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SYNTHESIS AND LIQUID CRYSTALLINE PHASE BEHAVIOUR OF A NOVEL METALLOMESOGENIC SIDE CHAIN LIQUID CRYSTAL POLYMER FREE FROM CROSS-LINKING

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Abstract A novel metallomesogen side chain liquid crystal polymer (MMSCLCP) derived from a new copper(II) co-ordination complex has been synthesised free from cross-linking and has been shown to exhibit a smectic A (S_A) mesophase. This is the first example of a true MMSCLCP derived from a co-ordination complex, previous examples being organometallic species.

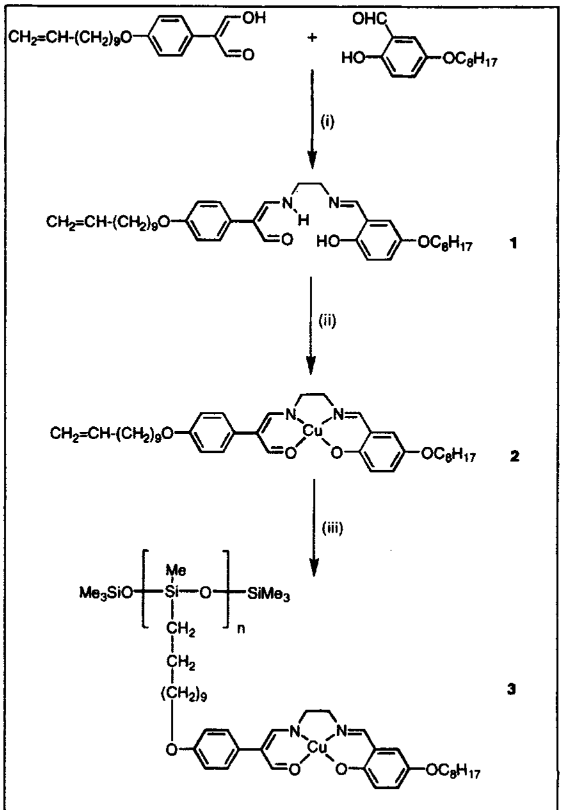
INTRODUCTION

Research into the liquid-crystalline behaviour of structurally anisotropic metal complexes or metallomesogens (MMs) has attracted significant attention in resent years[1-4]. In contrast, relatively little work has been carried out on polymeric MM systems, although recent reviews[5] have focused attention on this field of research. Only a small number of systems have been reported based on metallomesogenic side chain liquid crystal polymers (MMSCLCPs) and those systems reported to date are restricted by the chemistry involved in the formation of non-symmetrical metal-containing monomers. Polymerisation of symmetrical complexes leads to a cross-linked network and the liquid crystalline properties of the monomers are destroyed as the degree of cross-linking is increased. The exception is an organometallic ferrocene MMSCLCP described recently by Deschenaux and co-workers[6] which is derived from a mono-activated ferrocene precursor. However, there have been no examples to date of true MMSCLCPs derived from metal co-ordination complexes which are free from cross-linking.

SYNTHETIC PROCEDURES

We have recently devised a synthetic procedure for the preparation of non-symmetrical precursor ligands and subsequently the synthesis of metal complexes possessing a number of non-identical alkyl chains. This has allowed us to prepare monomers containing, for example, one ω-alkenic and one saturated hydrocarbon chain. Polymerisation can then occur at the single alkenic site and the problem of cross-linking is effectively eliminated. We have demonstrated this methodology in the synthesis of a mesomorphic homopolymer (**3**), the results of which will be discussed in this paper.

The unsymmetrical ligand (1) was prepared by the reaction of equimolar quantities of (4-undec-10-enylphenyl)malonaldehyde, 5-octoxysalicylaldehyde and 1,2-diaminoethane in dichloromethane under reflux with the azeotropic distillation of water. Column chromatography (dichloromethane/ ether) afforded 1 (R_f 0.44) as a yellow crystalline solid in 45 % yield. The unsymmetrical copper(II) complex (2) was obtained by the reaction of equimolar quantities of copper acetate monohydrate and 1 in refluxing methanol. Re-crystallisation twice from dichloromethane / ether afforded the pure complex as brown-violet rectangular plates in 77 % yield.

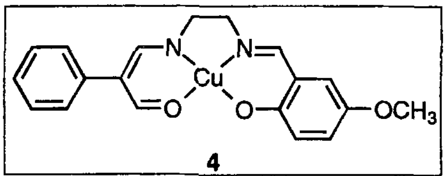


Reagents: (i) $H_2NCH_2CH_2NH_2$, CH_2Cl_2, reflux; (ii) $[Cu_2(OAc)_4.H_2O]$, CH_3OH (iii) $Me_3SiO(SiH(Me)_nOSiMe_3$, Wacker Platinum Catalyst, toluene

SCHEME 1 Synthesis of the polymer

A solution of a low polydispersity polysiloxane (n = 140), which had previously been separated by preparative gel permeation chromatography (GPC), in dry thiophene-free toluene was added to a Schlenk tube containing 2 (as a 10% molar excess in toluene) under an atmosphere of dry nitrogen. The catalyst (Wacker Platinum catalyst SLM 86003) was added and the resulting solution heated to 100 °C. When the reaction had proceeded to completion (as determined by infrared spectroscopy) the solvent was removed in vacuo and the remaining brown residue was dissolved in the minimum volume of dichloromethane, filtered through celite and precipitated by slow addition to methanol with vigorous stirring. The resulting suspension was stirred (1.5 h) and the brown product was separated by centrifugation, collected and air dried to give the polymer (3) in 30 % isolated yield. The purity of each intermediate was determined using standard techniques; elemental analysis, infrared spectroscopy and mass spectrometry. The ^{1}H NMR spectrum of the ligand was also determined. In each case satisfactory analyses were obtained.

