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Synthesis and characterization of a metal chelate-bridged quasi-ladder main chain discotic liquid crystal polymer

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Preliminary communication

Synthesis and characterization of a metal chelate-bridged quasi-ladder main chain discotic liquid crystal polymer

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A metal chelate-bridged quasi-ladder discotic liquid crystal polymer (DLCP) has been prepared by a controlled chelation reaction of cupric ions with β-diketone groups on two adjacent poly(AADK-HMM) chains, synthesized by the hydrosilylation of a bis-allyl group-terminated β-diketone monomer and 1,1,3,3-tetramethylhydrodisiloxane (HMM). X-ray diffraction patterns of the samples annealed in the mesomorphic state or cooled from the isotropic phase demonstrated the existence of an ordered columnar structure on short or long range scales, respectively. The fact that the molecular weight of the cupric complex is approximately twice that of the parent polymer indicates that the quasi-ladder double chain polymer is the predominant product although some terminal defects are present.

Columnar discotic liquid crystals were established as a new class of one-dimensional molecular materials capable of rapid charge transference in 1993 [1, 2]. A variety of metal-coordinated square-planar complexes [3], for example, a series of copper β-diketonates [4], exhibit columnar or lamellar mesophases. In a recent report, we first described the conductive behaviour of columnar bis(β-diketonate)copper(II) complexes with oligo(ethylene oxide) side groups and doped with $LiClO_4$ or iodine. Compared with the original state of the complex, the conductivity increased by two or three orders of magnitude reaching $10^{-5}\ \mathrm{S\,cm^{-1}}$ when heated into the columnar mesophase [5].

For technical application, liquid crystalline polymers containing rod-like (calamitic) units in the main chain or in side groups have been extensively investigated. However, polymers based on discotic mesogenic units have been much less explored. In polymeric discotic liquid crystals, disc-shaped mesogenic moieties are either segments in the main chain [6–9] or are attached to the polymeric backbone as pendant side groups [10, 11]. In addition, there have also been reports of discotic polymer networks [12–14] and elastomers [15].

This paper deals with a new kind of main chain discotic liquid crystal polymer with a quasi-ladder structure, prepared by the controlled cupric-chelation reaction between two polymer chains containing β-diketone ligand units. Although some authors have also described attempts to prepare metal-coordinating LCPs by introducing metal-coordinating units into the main chain [16] or by intermolecular chelation reactions [17, 18], the incorporation of metal ions always resulted in a 'negative effect' on liquid crystallinity due to random crosslinking. In contrast, we have prepared a series of metal-coordinating liquid crystal polymers with improved mesomorphic properties under controlled experimental conditions [19–24]. Here we report the first quasi-ladder-like main chain discotic LCP with a high metal content, good

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solubility and film-forming ability and which exhibits a columnar mesophase. The schematic structure of the polymer and the synthetic route used to prepare it are shown in figure 1.

The two precursor materials, *p*-allyloxyacetophenone (**1**) and methyl *p*-allyloxybenzoate (**2**), and the monomer, *bisallyloxyphenyl-p-propane-1,3-dione*, AADK (**3**) were synthesized by methods described by Ohta *et al.* [25]. The crude product was purified by column chromatography on silica with hexane–ethyl acetate (2 : 1) as eluent; pure AADK was obtained as a pale yellow crystal; m.p. 103.0°C, yield 66%. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): $\delta = 4.6$ (d, 4H, $-OCH_2-$), 5.3–5.5 (m, 4H, $CCH{=}\underline{CH}_2$), 5.9–6.2 (m, 2H, $-\underline{CH}{=}CH_2$), 6.7 (s, 1H, $-COCH{=}C$), 7.0, 8.0 (d, 8H, C_6H_4) and 17.1 (s, 1H, HO–C=). Elemental analysis: calc. for $C_{21}H_{20}O_4$ (336) C 75.02, H 5.95; found C 75.17, H 5.98%.

