THE UNIVERSITY OF HULL

Synthesis and characterization of gold nanoparticle composites with side chain liquid crystals

being a Thesis submitted for the Degree of Doctor of Philosophy (PhD) in Chemistry in the University of Hull

by

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Abstract

The properties of specifically designed nanocomposites are currently of high interest to scientists as they are different to those of materials in bulk. Of special interest are nanocomposites made up of gold nanoparticles and liquid crystalline materials. Since most applications of metal nanoparticles are based on their assemblies, controlling their self–assembly opens the potential to synergistic property combination of these composites, most actively discussed are currently those of optical metamaterials.

Here the results of the investigation of gold nanoparticle (AuNP)- and gold nanorod (AuNR)- side-chain liquid crystalline polymer chains (SCLCPs) are presented. The synthesis of these nanoystems were explored systematically. The preparation of SCLCPs, either by grafting to the NPs or by polymerisation from the preparation of an Au-NP macroinitiator were explored. The mode of polymerisation either free radical polymerisation or atom transfer radical polymerisation (ATRP) was varied.

Firstly, the AuNPs and AuNRs were synthesised and fully characterised. The sizes of AuNPs investigated were 2 nm and 3 nm while the average dimension of AuNRs investigated was 26 nm x 8 nm, with an aspect ratio of 3. These nano species were either functionalized directly with the LC thiol and/or functionalized with initiator and used as a macroinitiator in the polymerisation of different monomers.

The mesogenic compound used in the investigation was 4'-undecycloxybiphenyl-4-yl 4octyloxy-2-(pent-4-en-1-yloxy) benzoate. The alkene end of the mesogen was converted to polymerisable end group through a range of chemical reactions. The polymerisation of these polymers were investigated first by free radical polymerisation, before been polymerised using AuNP/AuNR-initiator modified to act as macroinitiators to obtain the targeted composites.

For polymer/nano composites, the optimum structural control of the composite was achieved by preassembling the inorganic nanoparticles with the organic polymer. With accurate compositional specification of the final composite, different methods were used for the synthesis which includes grafting of a polymer chain to the surface through a covalently linked monomer, or grafting polymer chains from polymerisation initiatorsmodified surfaces.

Based on these points, liquid crystalline polymeric composites were synthesised using both 'grafting from' and 'grafting to' methods. Disulfide functional initiator was prepared followed by methacrylate which was attached to the mesogen and polymerised. The Cu(I)Br/2,2'-bipyridine mediated atom transfer radical polymerisation of the methacrylate was first investigated and the polymer obtained fully characterised. The polymerizations of the methyacrylate mesogenic compounds were then investigated. The disulfide-containing polymers were cleaved to obtain active thiol-polymers which were coupled to the NPs to afford the composites.

The initiator-coupled AuNPs and AuNRs were used as the macroinitiator in the polymerization of the methacrylate mesogenic monomers in the 'grafting from' method. The mesogen, nanoparticles and the composites were analysed by TLC, ¹H NMR, ¹³C NMR, mass spectrometry, elemental analysis and SEM while the liquid crystalline properties of the mesogens were further determined by DSC, XRD and OPM techniques.

iv

The average gold nanoparticle size/distribution was determined by GPC and TEM. The properties of polymers were determined by GPC, mass spectrometry and NMR.

Table of contents

Title page	
Acknowledgement	i
Abstract	ii
Table of contents	iv
List of schemes	ix
List of tables	xi
List of figures	xiv

CHAPTER ONE: Introduction

1.1	Liquid crystals	1
1.2	Liquid crystal phases	5
1.3	Metal nanoparticles	12
1.4	Gold nanoparticles (AuNPs)	17
1.5	Properties of materials at nano-level	19
1.6	Introduction to liquid crystal-nanoparticle composites	22
1.7	AuNP grafted polymeric composites	25
1.8	Gold nanorods (AuNRs)	25
1.9	Liquid crystalline polymers	27
1.10	Polymerization	28
1.11	Atom Transfer Radical Polymerization (ATRP)	29
1.12	Methods for Characterisation of Nanoparticle Liquid Crystals	33

