Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Peter Styring & Isabel Saez (2004): Side chain liquid crystal polyacrylate and polymethacrylate nickel complexes free from covalent cross-linking, Molecular Crystals and Liquid Crystals, 411:1, 491-502

To link to this article: http://dx.doi.org/10.1080/15421400490436412

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 491/[1533]–502/[1544], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490436412

SIDE CHAIN LIQUID CRYSTAL POLYACRYLATE AND POLYMETHACRYLATE NICKEL COMPLEXES FREE FROM COVALENT CROSS-LINKING

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Non-symmetrical nickel(II) complexes containing a single acrylate or methacrylate motif have been synthesised and polymerised radically in tetrahydrofuran solution using AIBN as the initiator. This results in the incorporation of the metal complexes into a polyacrylate and a polymethacrylate as freely mobile side chains, free from cross-linking. Whilst the monomers are non-liquid crystalline, the polymers show smectic A liquid crystal phases.

Keywords: acrylate; inorganic complex; liquid crystal; metacrylate

INTRODUCTION

Metal-containing liquid crystals have been the focus of considerable attention in recent years because of the possibility of incorporating the unique properties of a metal into the conventional organic structure of a liquid crystal [1–3]. Further attempts have been made to incorporate metal-containing liquid crystals (metallomesogens) into polymeric structures [3,4], however except for a few examples this has resulted in covalent cross-linking to give non-mesomorphic networks. Deschenaux and co-workers [5–7] have reported a number of polymeric metallomesogen based on the organometallic ferrocene core. Serrano and co-workers have also

We thank EPSRC for financial support to IMS. We also thank The University of Hull Analytical Services and Mrs. Julie Haley for spectroscopic and calorimetric data.

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been active in incorporating both catamitic [8] and discotic [9] metallomesogens into polymeric structures. Ghedini and co-workers have also shown that it is possible to synthesise side-chain metallomesogenic polymers that are free from cross-linking using organometallic species such as cyclopalladated complexes [10] pi-allyl complexes [11]. Some polymers derived from non-symmetric phthalocyanine macrocycles [12] have also been reported as have a number of siloxane materials synthesised by ourselves [13–15].

We were interested to see if liquid crystal polymers with organic backbones could also be prepared with metal-containing side chains, free from covalent cross-linking. Two examples of such polymers derived from nickel(II) co-ordination complexes are reported here for the first time.

EXPERIMENTAL

Analysis of Materials

Confirmation of the structures of the intermediates and products was obtained by ^{1}H NMR spectroscopy (JEOL JNM-GX270 FT spectrometer operating at 270 MHz), infrared spectroscopy (Perkin-Elmer 783 or 983 spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 automated GC/MS). The progress of the reactions and the purity of a number of organic products was checked using a Perkin-Elmer 8320 capillary gas chromatography equipped with a BP1 capillary column (12 m). The transition temperatures of all mesogens were determined using an Olympus BH-2 polarising light microscope in conjunction with a Mettler FP52 heating stage and Mettler FP5 temperature control unit. The transition temperatures were confirmed and enthalpies determined by thermal analysis using a Perkin-Elmer DSC7-UNIX/PC differential scanning calorimeter. Diethyl ether was dried and stored over sodium wire. THF was dried by distillation from sodium wire and benzophenone and stored over 4A molecular sieves. Ethanol was dried by distillation from magnesium and stored over 4A molecular sieves. Toluene was dried by distillation from and stored over 4A molecular sieves.

Monomer Synthesis

11-Bromo-1-tetrahydropyranyloxyundecane (1)

11-Bromo-1-undecanol (50 g, 0.199 mol) (Aldrich) was dissolved in dichloromethane (500 mL) and the mixture cooled to 0°C. Dihydropyran (22.15 mL, 0.242 mol) was added dropwise over a period of two hours. The reaction was started by addition of a few crystals of 4-toluenesulphonic acid at the beginning of the addition. After the addition was complete, the

reaction mixture was stirred during 15 min, and stopped by addition of $NaHCO_3$ (0.5 g). After evaporation of the dichloromethane, the pale yellow syrup obtained was dissolved in ethyl acetate and purified by filtration through silica gel. Yield = 65.3 g (98%).