Poly(bispropyloxyphenyl-p-propane-1,3-dione-p-1,1,3,3-tetramethylsiloxyl), poly(AADK-HMM) (**4**), was synthesized via the hydrosilylation reaction of AADK and 1,1,3,3-tetramethylhydrosiloxane (HMM) using a stoichiometric ratio of 1 : 1 with dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2) as catalyst and methylthiophene-free toluene as solvent. The progress of the hydrosilylation reaction was monitored by ^{1}H NMR spectroscopy. The product was viscous and partially

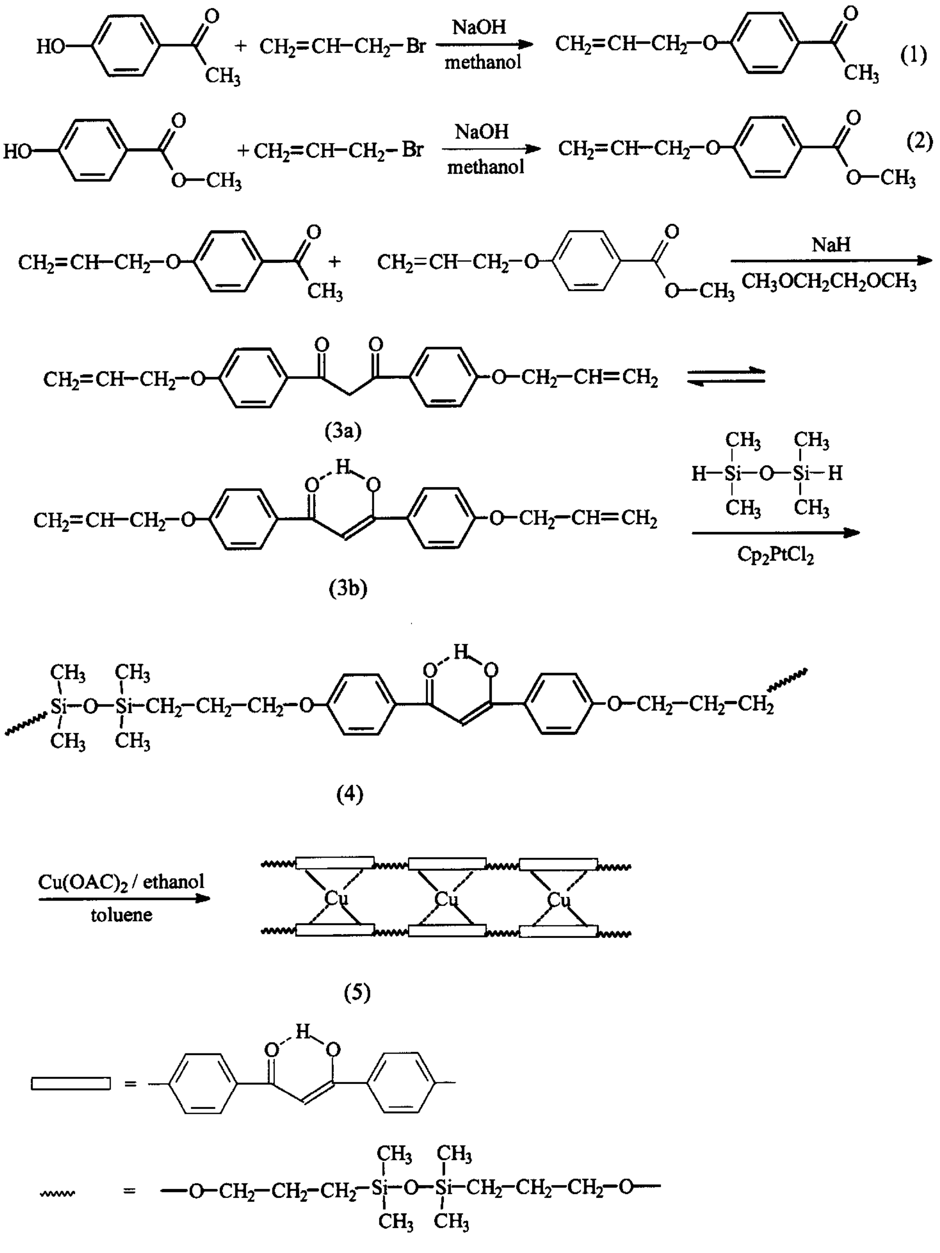

Figure 1. Synthetic route to obtain the β-diketone-containing parent polymer and the corresponding cupric complexes.

solid after evaporating the solvent. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): $\delta = 0–0.2$ (12H, s, $SiCH_3$), 0.6–0.7 (4H, $SiCH_2$), 1.6–2 (4H, $-OCH_2\underline{CH_2}-$), 3.9–4.1 (4H, $-OCH_2-$), ~6.7 (1H, $-COCH=C$), 6.9–7.0, 7.9–8.0 (8H, C_6H_4) and 17.1 (1H, HO–C=).