1.13	Earlier works	.40
Refere	nces	.42

CHAPTER TWO

Project target

CHAPTER THREE: Synthesis Gold nanoparticles and gold nanorods

3.1	Introduction	.52
3.2	Synthesis of AuNPs	53
3.4	1-Docanethiol capped gold nanoparticles	.58
3.5	Gold nanorods (AuNRs)	65
3.6	Experimental procedures	.68
Refere	nces	.72

CHAPTER FOUR: Composites of gold nanorods and organic mesogens

4.2	Synthesis of the mesogens73
4.3	Synthesis of 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-mercaptopentyl)oxy)-4-
(octyle	(4.9)
4.4	Synthesis of AuNP-4'-(Undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-mercaptopentyl)oxy)-
4-(oct	yloxy) benzoate liquid crystal composite (4.10)77
4.5	Synthesis of AuNP-Ethoxysilane composite (4.13)77
4.6	Results and Discussion79

4.7	Gold nanoparticle-4'-(Undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-mercaptopentyl)	oxy)-4-
(octyl	loxy) benzoate liquid crystal	.86
4.8	AuNP-ES Nanocomposite (composite 4.13)	99
4.9	Ethoxysilane mesogen (compound 4.11)	99
4.10	Conclusion	.105
4.11	Experimental Procedure	108
	References	127

CHAPTER FIVE: Side chain liquid crystalline polymers

5.1	Introduction	129
5.2	Side chain liquid crystal polymers	.130
5.3	Synthesis of side chain thiol polymer	.146
5.4.1	Conclusion	151
5.5	Experimental procedures	152
	References	.172

CHAPTER SIX: Composites of gold nanoparticles and side chain liquid crystalline polymers

6.1	Synthesis of AuNP-polymer liquid crystalline composites	.173
6.2	Synthesis of AuNP-polymer liquid crystalline composites	175
6.3	Synthesis of composite 6.15	178
6.4	Synthesis of composite 6.18	180
6.5	Synthesis of composite 6.20	182

6.6	Synthesis of composite 6.21	
6.7	Synthesis of composite 6.27	
6.8	Results and Discussion	
6.9.2	Polymer grafting from AuNP macroinitiator surface	200
6.10	Composite 6.15	208
6.11	Composite 6.18	215
6.12	Composite 6.19	221
6.13	Composite 6.20	224
6.14	Composite 6.26	231
6.15	General discussion	240
6.16	Conclusion	243
Expe	rimental procedures	
	References	270

CHAPTER SEVEN: Composites of gold nanorods and side chain liquid crystalline

Polymers

7.1	Introduction	.272
7.1.1	Gold nanorod synthesis and ligand exchange	.273
7.2	Synthesis of composite 7.2	.275
7.3	Total replacement of CTAB on AuNRs (7.3)	.282
7.4	Polymerization at 60 °C (composite 7.4)	286
7.5	Polymerization with a longer chain macroinitiator	.294
7.6	Synthesis of composite 7.11	.297

7.7	Synthesis of composite 7.14	
7.8	Experimental procedures	
	References	
	General conclusions	
	Outlook	327
	Compounds identity	

List of schemes

Scheme 1.1:	Mechanism of metal complex-mediated ATRP30
Scheme 4.1:	Synthesis of thiol mesogens 4.974
Scheme 4.2:	Synthetic routes for composites 4.1378
Scheme 4.3:	Synthesis of Methyl-2,4-dihydroxybenzoate108
Scheme 4.4:	Synthesis of Methyl-2-dihydroxy-4-octyloxybenzoate109
Scheme 4.5:	Synthesis of Methyl-4-octyloxy-2-(pent-4-en-1-yloxy) benzoate110
Scheme 4.6:	Synthesis of 4-Octyloxy-2-(pent-4-en-1-yloxy) benzoic acid111
Scheme 4.7:	Synthesis of 4-Hydroxy-4'-undecycloxybiphenyl112
Scheme 4.8:	Synthesis of 4'-Undecycloxybiphenyl-4-yl 4-octyloxy-2-(pent-4-en-1-
	yloxy)benzoate114
Scheme 4.9:	Synthesis of 4'-(undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-acetylthio)pentyl)oxy)-
	4-(octyloxy) benzoate116
Scheme 4.10:	Synthesis of 4'-(undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-mercaptopentyl)oxy)-4-
	(octyloxy) benzoate118
Scheme 4.12:	Synthesis of 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 4-(octyloxy)-2-((5-
(triethoxysilyl)pentyl)oxy)benzoate (4.13)125
Scheme 4.13:	Reacting AuNPMUD with 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 4-(octyloxy)-2-
((5-(triethoxys	silyl)pentyl)oxy)benzoate (AuNP-7ES)126
Scheme 5.1:	Synthesis of monomer 20130
Scheme 5.2:	Polymerization of 5.6131
Scheme 5.3:	Synthesis of monomer 5.9
Scheme 5.4:	Polymerization of 5.9