4-(11-Tetrahydropyranyloxyundecyloxy)phenol (2)

Potassium hydroxide (4.72 g, 65 mmol) was dissolved in absolute ethanol (300 mL) under an atmosphere of dry nitrogen and hydroquinone (19.5 g, 177 mmol) was added. The reaction mixture was heated under reflux while a solution of 11-bromo-1-tetrahydropyranyloxyundecane (19.81 g, 59 mmol) in ethanol (50 mL) was added dropwise. The reaction mixture was refluxed (20 h), the solvent was then evaporated off and the residue extracted with diethyl ether (3×300 mL), washed with saturated aqueous NaCl (150 mL) and dried over $MgSO_4$. The solvents were evaporated under vacuum and the residue extracted with *n*-heptane to afford a first crop of pure phenol. The remaining crude material was purified by column chromatography on flash grade silica gel (diethyl ether/hexane, 2:3; $R_f = 0.27$). Yield = 12.65 g (59%).

^{1}H NMR ($CDCl_3$): δ 6.76 (m, 4H, aromatic); 4.90 (s, 1H, O*H*); 4.60 (m, 1H, C*H*O-CH_2 THPO); 3.89 (t(J = 7 Hz), 2H, CH_2O); 3.74, 3.52, 3.40 (m, 4H, CH_2O THPO); 1.75–1.50 (m, 4H, CH_2-CH_2-O); 1.30 (m, 20H, (CH_2)).

2-Hydroxy-5-(11-tetrahydropyranyloxyundecyloxy)-benzaldehyde (3)

Anhydrous tin(IV) chloride (0.23 mL, 2.0 mmol) was added to a solution of tetrahydropyranyloxy phenol (7.35 g, 20.0 mmol) in sodium dried, degassed toluene (250 mL) under a nitrogen atmosphere. Tri-*n*-butylamine (1.90 mL, 8.0 mmol) was added at room temperature. The solution turned yellow and was stirred for 1 h before paraformaldehyde (BDH) (1.32 g, 44 mmol) was added and the yellow suspension heated to 105°C (3 h). The brown solution was cooled, poured onto saturated aqueous NaCl (200 mL) and acidified to pH 2 with 10% HCl. The product was extracted with ether (3×100 mL) and the combined organic layers dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (flash grade silica gel; petroleum ether 40–60°C/diethyl ether, 1:1). The salicylaldehyde was isolated as a yellow solid ($R_f = 0.45$). Yield = 2.79 g (36%).

^{1}H NMR ($CDCl_3$): δ 10.64 (s, 1H, O*H*); 9.85 (s, 1H, C*H*O); 7.20–6.80 (m, 3H, H_a, H_b, H_c); 4.60 (m, 1H, C*H*O-CH_2 THPO); 3.93 (t(J = 7 Hz), 2H, CH_2O); 3.74, 3.52, 3.38 (m, 4H, CH_2O THPO); 1.80–1.50 (m, 4H, CH_2-CH_2-O); 1.30 (m, 20H, (CH_2)).

8-(3-(11-Tetrahydropyranyloxyundecyloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-2,7-dien-1-al (5)

1,2-Diaminoethane (0.25 mL, 3.87 mmol) was added to a vigorously stirred solution of phenylmalonaldehyde (0.573 g, 3.87 mmol) in dichloromethane (350 mL). A white precipitate formed immediately. 5-(Tetrahydropyranyloxyundecyloxy)salicylaldehyde (1.520 g, 3.87 mmol) was added and the resulting yellow suspension stirred at room temperature for 18 h and refluxed using a Dean-Stark apparatus until a clear yellow solution was obtained (approximately 6 h). The yellow solution was evaporated *in vacuo* and the residue purified by column chromatography (flash grade silica gel, Cl_2CH_2/THF, 4:1). The band with $R_f = 0.75$ yielded the symmetrical salen derivative. The band with $R_f = 0.50$ was collected and the product recrystallised from hot methanol to yield yellow microcrystals of **5**. Yield = 0.371 g (34%).

Microanalysis: Calcd for $C_{34}H_{48}O_5N_2$: C 72.31; H 8.56; N 4.95. Found: C 72.33; H 8.77; N 5.03. MS (EI): m/z 565 (M^+); 480 (M^+-THP).

