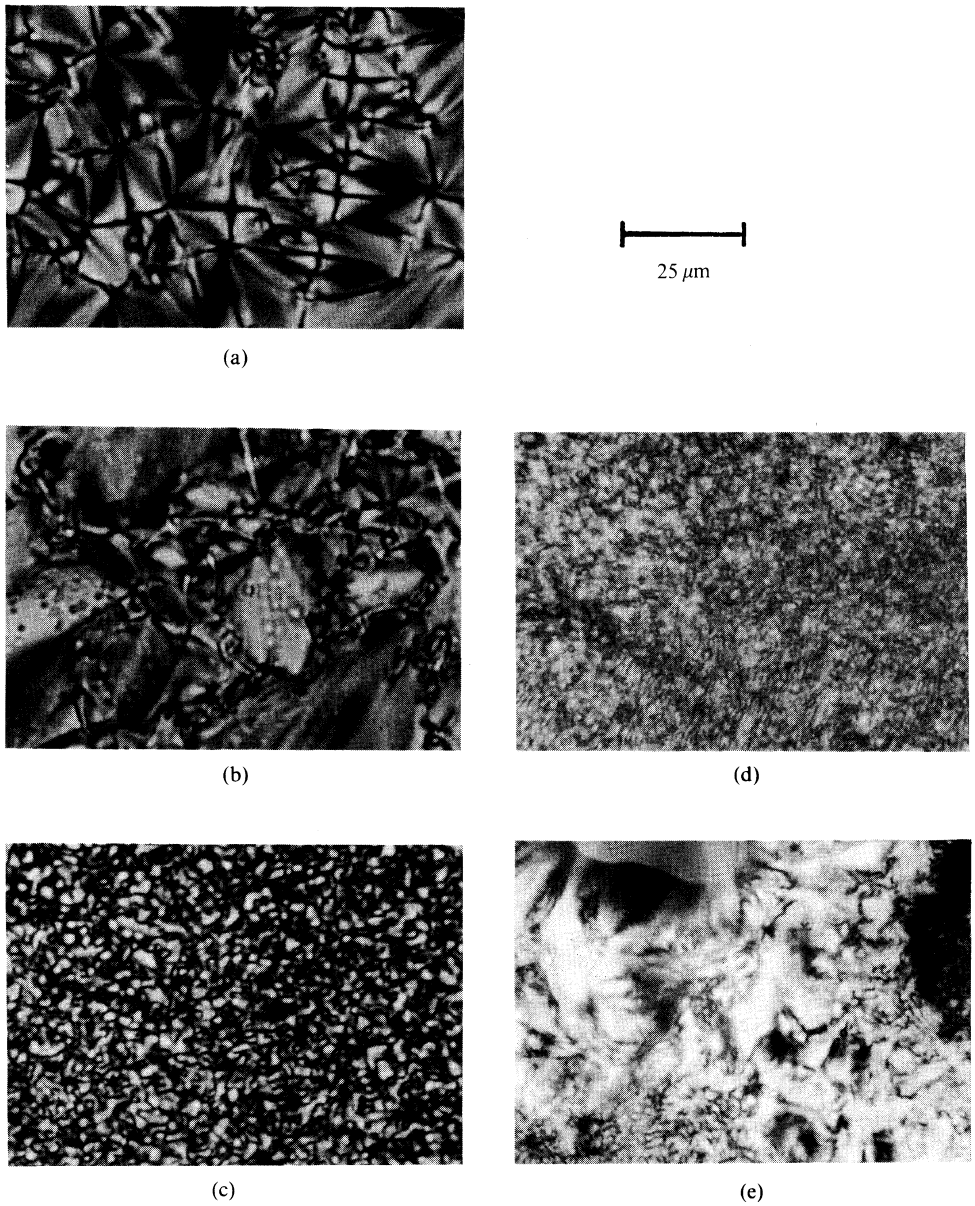



**Figure 2.** Polarization micrographs of **1** and **2a**—**d**. (a), **1** at 100°C; (b), **2a** at 170°C; (c), **2b** at 160°C; (d), **2c** at 100°C; (e), **2d** at 160°C.

## RESULTS AND DISCUSSION

Polymer **1** is a new type of side chain LCP which contains mesogenic β-diketone that can form complex with most metal ions. Since a complexation with **1** and copper ion gives an insoluble precipitate, it is thought that the precipitate (**2a**—**d**) is a crosslinking polymer formed by complexation. The mole percentage of the copper-chelated side chain in the polymer is indicated in Table I.

Phase behavior was studied by polarization

microscopy, DSC measurement and X-ray diffraction. The thermal behavior of **1** was characterized by glass transition at 15°C and isotropic transition at 170°C. In the case of **2a** and **2b** in which many free ligands are still present, thermal behavior was essentially the same as that of **1**, whereas **2c** and **2d** decomposed at 240°C and 220°C, respectively, without isotropic melt.

Polarization micrographs of **1** and **2a—d** are shown in Figure 2. Polymer **1** exhibited a fan-shaped texture with focal conics characteristic of the smectic mesophase between the glass transition and the isotropic one, whereas **2b** and **2c** showed a schlieren texture. Both fan-shaped and schlieren textures were observed in the micrograph of **2a**. The X-ray diffraction patterns of **1**, **2a**, **2b**, and **2c** indicating the presence of both a short range (4.3 Å for **1** and **2a—c**) and a long range order (25.7 Å for **1** and **2a**, 28.0 Å for **2b** and **2c**) suggest these polymers to be smectic LCP. The observed fan-shaped and schlieren textures for **2a** are possible due to the liquid crystallinity of the mesogenic free $\beta$-diketone ligand and mesogenic copper bis($\beta$-diketonate) complex, respectively. Polymer **2d** containing 92 mol% of copper-chelated side chain also showed a birefringent texture. Furthermore, the X-ray pattern of **2d** at room temperature showed a diffuse ring at a wide scattering angle (4.2 Å) and a diffuse halo ring at a small angle (28 Å). It would thus appear that **2d** is also smectic LCP, but this remains to be confirmed.

## REFERENCES


1. H. Finkelmann, "Polymer Liquid Crystals," A. Ciferri, W. R. Krigbaum, and R. B. Meyer, Ed., Academic Press, New York, N.Y., 1982, p 35.
2. A. Ciferri, "Polymer Liquid Crystals," A. Ciferri, W. R. Krigbaum, and R. B. Meyer, Ed., Academic Press, New York, N.Y., 1982, p 63.
3. M. G. Dobb and J. E. McIntyre, *Adv. Polym. Sci.*, **60/61**, 63 (1984).
4. H. Finkelmann and G. Rehage, *Adv. Polym. Sci.*, **60/61**, 100 (1984).
5. V. P. Shibaev and N. A. Platé, *Adv. Polym. Sci.*, **60/61**, 175 (1984).
6. K. Hanabusa, J. Higashi, T. Koyama, H. Shirai, N. Hojo, and A. Kurose, *Makromol. Chem.*, **190**, 1 (1989).
7. K. Hanabusa, T. Suzuki, T. Koyama, H. Shirai, N. Hojo, and A. Kurose, *Makromol. Chem.*, in press.
8. C. Carfagna, U. Caruso, A. Roviello, and A. Sirigu, *Makromol. Chem., Rapid Commun.*, **8**, 345 (1987).
9. M. Portugall, H. Ringsdorf, and R. Zentel, *Makromol. Chem.*, **183**, 2311 (1982).
10. M. E. B. Jones, M. F. Lynch, D. A. Thornton, and R. F. Webbs, *Makromol. Chem.*, **50**, 232 (1961).