Scheme 5.5:	Synthesis of monomer 5.14
Scheme 5.6:	Polymerization of 5.15134
Scheme 5.7:	Synthesis of polymer 5.17147
Scheme 5.8:	Synthesis of but-3-en-lyl methacrylate (5.3)152
Scheme 5.9:	Synthesis of 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 4-(octyloxy)-2-((5-(1,1,3,3-
tetramethyldis	siloxanyl)pentyl)oxy)benzoate (5.5)154
Scheme 6.1:	Synthetic routes for composite
Scheme 6.2:	Synthetic routes for composite 6.15179
Scheme 6.3:	Synthetic routes for composite 6.18181
Scheme 6.4:	Synthetic routes for composite 6.20182
Scheme 6.5:	Synthetic routes for composite 6.21
Scheme 6.6:	Synthetic routes for composite 6.27
Scheme 7.1:	Synthetic routes for composite 7.2
Scheme 7.2:	Synthetic routes for composite 7.4
Scheme 7.3:	Synthetic routes for composite 7.11
Scheme 7.4:	Synthetic routes for composite 7.11
Scheme 7.5:	Synthetic routes for composite 7.14

List of tables

Table 1.1: Properties of Nanoparticles
Table 3.1: Volume requirement for each molar ratio of the ligands
Table 3.2: Maximum wavelength (nm) for corresponding AuNPs
Table 3.4: Size distribution of AuNPs61
Table 3.5: Changes in concentration of 1-Dodecanethiol and temperature of AuNPs64
Table 3.6: Size distribution of AuNRs
Table 4.1: Yield and elemental analysis results of compounds
Table 4.2: Thermal behaviour of compounds 4.7, 4.8, 4.9.82
Table 4.3. Transition temperature4.7, 4.8, 4.9.83
Table 4.4: Size distribution of composite 4.10. 89
Table 4.6: Sizes of compound 4.12
Table 4.7: Elemental analysis of compound 4.12
Table 4.8: Sizes of composite 4.13
Table 4.9: XRD data of composite 4.13
Table 4.10. Elemental analysis of composite 4.13104
Table 4.11: Elemental analysis and TGA results for the composites
Table 4.12: N_{Au} , N_L and M_w for the nanocomposites107
Table 5.1: Comparative data of 5.7, 5.10 and 5.15

Table 5.2: Liquid crystalline properties of the intermediates, monomer and polymers136
Table 5.3: Thermal behaviour of polymers under nitrogen and in air
Table 6.1: Results of polymerization monitored by GPC
Table 6.2: Thermal properties of 5.5 and 5.6
Table 6.3: Size distribution of 6.9. 198
Table 6.4: XRD data of composite 6.9
Table 6.5: XRD data of 6.12
Table 6.6: Elemental analysis of 6.15
Table 6.7: XRD data of 6.15
Table 6.8: properties of 6.16.
Table 6.9: Elemental composition of 6.20
Table 6.10: XRD data of composite 6.20. 231
Table 6.11: Elemental composition of 6.26
Table 6.12: XRD data of composite 6.26
Table 6.13: Elemental analysis and TGA results for the composites
Table 6.14: N _{Au} , N _L and M _w for the nanocomposites243
Table 7.1: Size distribution of 7.2