^{1}H NMR ($CDCl_3$): δ 12.44 (s, 1H, O*H*); 10.49 (m broad, 1H, N*H*); 9.47 (d, (J = 4 Hz), 1H, C*H*O); 8.31 (s, 1H, C*H*=N); 7.30–6.75 (m, 9H, aromatic C_6H_5, H_a, H_b, H_c, NC*H*=C); 4.58 (m, 1H, C*H*O-CH_2 THP); 3.88 (t (J = 7 Hz), 2H, CH_2O); 3.87–3.34 (m, 4H, CH_2-N=CH and CH_2-NH; 4H, CH_2O THP); 1.80–1.50 (m, 4H, CH_2-CH_2-O); 1.30 (m, 20H, (CH_2)).

[8-(3-(11-Tetrahydropyranyloxyundecyloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-1,3,7-trienato]-(2-) nickel(II) (6)

Nickel acetate dihydrate (110.1 mg; 0.44 mmol) was added to a solution of the tetrahydropyranyloxy ligand **5** (0.250 g; 0.44 mmol) in methanol (20 mL) that was at reflux. Red microcrystals formed immediately. The suspension was heated for 1 h at reflux. After cooling to room temperature, the red-brown needles formed were filtered off and recrystallised from methanol. Yield = 0.210 g (76%).

Mesomorphism: Cryst (134 SmA) 158 Iso °C.

Microanalysis: Calcd for $C_{34}H_{46}O_5N_2Ni$: C 65.71; H 7.45; N 4.50. Found: C 64.99; H 7.61; N 4.31. MS (EI): m/z 621 (M^+); 593 (M^+-CHO); 536 (M^+-THP). 365 (M^+-THP-$(CH_2)_{11}O$).

IR (KBr disc, υ cm^{-1}): 1609 (vs, sharp; C=N, C=O and C=C-N coordinated).

^{1}H NMR ($CDCl_3$): δ 7.45–7.10 (m, 8H; aromatic C_6H_5, *H*C=N, *H*C=O and NC*H*=C); 6.93 (s, broad, 2H, H_a, H_b); 6.52 (m, 1H, H_c); 4.67 (m, 1H, C*H*O-CH_2 THP); 3.88 (t, (J = 7 Hz), 2H, CH_2O); 3.87–3.68 (m, 2H, CH_2O); 3.55–3.28 (m, 4H, CH_2-N=CH and CH_2-NH; 2H, CH_2O THP); 1.80–1.50 (m, 4H, CH_2-CH_2-O); 1.30 (m, 20H, (CH_2)).

[8-(3-(11-Hydroxyundecyloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-1,3,7-trienato](2-) nickel(II) (7)

The tetrahydropyranyloxy protected nickel complex **6** (0.500 g, 0.848 mmol) was dissolved in Cl_2CH_2/MeOH (1:1, 20 mL) and 4-toluenesulphonic acid monohydrate (16 mg, 0.0848 mmol) was added. The solution was heated to reflux in air for 12 h. The reaction mixture was then cooled to room temperature and the solvents evaporated. The residue was subjected to column chromatography on flash grade silica gel, eluting with Cl_2CH_2/THF (4:1). The alcohol-terminated nickel complex ($R_f = 0.33$) was isolated as golden-red needles from methanol (0.217 g). The isolated unreacted starting nickel complex ($R_f = 0.66$) was subjected to hydrolysis as above, to yield a second crop of the alcohol (0.089 g). Combined yield = 0.300 g (85%).

Melting point: 210°C.

Microanalysis: Calcd for $C_{29}H_{38}O_4N_2Ni$: C 64.83; H 7.12; N 5.21. Found: C 64.62; H 7.05; N 4.92. MS (EI): m/z 536 (M^+-1). IR (KBr disc, υ; cm^{-1}): 3423 (vs, broad; OH); 1606, 1592 (vs, sharp; C=N, C=O and C=C-N coordinated).

^{1}H NMR ($CDCl_3$): δ 7.45–7.10 (m, 8H; aromatic C_6H_5, *H*C=N, *H*C=O and NC*H*=C); 6.93 (s, broad, 2H, H_a, H_b); 6.53 (m, 1H, H_c); 3.83 (t, (J = 7 Hz), 2H, CH_2O-Ph); 3.65 (q broad (J = 6 Hz), 2H, CH_2-OH); 3.40 (m, 2H, CH_2-N=CH); 3.31 (m, 2H, CH_2-NH); 1.73 (m, 2H, CH_2-CH_2-O); 1.30 (m, 16H, $(CH_2)_8$).