Bis[poly(bispropyloxyphenyl-p-propane-1,3-dione-p-1,1,3,3-tetramethylsiloxyl)]copper(II) complex, poly(AADK-HMM)-Cu (**5**), was prepared by the controlled coordination reaction of poly(AADK-HMM) in dilute toluene solution with cupric acetate in ethanol. The reaction mixture was stirred at room temperature and a green solid with film-forming abilities was obtained after evaporating the solvent. The product was purified by precipitation from toluene using methanol. The cupric content was determined by UV spectroscopy; the results indicated that about 71–72% of the β-diketone groups chelated cupric ions and so some defects are in the structure.

The molecular mass of both the parent polymer, poly(AADK-HMM) and its cupric complex, poly(AADK-HMM)-Cu were determined by vapour pressure osmometry (using a VPO, Knauer) and are listed in the table. The molecular mass of the cupric complex is approximately twice that of the parent poly(AADK-HMM). This indicates that the metal chelate-bridged double chain polymer with a quasi-ladder structure is the predominant product. However, terminal defects caused by the molecular mass distribution and structural irregularities from the chelation reaction make the molecular mass of the complex less than the stoichiometric value.

Table. Comparison of the molecular masses of the parent polymer (AADK-HMM) and its Cu-complex by VPO measurements[a].

Poly(AADK-HMM)		Poly(AADK-HMM)-Cu		
Solvent	M_w	Solvent	M_w	Cu content/%[b]
Toluene	5716	Toluene	10815	71.4
THF	3396	THF	5988	70.0

[a] Standard: poly-methyl-hydrogen silicon oil (M_w = 2262).

[b] Stoichiometric saturated Cu-content based on the bis-β-diketone is defined as 100%.

The DSC traces, measured using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 10°C min^{-1}, of poly(AADK-HMM)-Cu are shown in figure 2. It is seen that during the first heating, there is no melting transition but instead the polymer goes directly from a glassy state into the mesophase at about 70°C and clears at about 125°C. In the second heating, the isotropic transition moves to a much higher temperature and the T_g cannot be observed.

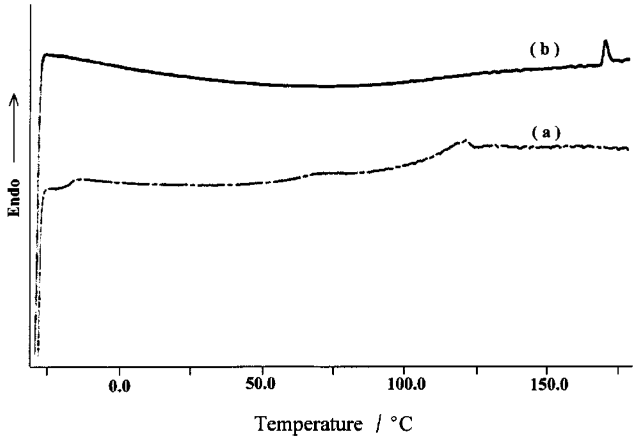

Figure 2. DSC traces of poly(AADK-HMM)-Cu complex: (*a*) first heating run, (*b*) second heating run.

Flake and ribbon-like optical textures are observed under the polarized light microscope as shown in figure 3. This picture is similar to those observed on our previous studies of 'fishbone' or 'rowboat'-like mesogenic polymers with ladder-like main chains [19–21, 26]. A characteristic optical texture used to identify for low molar mass discotic liquid crystals is not observed due to the restricted nature of the double main chain.