Table 7.2: Average dimension and A/R of 7.2.	278
Table 7.3: Elemental composition 7.2.	.279
Table 7.4: Size distribution of 7.3.	.284
Table 7.5: Average dimension and A/R of 7.3	.285
Table 7.6: Elemental composition of 7.3	285
Table 7.7: Size distribution of 7.4	.290
Table 7.8: Average dimension and A/R of 7.4	291
Table 7.9: Average dimension and A/R of 7.4	.291
Table 7.10: Elemental composition of 7.11	299
Table 7.11: Elemental composition	.303
Table 7.12: Elemental composition of 7.14	313

List of figures

Figure 1.1: Cholesteryl benzoate
Figure 1.1.1: Examples of lyotropic liquid crystals
Figure 1.2: Example of calamitic liquid crystal4
Figure 1.3: Example of discotic liquid crystal5
Figure 1.4: Thermotropic LC phases5
Figure 1.5: Appearance of liquid crystal phases in a temperature profile6
Figure 1.6: Structure of nematic phase7
Figure 1.7: Structures of SmA and SmC phases7
Figure 1.8: Order of molecules in smectic A mesophase
Figure 1.9: Order of molecules in smectic C mesophase
Figure 1.10: The chiral smectic C phase9
Figure 1.11: Structure of the Cholesteric Phase10
Figure 1.12: Phase changes with temperature11
Figure 1.13: (a) Marvellous funerary mask of Tutankhamun (b)-(c) The Lycurgus Cup (c)
Medieval Stained Glass13
Figure 1.14. NP formation16
Figure 1.15: Different colours of gold nanoparticles are the result of SPR20
Figure 1.17: SPR of plasmonic materials21
Fig. 1.18 Schematic of plasmon oscillation

Figure 1.19: General template of MCLCPs and SCLCPs27
Figure 1.20 DSC plot with phase sequence of 80CB35
Figure 1.22: X-ray diffractometer features
Figure 1.23: Schematic outline of a TEM
Figure 1.24: AuNP covered with mesogen
Figure 2.1: Summary of project target
Figure 3.1: Schematic representation of AuNP preparation
Figure 3.2: Plasmonic behaviour of AuNPs (a)
Figure 3.3: Plasmonic behaviour of AuNPs(b)
Figure 3.4 (a): ¹ H NMR spectra of free 1-Dodecanethiol
Figure 3.4 (b): ¹ H NMR spectra of gold nanoparticle capped with 1-Dodecanethiol59
Figure 3.5: TEM images of AuNPs60
Figure 3.6: Size distribution of the AuNPs
Figure 3.7: The UV-Vis of AuNPs (a) 2 nm (b) 3 nm63
Figure 3.8: Size distribution of AuNPs
Figure 3.9: AuNRs as prepared66
Figure 3.10 is the TEM image of the AuNRs
Figure 3.11: UV-vis spectrum of AuNRs
Figure 4.1: Synthesis of the AuNP composite75
Figure 4.2: Synthesis of composite 4.1377
Figure 4.3: ¹ H NMR of 4.7, 4.8 and 4.981
Figure 4.4-4.6: DSC heating and cooling curve of compound 4.7, 4.8, 4.9

Figure 4.7: POM textures observed of 4.7, 4.8, and 4.9	35
Figure 4.8: ¹ H NMR of compound 4.9	85
Figure 4.9-4.11: ¹ H NMR of composite 4.10 (2 nm), 4.10 (3 nm), direct mesogen-capped A	uNP
LC	7
Figure 4.12a: TEM image of composite 4.108	39
Figure 4.12b: Size distribution of composite 4.109	0
Figure 4.13: OPM image of composite 4.109)0
Figure 4.14: SEM images of 4.10	91
Figure 4.15: DSC heating and cooling curve of coupled 4.10 (2 nm)9	91
Figure 4.16: DSC heating and cooling curve of composite 4.10 (3 nm)9	92
Figure 4.17: TGA thermogram of 4.10 (3 nm)	93
Figure 4.17: TGA thermogram of 4.10 (2 nm)	93
Figure 4.18: UV-vis of 4.10 (a) 2 nm (b) 3 nm9	94
Figure 4.19: ¹ H NMR of 11-mercapto-1-undecanol and compound 4.1	95
Figure 4.19: TEM of 4.129	96
Figure 4.20: Compound 4.12 size distribution	97
Figure 4.21: TGA thermogram of compound 4.12	98
Figure 4.22: UV-vis of compound 4.12	98
Figure 4.23: ¹ H NMR of mesogen 4.11 and nanocomposite 4.13	99
Figure 4.24: TEM of 4.131	00
Figure 4.25: DSC of composite 4.131	.01
Figure 4.26: POM texture of composite 4.131	.01
Figure 4.27: XRD of composite 4.131	02