[8-(3-(11-Acryloxyundecyloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-1,3,7-trienato](2-) nickel(II) (8)

The alcohol-terminated nickel complex **7** (0.300 g, 0.558 mmol) was dissolved in a mixture of sodium dried toluene and dichloromethane 1/1 (30 mL) under a dry nitrogen atmosphere. Acryloyl chloride (Fluka) (0.054 mL, 0.669 mmol) was added and the solution stirred for 5 minutes. Triethylamine (0.093 mL, 0.669 mmol) was added and a few crystals of hydroquinone were added to stabilise the solution. The red suspension was stirred at room temperature (18 h). On cooling to room temperature, the solvent was evaporated *in vacuo* at room temperature and the residue purified by flash column chromatography on silica gel using Cl_2CH_2/THF (9:1) as the eluent system to yield red crystals of **8**. Yield = 0.130 g (40%).

Melting point = 185°C.

Microanalysis: Calcd for $C_{32}H_{40}O_5N_2Ni.1/2\ CH_2Cl_2$: C 61.59; H 6.51; N 4.41. Found: C 60.78; H 6.43; N 4.37. MS (EI): m/z 591 (M^+); 365 (M^+-$(CH_2)_{11}OCOCH{=}CH_2$).

IR (KBr disc, υ cm^{-1}): 1710 (vs, sharp, COO); 1620 (sh), 1608 (vs, sharp; C=N, C=O and C=C-N coordinated).

^{1}H NMR ($CDCl_3$; 400 MHz): δ 7.45–7.10 (m, 8H; aromatic C_6H_5, *H*C=N, *H*C=O and NC*H*=C); 6.93 (s, broad, 2H, H_a, H_b); 6.53 (m, 1H, H_c); 6.39 (d, ($J_{trans} = 17$Hz)d($J_{de} = 1$Hz), 1H, $\boldsymbol{H}_e$); 6.12 (d, ($J_{trans} = 17$Hz), d, ($J_{cis} = 10$Hz), 1H, H_f); 5.81 (d, ($J_{cis} = 10$Hz), d, ($J_{de} = 1$Hz), 1H, H_d); 4.15 (t, (J = 7 Hz), 2H, C*H*$_2$-OCO); 3.82 (t, (J = 7Hz), 2H, C*H*$_2$O-Ph); 3.39 (t, (J = 6 Hz), 2H, C*H*$_2$-N=CH); 3.30 (t, (J = 6 Hz), 2H, C*H*$_2$-NH); 1.95 (s, 3H, C*H*$_3$-CH =); 1.69 (m, 2H, C*H*$_2$-CH$_2$-O); 1.33 (m, 16H, (C*H*$_2$)$_8$).

[8-(3-(11-Methacryloxyundecyloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-1,3,7-trienato](2-) nickel(II) (9)

The alcohol-terminated nickel complex **7** (0.185 g, 0.345 mmol) was dissolved in sodium dried toluene (30 mL) under nitrogen atmosphere. Methacryloyl chloride (0.033 mL, 0.345 mmol) was added and the solution stirred for 5 minutes. A few crystals of hydroquinone were added to stabilise the solution then triethylamine (0.048 mL, 0.345 mmol) was added and the red suspension stirred at room temperature (18 h). The solvent was evaporated *in vacuo* at room temperature and the residue purified by flash column chromatography on silica gel using Cl_2CH_2/THF (9:1) as the eluent system to yield red crystals of **9**. Yield = 0.124 g (60%).

Melting point = 185°C.

Microanalysis: Calcd for $C_{33}H_{42}O_5N_2Ni$: C 65.47; H 6.98; N 4.62. Found: C 65.31; H 7.03; N 4.53. MS (EI): m/z 605 (M^+); 368 (M^+-$(CH_2)_{11}$OCO-MeCH=CH_2). IR (KBr disc, υ; cm^{-1}): 1710 (vs, sharp, COO); 1620 (sh), 1608 (vs, sharp; C=N, C=O and C=C-N coordinated).

^{1}H NMR ($CDCl_3$): δ 7.45–7.10 (m, 8H; aromatic C_6H_5, *H*C=N, *H*C=O and NC*H*=C); 6.93 (s, broad, 2H, H_a, H_b); 6.53 (m, 1H, H_c); 6.10 (s, 1H, *cis*-C*H*=C(COO)); 5.55 (m, 1H, *trans*-CH=C(COO)); 4.14 (t, (J = 7 Hz), 2H, C*H*$_2$-OCO); 3.82 (t, (J = 7 Hz), 2H, C*H*$_2$O-Ph); 3.40 (m, 2H, C*H*$_2$-N=CH); 3.32 (m, 2H, C*H*$_2$-NH); 1.95 (s, 3H, C*H*$_3$-CH=); 1.70 (m, 2H, C*H*$_2$-CH$_2$-O); 1.30 (m, 16H, (C*H*$_2$)$_8$).