We tested the feasibility of performing platinum catalysed hydrosilylation of alkenes in the presence of a copper(II) centre prior to embarking on the polymerisation of the liquid crystalline monomer. Hydrosilylation of a standard terminal alkene substrate ($RO\text{-}C_6H_4\text{-}OR$; $R = CH_2{=}CH\text{-}(CH_2)_8\text{-}$) with $(CH_3)_3SiOSi(CH_3)_2H$, catalysed by Karsted catalyst [bis(divinyltetra-methyldisiloxane)platinum(0) as a 3% solution in xylene] (Petrach) was studied in the presence of a 20% molar ratio of the closely related copper(II) complex, 4. The presence of 4 did not inhibit nor retard the platinum catalysis, nor did it affect the distribution of the hydrosilylation products.[7]



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In a separate experiment, the hydrosilylation reaction was followed by infrared spectroscopy, monitoring both the disappearance of the Si-H stretch at 2169 cm^{-1}, and also the relative ratio of the absorptions due to the Si-H stretch from the polymer backbone and the copper co-ordinated imino C-N stretch (1627 cm^{-1}). The reaction was found to proceed slowly at 60 and 80 °C, however when the reaction temperature was then increased to 100 °C completion was achieved when the mixture was stirred for 4 hours. Since the CO band is sensitive to co-ordination, typically decreasing by for 4 hours. Since the CO band is sensitive to co-ordination, typically decreasing by approximately 20 cm^{-1} on co-ordination to a metal (1657cm^{-1} in the ligand and 1626 cm^{-1} in the complex), it can be concluded that the monomeric complex did not degrade during the hydrosilylation procedure as there was no trace of free ligand in the IR spectrum. The complete occupancy of the Si-H sites and the absence of cross-linking was confirmed in related diamagnetic nickel(II) complexes by NMR (^{1}H and ^{29}Si), FAB-MS and gel permeation chromatography.[7]

A polysiloxane of low polydispersity was chosen for this study so that accurate structure-property correlations could be formulated and work is continuing in the study of new systems based on diverse monomers and a variety of transition metal centres. The thermal behaviour of the free ligand, unsymmetrical monomer, and polymer was investigated by polarised light microscopy using a Zeiss Universal microscope equipped with a Mettler FP82HT micro-furnace and FP90 temperature processor and by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-2C calorimeter interfaced to a TADS data station. The calorimeter was calibrated using pure indium metal as the reference material.

The unsymmetrical ligand (1) was found to be non-mesomorphic, melting directly to the isotropic liquid at 136.0 °C. However, complexation to Cu^{2+} gave a material which showed a smectic A (S_A) phase at 163.7 °C and which remained until the onset of decomposition at 198.5 °. The use of a metal ion in the promotion of liquid crystalline phase stability is clearly demonstrated here. ^{1}H NMR studies in $CDCl_3$ solution at room temperature have shown the free ligand to adopt the conformation shown in Fig. 1 where the ethylene diamine linking group adopts an all-*trans* conformation with the chelate groups on opposite sides of the molecular core, each stabilised by intra-molecular hydrogen bonding. This has been confirmed by single crystal X-ray diffraction on related ligands of the same general core structure.[8] The overall shape is non-

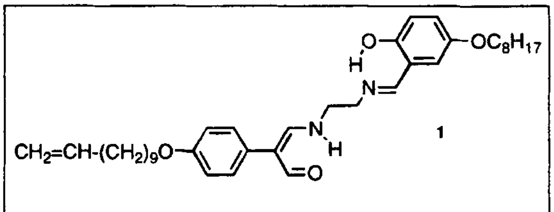

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FIGURE 1 The structure of the free ligand anisotropic due to molecular broadening and phase formation is suppressed. The metal ion acts as a template, bringing the two aromatic sections of the molecule together so that the chelate groups are on the same side of the molecular core, resulting in a rigid, anisotropic, square planar structure. Polymerisation onto the polysiloxane backbone causes a small increase in the stability of the crystal phase, the polymer melting at 177 °C, and a slight decrease in the clearing point to 192 °C. However, it should be noted that the polymer is more thermally stable than the monomer and clearing occurs without significant decomposition. It is also interesting to note that the smectic A phase is preserved on polymerisation of the monomer. The transitions temperatures of the polymer are quoted to the nearest degree as the broad nature of the transitions and dark colour of the material made an accurate assignment impossible.

TABLE Mesomorphism and transition temperatures

		Transition Temperatures (°C)			
Compound	**K**		**S_A**		**Iso**
1	•	136	•	•	•
2	•	163.7	•	198.5	•
3	•	177	•	192	•

CONCLUSIONS

We have demonstrated the first practical example of the synthesis of a non-cross-linked side chain liquid crystal polymer derived from a metallomesogen (MM) monomer[9]. By using a fractionated polysiloxane of known degree of polymerisation (DP) we will be able to relate the properties of this material to other polymers derived from MM monomers containing a variety of metal centres and thereby build an understanding of structure-property correlations in MMSCLCPs. By combining the unique properties of MMs with the processability of SCLCPs we hope to devise new materials with applications in areas unique to conventional organic liquid crystals.

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