Figure 4.28: TGA thermogram of composite 4.13103
Figure 4.29: UV-Vis spectrum of composite 4.13104
Figure 5.1: POM textures of monomers and polymers
Figure 5.2: DSC curves monomers and polymers
Figure 5.3: DSC heating and cooling curves for 5.7
Figure 5.4: DSC heating and cooling curves for 5.10
Figure 5.5: DSC heating and cooling curves for 5.15140
Figure 5.6: TGA (in nitrogen) thermograph of 5.7, 5.10 and 5.15142
Figure 5.7: TGA (in air) thermograph of 5.7, 5.10 and 5.15143
Figure 5.8: ¹ H NMR of monomer 5.12148
Figure 5.9: ¹ H NMR of polymer 5.16148
Figure 5.10: ¹ H NMR of 5.13149
Figure 5.11: ¹ H NMR of monomer 5.19149
Figure 57: POM textures of 5.17150
Figure 6.1: The general template of the composites173
Figure 6.2: Removal of catalyst (Cu(I)Br) from polymer185
Figure 6.3: Crude polymer
Figure 6.3: Increase in Mn with (a) reaction time (min); (b) conversion (%)187
Figure 3.38: ln([M] ₀ /[M]) vs time (min)188
Figure 6.5: Rate of monomer consumption
Figure 6.6: The ¹ H NMR of compound 4.7, 5.5 and 5.6190
Figure 6.7: Texture observed from POM for 5.5 and 5.6 after cooled by cardice192
Figure 6.8: Transition of compound 5.5 to isotropic after cooled by liquid N ₂ 192

Figure 6.9: DSC for 5.5 and 5.6193	
Figure 6.10: ¹ H NMR of 6.8	
Figure 6.11: Transition of compound 5.5 to isotropic after cooled by liquid N ₂ 195	
Figure 6.12: DSC heating and cooling curves of 6.8195	
Figure 6.13: ¹ H NMR of 24 and 6.9196	
Figure 6.14: SEM images of 6.9197	
Figure 6.15: EDS of 6.9197	
Figure 6.16: TEM image of 6.9198	
Figure 6.17: POM image of 6.9199	
Figure 6.18: UV-Vis spectrum of 6.9	
Figure 6.19: XRD of composite 6.9200	
Figure 6.20: ¹ H NMR of 6.3, 6.10 and 6.11201	
Figure 6.21: UV-vis of 6.11	
Figure 6.22: TGA thermogram of 6.11203	
Figure 6.23: ¹ H NMR of 6.12204	
Figure 6.24: TEM of 6.12204	
Figure 6.25: ¹ H NMR of 6.12205	
Figure 6.26: POM texture of 6.12205	
Figure 6.27: DSC heating and cooling curves for 6.12	
Figure 6.28: XRD of 6.12	
Figure 6.29: 1H NMR of 4.7, 5.8 and 5.9	
Figure 6.30: SEM image of composite 6.15	
Figure 6.32: POM image of 6.15	