Polymerisation Reactions

Polymerisation reactions were carried out in sodium/benzophenone-dried THF, using AIBN as radical initiator, under nitrogen atmosphere. In both cases, the final polymer was precipitated from dichloromethane into a large volume of methanol with vigorous stirring. Absence of initial monomer was checked at this stage by thin layer chromatography. The polymers were recovered by filtration and dried under vacuum for several hours. The ^{1}H NMR spectra of the polymers showed broad resonances, typical of polymers, however resolution was sufficient to allow relative integrations

to be calculated: the absence of unreacted monomer was confirmed in both cases.

Poly[8-(3-(11-acryloxyundecyloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-1,3,7-trienato](2-) nickel(II)] (10)

The acrylate monomer **8** (84 mg, 0.142 mmol) and 66 μL of a solution of AIBN (0.1 g) in dry THF (10 mL) [inititor/monomer ratio = 3 mol%] were placed in a Schlenck tube that was evacuated then filled with nitrogen several times. Freshly distilled dry THF (6 mL) was added and the solution subjected to three freeze-thaw cycles, then flushed with nitrogen. The tube was placed in an oil bath at 70°C to initiate the polymerisation. After 48 h the reaction solution was cooled to room temperature, whereupon a fine ochre coloured solid precipitated out. The whole mixture was evaporated to dryness, the residue dissolved in CH_2Cl_2 (3 mL) and precipitated into methanol (200 mL) with vigorous stirring. This procedure was repeated once more, until the solid showed no trace of acrylate monomer by TLC. The red-ochre solid was filtered off and dried under vacuum. Yield = 44 mg (53%).

Mesomorphism: Cryst 167 SmA 260 dec °C.

Microanalysis: Calcd for $C_{32}H_{40}O_5N_2Ni$: C 64.99; H 6.81; N 4.73. Found: C 64.24; H 6.96; N 4.45. IR (KBr disc, υ; cm^{-1}): 1710 (vs, sharp, COO); 1620 (sh), 1608 (vs, sharp; C=N, C=O and C=C-N coordinated).

^{1}H NMR ($CDCl_3$; 400 MHz): δ 7.45–7.10 (m, 8H; aromatic C_6H_5, *H*C=N, *H*C=O and NC*H*=C); 6.89 (s, broad, 2H, H_a, H_b); 6.40 (broad, 1H, H_c); 4.05 (s, 2H, CH_2-OCO); 3.76 (s, br, 2H, CH_2O-Ph); 3.34 (s, br, 4H, CH_2-N=CH, CH_2-NH); 2.51–2.00 (br, CH2-C*H*-OCO); 1.84 (br, C*H*2-C*H*-OCO); 1.69 (m, br, 2H, CH_2-CH_2-O); 1.60 (m, br, 2H, CH_2-CH_2-O); 1.33 (m, 16H, (CH_2)$_8$).

Poly[8-(3-(11-methacryloxyundecyloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-1,3,7-trienato](2-) nickel(II)] (11)

Polymer **11** was prepared following the procedure described above from the methacryloxy nickel complex (80 mg, 0.132 mmol) and AIBN (0.2 mg, 1 mol%) in THF (6 mL). Yield = 50 mg (62%).

Mesomorphism: g 129 E/B 189 SmA 195 Iso °C.