Figure 4 shows the X-ray diffraction pattern; measured using a PW1710 BASED, of poly(AADK-HMM)-Cu cooled from about 80°C, after previously annealing for

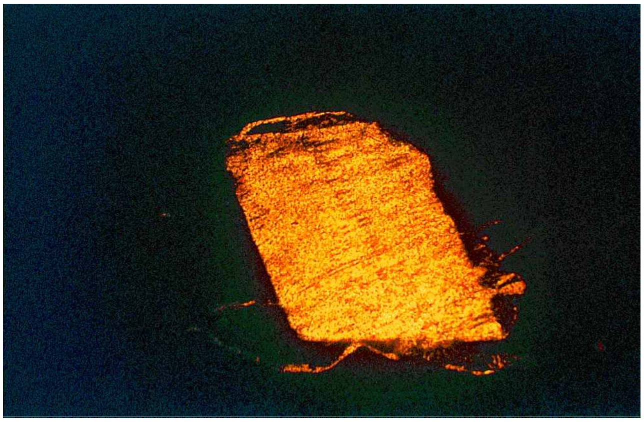

Figure 3. Photomicrograph of the texture of the mesophase of poly(AADK-HMM)-Cu.

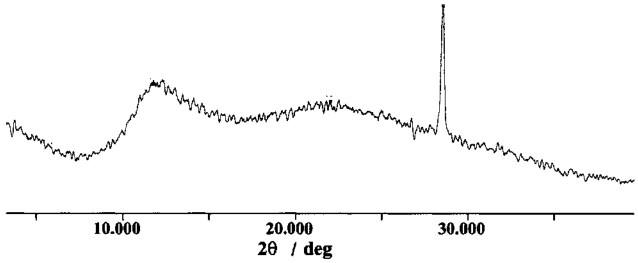

Figure 4. XRD trace of poly(AADK-HMM)-Cu cooled from 80°C.

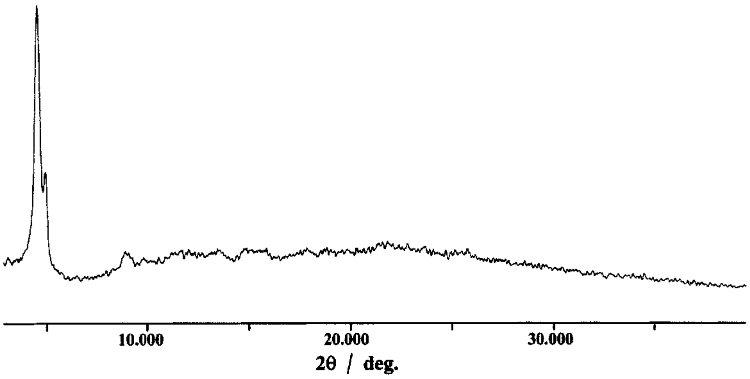

Figure 5. XRD trace of poly-(AADK-HMM)-Cu cooled from the isotropic phase.

1–2 hours. The pattern shows two diffuse diffraction peaks in the wide angle region. These correspond to average spacings of about 7.6 and 4.0 Å. The former spacing corresponds to the width of the ladder-like chain as well as the vertical length of the discotic units. The latter spacing is associated with the average interchain distance. In addition, a sharp peak occurs at $2\theta \sim 28°$ in the wide angle region, corresponding to a spacing of about 3.1 Å. This reflection can be attributed to the ordered columnar packing of the square-planar chelate cores on the short range scale.

Figure 5 shows the X-ray diffraction trace of a film sample cooled from the isotropic state; in the small angle region there are two strong, sharp and partly overlapping peaks with 2θ values of 4.4° and 4.8°, corresponding to spacings of 19.98 and 18.24 Å, respectively. In general, the presence of two small angle reflections suggests the formation of a rectangular superstructure ordered on a long range scale.

4. Conclusion

Under controlled experimental conditions we have prepared the first of a new class of discotic main chain liquid crystal polymers with quasi-ladder structures by the chelation reaction of cupric ions with two adjacent polymer chains containing β-diketone ligand units. XRD patterns proved the existence of an ordered columnar structure on short or long range scales in samples cooled from the mesomorphic or isotropic phases, respectively.

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