Figure 6.33: DSC curves of composite 6.15	211
Figure 6.34: UV-vis of composite 6.15	212
Figure 6.35: TGA thermogram of 6.15	213
Figure 6.36: XRD of 6.15	214
Figure 6.37: ¹ H NMR of Polymer 6.16 and 6.17	216
Figure 6.38: UV-Vis of 6.16	217
Figure 6.39: TGA thermogram for 6.17	218
Figure 6.40: ¹ H NMR of 6.18	219
Figure 6.41: UV-vis for 6.18	219
Figure 6.42: POM textures for 6.18	220
Figure 6.43: DSC heating and cooling curves for 6.18	220
Figure 6.44: TGA thermogram of 6.18	221
Figure. 6.45: ¹ H NMR of 6.19	222
Figure 6.46: SEM textures for 6.19	222
Figure 6.47: EDS of 6.19	223
Figure 6.48: POM textures for 6.19	
Figure 6.49: ¹ H NMR of 6.20	224
Figure 6.50: POM textures for 6.20	225
Figure 6.51: EDS of 6.20	226
Figure 6.52: TEM images for 6.18	226
Figure 6.53: UV-vis of 6.20	228
Figure 6.54: POM textures for 6.20	229
Figure 6.55: DSC curves of 6.20	229

Figure 6.56: TGA thermogram of 6.20	230
Figure 6.57: XRD for 6.20	231
Figure 6.58: POM textures for 6.22	
Figure 6.59: POM textures for 6.25	232
Figure 6.60: DSC curves of 6.25	233
Figure 6.61: ¹ H NMR of 6.25 and composite 6.26	234
Figure 6.62: SEM images for 6.26	235
Figure 6.63: EDS of 6.26	
Figure 6.64: TEM images for 6.26	236
Figure 6.65: UV-vis of 6.26	237
Figure 6.66: POM textures for 6.26	238
Figure 6.67: DSC curves of 6.26	
Figure 6.68: TGA thermogram of 6.26	
Figure 6.69: XRD data for 6.26	240
Figure 7.1: Application of polymeric materials	273
Figure 7.2: Thiol ligand exchange of CTAB on AuNRs	274
Figure 7.3: (a) CTAB-capped AuNRs on chloroform (b) after exchanged with DI	OT in
chloroform under water	
Figure 7.4: SEM images of 7.2	
Figure 7.5: EDS of 7.2	
Figure 7.6: TEM images of composite 7.2	277
Figure 7.7: Chart showing the lengths, widths and A/R of 7.2	278
Figure 7.8: UV-vis of 7.2	279

Figure 7.9: POM textures of composite 7.2 (x 400)	
Figure 7.10: DSC curves of 7.2	281
Figure 7.11: TGA thermogram of 7.2	
Figure 7.12: CTAB capped AuNRs in water (left vial), 7.3 in toluene on water (right	nt
vial)	
Figure 7.13: TEM images of 7.3	
Figure 7.14: Chart showing the lengths, widths and A/R of 7.3	
Figure 7.15: UV-vis of 7.3	
Figure 7.16: ¹ H NMR of 7.4	
Figure 7.17: SEM images of 7.4	
Figure 7.18: EDS of 7.4	
Figure 7.19: TEM images of 7.4	
Figure 7.20: Chart showing the lengths, widths and A/R of 7.4	
Figure 7.21: UV-vis of 7.4	
Figure 7.22: POM textures of 7.4	
Figure 7.23: TGA thermograph of 7.4	293
Figure 7.24: Composite 7.10 in toluene and on water	
Figure 7.25: UV-vis of 7.10 in toluene	296
Figure 7.26: UV-vis of 7.10 in THF	
Figure 7.27: ¹ H NMR of 7.11	297
Figure 7.28: SEM images of 7.11	

Figure 7.29: EDS of 7.11	
Figure 7.30: UV-vis of 7.11	299
Figure 7.31: POM images of 7.11	
Figure 7.32: DSC curves of 7.11	
Figure 7.33: TGA thermogram of 7.11	
Figure 7.34: SEM images of 7.13	
Figure 7.35: EDS of 7.13	
Figure 7.36: UV-Vis of 7.12 in toluene	
Figure 7.37: UV-Vis of 7.12 in THF	
Figure 7.38: UV-Vis of 7.13 in toluene	
Figure 7.39: UV-Vis of 7.13 in THF	
Figure 7.40: POM images of 7.12 and 7.13	
Figure 7.41: DSC curves of 7.12	
Figure 7.42: DSC curves of 7.13	
Figure 7.43: TGA thermogram of 7.12	
Figure 7.44: TGA thermogram of 7.12	
Figure 7.45: POM images of 7.12 mixtures	
Figure 7.46: DSC curves of 7.12	