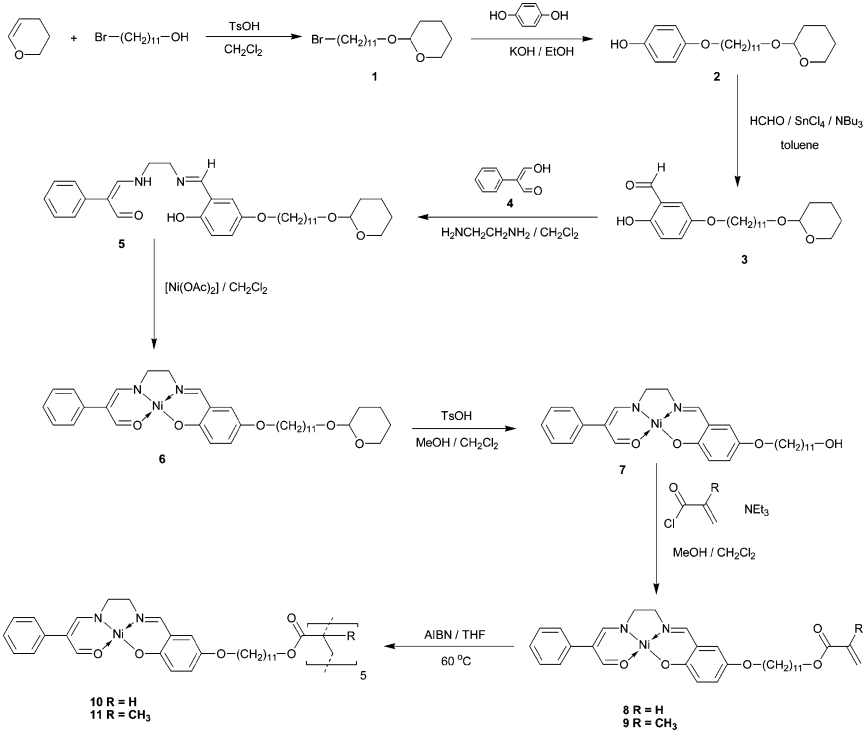
Microanalysis: Calcd for $C_{33}H_{42}O_5N_2Ni$: C 65.47; H 6.98; N 4.62. Found: C 65.11; H 6.83; N 4.61. IR (KBr disc, υ; cm^{-1}): 1710 (vs, sharp, COO); 1620 (sh), 1608 (vs, sharp; C=N, C=O and C=C-N coordinated).

^{1}H NMR ($CDCl_3$): δ 7.45–6.50 (m, 11H; aromatic C_6H_5, *H*C=N, *H*C=O, NC*H*=C, H_a, H_b, H_c); 4.05 (s, br, 2H, CH_2-OCO); 3.76 (s, br, 2H, CH_2O-Ph); 3.34 (s, br, 4H, CH_2-N=CH, CH_2-NH); 2.51–1.50 (br, several signals, CH_2-C*H*-OCO, CH_2-C*H*-OCO); CH_2-CH_2-O, CH_2-CH_2-O); 1.33 (m, 16H, (CH_2)$_8$).

RESULTS AND DISCUSSION

Synthesis

The synthesis of the nickel-containing monomers proved more difficult than the analogous monomers used in the siloxane syntheses [13–15], requiring the use of a tetrahydropyranyl (THP) protecting group from an early stage of a linear synthesis as shown in Scheme 1. 11-Bromodecanol was protected with dihydropyran to give the THP intermediate **1** which was used to alkylate hydroquinone to **2** in good yield. This was then formylated, again in good yield, using paraformaldehyde and tin(IV) chloride to give the substituted salicylaldehyde **3** which was condensed with equimolar quantities of 2-phenylmalonaldehyde (**4**) and 1,2-diaminoethane to give **5** in reproducible yields of up to 30%. Complex **6** was formed in 80% yield and then deprotected to give the hydroxy-terminated complex **7** in 85% yield. The acrylate (**8**) and methacrylate (**9**) monomers were prepared by reacting **7** with acryloyl chloride or methacryloyl chloride respectively



SCHEME Synthetic pathway to the nickel(II)-containing monomers and polymers.

in quantitative yields. Polymerisation was achieved using AIBN as the radical initiator in THF solvent at 60°C. The polymers were obtained pure in approximately 50% yield as dark brown waxy solids by repeated precipitations from dichloromethane/methanol. The average degree of polymerisation for both the methacrylate and acrylate was determined to be 5 by ^{1}H NMR (270 MHz) using end group analysis based on the relative integrations of the signals. This was disappointing but can be attributed to the low solubilities of the products in THF at 60°C, resulting in premature precipitation and therefore termination of the reaction. Alternatively, it could be that the metal plays a key role in the polymerisation process by hindering the radical process and so either terminating the reaction or retarding it to an extent where only short chains are formed [9,10]. The average molecular weights (M_n) of the polymethacrylate and polyacrylate are 3027.6 and 2957.5 daltons respectively. Alternatively, intermolecular metal–metal interactions of the type reported previously for the siloxane systems [8] may also result in non-covalent networks that cause premature precipitation, although this might not be such an important factor bearing in mind the relatively low concentration of the reaction solution. Efforts are now being focussed on to the feasibility of performing solid-state polymer synthesis from a monomer melt under UV irradiation.

Mesomorphic Properties

The melting behaviour of the materials prepared was investigated by hot-stage polarising light microscopy and transitions confirmed by differential scanning calorimetry. All intermediates and the ligand were found to exhibit simple melting behaviour, with the exception of the THP protected nickel complex (**6**), which exhibited a monotropic smectic A phase on cooling from the isotropic liquid as shown in Table 1. Removal of the THP protecting group gave the terminal hydroxy-substituted complex which was non-mesomorphic, undergoing simple melting at 210°C. Esterification gave either the methacrylate (**8**) or acrylate (**9**) monomers, which again underwent simple melting at 185 and 154°C respectively.

On polymerisation we were surprised to discover that the materials were liquid crystalline despite the simple melting behaviour of the monomers. The polymethacrylate (**10**) was a waxy solid at room temperature which underwent a glass transition, characterised by a second order thermal event of the DSC thermogram, at 167°C, only 13°C higher than the melting point of the monomer. Observation of the optical texture by polarised light microscopy revealed a smectic A phase characterised by small focal conic defects. A good cooling texture could not be obtained because the sample rapidly decomposed at 260°C and consequently a value for the enthalpy could not be determined. It is recognised that the increased flexibility of

TABLE 1 Transition Temperatures of the Nickel(II)-Containing Intermediates, Monomers and Polymers (°C) with Transition Enthalpies (kJ mol^{-1}) Given in Parentheses

Material	Cryst	g		E/B		SmA		Iso
6	•	–		–	(134	•)	158	•
7	•	–		–		–	210	•
8	•	–		–		–	185	•
9	•	–		–		–	154	•
10	–	•		–	167 T_g	•	260 *	dec
11	–	•	129 T_g	•	189 (9.1)	•	195 (0.1)	•

*Peak not observed due to broad decomposition.

the polyacrylate backbone relative to the polymethacrylate results in a decrease in the glass transition and liquid crystalline phase transition temperatures [16]. Consequently the polyacrylate (**11**) exhibited a glass transition temperature at 129°C to give an anisotropic plastic crystal phase. A first order endothermic transition to a smectic A phase was observed at 189°C (9.1 kJ mol^{-1}), which was stable up to 195°C (9.1 kJ mol^{-1}) when the isotropic liquid phase formed without decomposition. This allowed us to achieve some good optical textures by slowly annealing from the isotropic liquid over a period of several hours. The focal conic texture confirmed the smectic A phase, while the lower temperature ordered phase

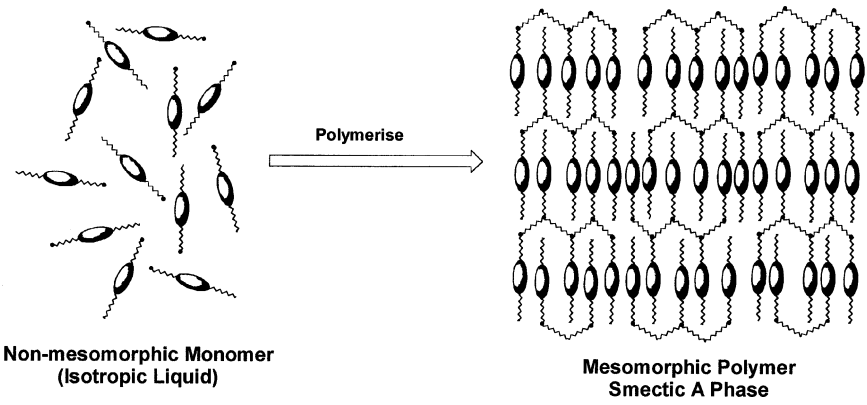


FIGURE 1 Schematic representation of self-organisation of the mesogenic complexes on polymerisation.

was most likely an E or B phase based on the fine mosaic texture observed, however without X-ray diffraction data we were unable to differentiate between the two. Studies are currently in progress to characterise the liquid crystalline phases of the polymers by small angle X-ray scattering (SAXS) studies as a function of temperature over the range of mesophase existence. Preliminary results have been obtained using unaligned samples, however the SAXS patterns are poor; giving in the case of the methacrylate at 140°C a broad, diffuse reflection corresponding to a layer spacing of approximately 28 Å consistent with molecular dimensions. No lateral spacings could be assigned. It was not possible to obtain good data for the acrylate because of decomposition.