Figure 7.47: DSC curves of 7.13	
Figure 7.48: ¹ H NMR of 7.14	
Figure 7.49: SEM images of 7.14	
Figure 7.50: EDS of 7.14	
Figure 7.51: UV-vis of 7.14	313
Figure 7.52: POM images of 7.14	314
Figure 7.53: DSC curves of 7.14	
Figure 7.54: TGA thermograph of 7.14	

CHAPTER ONE

INTRODUCTION

Scientists are absolutely fascinated by nanoparticles (NPs) based on their special properties such as size and shape-dependent optical electronic properties whose genesis is the localised surface plasmon resonance (LSPR)¹. LSPR strongly depend on the particle size, shape, topology, environment, and the nature of the light (propagation direction with respect to particles orientation and polarization)². Therefore functionalizing NPs with different types of molecules should control their assembly³ in addition to giving novel nano-platforms for diverse application such as nano-detection. Materials of best functions are low molecular mass mesogens, dendrimers and/ or polymers since they introduce anisotropic properties to the NPs thereby generating their self-assembly properties.

1.2 Liquid crystals

The history of liquid crystals dates back to 1888 when Austrian chemist, Friedrich Reinitzer discovered that cholesteryl benzoate (Fig. 1.1) seemed to have two melting points (145.5 °C and 178.5 °C). The solid crystal melted into a cloudy liquid at 145.5 °C and eventually gave a clear liquid at 178.5 °C.



Figure 1.1: Cholesteryl benzoate.

When contacted to unravel the puzzle, Otto Lehmann, a German physicist, discovered that the cloudy liquid has a unique kind of order and that it was a new state of matter, thereby coined its name 'fliessende krystalle' meaning 'Liquid Crystal'⁴.

The liquid crystal state is considered to be the 'fourth state of matter' along with solid, liquid and gas. Crystals and liquids are the most common condensed phases of matter and the only difference is the ordering of their molecules. While the molecules in crystal are both positionally and orientationally ordered in three dimensions thereby occupying specific sites in a lattice, those in a liquid are not. Liquid crystals constitute a fascinating class of condensed matter characterised by both fluidity and long-range order (some degree of orientational and sometimes positional order)^{5,6}.

Liquid crystals represent a number of different states of matter in which the degree of molecular order lies intermediate between the almost perfect long-range positional and orientational order found in solid crystals and the statistical long-range disorder found in ordinary isotropic amorphous liquids and gases⁷.

The properties in a normal liquid are isotropic, that is they are the same in all directions but in liquid crystals, they strongly depend on direction thereby anisotropic.

1.1.1 Types of liquid crystals

There are two main types of liquid crystals, namely, lyotropic and thermotropic liquid crystals.

1.1.1.1 Lyotropic liquid crystals are those in which the formation of mesophase depending the concentration and the solvent. They are amphiphile of two-component which can mixed with a solvent. They have two distinct moieties, a hydrophilic polar "head" and a hydrophobic "tail" and the examples molecules are found in soaps and phospholipids (present in cell membranes) as shown Fig. 1.1.1 below.



(a) Illustration of sodium dodecylsulfate forming micelles.



(b) Illustration of phospholipids (lecithin) forming bilayer lyotropic liquid crystal as present in cell membranes.

Figure 1.1.1: Examples of lyotropic liquid crystals.

1.1.1.2 Thermotropic liquid crystals are those in which the individual molecules built up without the requirement for any further molecular species (specifically solvent molecules) for the liquid crystal phase formation.

The fundamental thermodynamic control parameter determining the phase is the temperature. The liquid crystal phase is stable for a certain temperature interval⁵. The two key temperature values are those defining the beginning (melting point, T_m , from crystalline solid) and end of liquid crystalline order (the clearing point, T_c , into isotropic liquid)⁶.