The fact that only orthogonal smectic phases are observed is consistent with results obtained for polymeric siloxane materials derived from structurally similar nickel [13,14] and copper [15] complexes. Although not covalently bonded, we have shown by single crystal and small angle X-ray scattering [14] that intermolecular metal–metal or metal–ligand interactions promote layer formation and stabilise orthogonal liquid crystal phases. In the case of the materials reported here, immobilisation of the non-liquid crystalline monomer complexes on a short polymer backbone serves to bring the cores into close proximity. This allows for intermolecular interactions and so promotes smectic phase formation (Figure 1). As the monomers are themselves non-liquid crystalline, the polymer backbone may be regarded as acting as a template self-organisation and hence mesophase stabilisation. A similar effect has been noted by Bazuin and co-workers [17] in the case non-covalent, but ionic complexation of non-liquid crystalline monomers to a poly(sulfonate) backbone.

CONCLUSIONS

Two polymers based on organic (meth)acrylate backbones have been synthesised and have been shown to exhibit liquid crystalline phases. Whilst the degree of polymerisation is low (DP = 5) we have demonstrated a proof of principle in that we have shown that anisotropic inorganic monomers can be polymerised using conventional chemistries to produce assemblies in which the complex is immobilised at one point whilst the remainder of the molecule is not covalently cross-linked. Furthermore, we have shown that immobilisation of the complexes onto a backbone actually promotes liquid crystalline phase behaviour through self-assembly of the non-mesomorphic monomers. This has now opened up a number of possibilities for future work including co-polymerisation with organic monomers and investigations into the application of such polymers as immobilised catalysts in organic chemistry.

REFERENCES

[1] Serrano, J. L. (1996). (Ed.), *Metallomesogens: Synthesis, Properties and Applications*, Wiley: Weinheim.
[2] Giroud, A. M. & Maitlis, P. M. (1991). *Angew. Chem. Int. Ed. Engl.*, *30*, 375.
[3] Hudson, S. A. & Maitlis, P. M. (1993). *Chem. Rev.*, *93*, 861.
[4] Oriol, L. & Serrano, J. L. (1995). *Adv. Mater.*, *7*, 348.
[5] Deschenaux, R., Kosztics, I., Scholten, U., Guillon, D., & Ibn-Elhaj, M. (1994). *J. Mater. Chem.*, *4*, 1351.
[6] Deschenaux, R., Jauslin, I., Scholten, U., Turpin, F., Guillon, D., & Heinrich, B. (1998). *Macromolecules*, *31*, 5647.
[7] Turpin, F., Guillon, D., & Deschenaux, R. (2001). *Mol. Cryst., Liq. Cryst.*, *362*, 171.
[8] Valdebenito, N., Oriol, L., Barbera, J., Diaz, F., & Serrano, J. L. (2000). *Macromol. Chem. Phys.*, *201*, 2573.
[9] Oriol, L., Pinol, M., Poelsma, S., Serrano, J. L., & Vinuales, A. (2000). *J. Polym. Sci. Part A-Polym. Chem.*, *38*, 4466.
[10] Ghedini, M., Aiello, I., & Roviello, A. (1997). *Acta Polym.*, *48*, 400.
[11] Ghedini, M., Panunzi, B., & Roviello, A. (1998). *Liq. Cryst.*, *25*, 225.
[12] van der Pol, J. F., Neeleman, E., Nolte, R. J. M., Zwikker, J. W., & Drenth, W. (1989). *Makromol. Chem.*, *190*, 2727.
[13] Saez, I. M. & Styring, P. (1996). *Adv. Mater.*, *8*, 1001.
[14] Saez, I. M., Styring, P., Mehl, G. H., & Sinn, E. (1998). *J. Organomet. Chem.*, *551*, 299.
[15] Saez, I. M. & Styring, P. (1997). *Mol. Cryst. Liq. Cryst.*, *299*, 163.
[16] Percec, V. & Pugh, C. (1989). Side chain liquid crystal polymers. In: McArdle, C. B., (Ed.) Blackie: Glasgow, London.
[17] Bazuin, C. G. & Tork, A. (1995). *Macromolecules*, *28*, 8877.