Thermotropic liquid crystals are subdivided into two depending on the nature of the molecules contained:

i. Calamitic liquid crystals: these contain molecules that are rod-like (i.e one molecular axis is much longer than the other two). They are molecules often containing two or more rings which may or may not have a connector, but have hydrocarbon as the terminal ends (although not always). An example is shown in Figure 1.2.

$$C_5H_{11}$$
 — CN Cryst 24 N 35 Iso (°C)

4'-pentyl-4-biphenylcarbonitrile

Figure 1.2: Example of calamitic liquid crystal

ii. Discotic liquid crystals: are those with disc-like molecules (i.e molecules with one axis much shorter than the two others). An example is shown in Figure 1.3.





Figure 1.3: Example of discotic liquid crystal.

1.2 Liquid crystal phases

The liquid crystal phases (mesophases) are characterised by the type of molecular ordering. Order can be positional (molecules arranged in any sort of ordered lattice) or orientational (molecules mostly pointing in the same direction).The order can be short-range (between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimension).

All thermotropic liquid crystals have an isotropic phase at higher temperatures (heat driven). Here, they are characterised by random and isotropic molecular ordering (little to no long-range order), and fluid-like flow behaviour (Figure 1.4).



Appearance of a liquid crystal phases in a temperature profile

Figure 1.4: Thermotropic LC phases⁸.

Under other conditions (e.g lower temperature), a liquid crystal might exhibit one or more phases with significant anisotropic orientational structure and short-range orientational order while still having an ability to flow (Figure 1.5).



Figure 1.5: Appearance of liquid crystal phases in a temperature profile.

There are two main types of mesophases commonly exhibited by calamitic liquid crystals and these are the nematic and smectic phases.

(i) Nematic Phase

The simplest liquid crystal phase is the nematic phase. The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction (along the director, \mathbf{n}). The molecules are basically ordered in one-dimension, with the local preferred direction along one axis. Nematics are optically uniaxially systems with optical axis parallel to \mathbf{n} .



Figure 1.6: Structure of nematic phase (the arrow point gives the director, **n**).

(ii) Smectics Phases

The smectic mesophases are more ordered than the nematic phase. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to organise themselves in layers or planes. Molecules in these phases show a degree of translational order not present in the nematic phase. Motion is restricted to within these planes, and separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic phase.



Figure 1.7: Structures of (a) SmA and (b) SmC phases.

The smectic phases exhibit polymorphism, i.e. there are many different types of smectic phase, but the common ones are smectic A (SmA), smectic B (SmB), smectic C (SmC) and chiral smectic C (SmC*).

In the smectic A mesophase, the director is perpendicular to the smectic plane, and there is no particular positional order in the layer.



Figure 1.8: Order of molecules in smectic A mesophase.

In the smectic-C mesophase, molecules are arranged as in the smectic-A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane.



Figure 1.9: Order of molecules in smectic C mesophase.

There is a chiral variation of the smectic C mesophase generally known as chiral smectic C phase (SmC*). Consistent with the smectic C, the director makes a tilt angle with respect to the smectic layer. The difference is that this angle rotates from layer to layer forming a helix. In other words, the director of the smectic C* mesophase is not parallel or perpendicular to the layers, and it rotates from one layer to the next.

Chiral Smectic C



Figure 1.10: The chiral smectic C phase (where the director tilt of each layer precesses around a circle upwards through the structure).

In some smectic mesophases, the molecules are affected by the various layers above and below them. Therefore, a degree of three dimensional order is observed. Smectic-G is an example demonstrating this type of arrangement.

(iii) Cholesteric Phases

The cholesteric (or chiral nematic) liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center which produces intermolecular forces that favour alignment between molecules at a slight angle to one another. This leads to the formation of a structure which can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted with respect to those above and below. In this structure, the directors actually form in a continuous helical pattern about the layer normal.



Figure 1.11: Structure of the Cholesteric Phase.

The molecules shown are merely representations of the many chiral nematic mesogens lying in the slabs of molecular thickness with a distribution of orientation around the director.

An important characteristic of the cholesteric mesophase is the pitch. The pitch, p, is defined as the distance it takes for the director to rotate one full turn in the helix as illustrated above. A byproduct of the helical structure of the chiral nematic phase is its ability to selectively reflect light of wavelengths equal to the pitch length, so that a colour will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum. There is a temperature dependence of the gradual change in director orientation between successive layers, which modifies the pitch length resulting in an alteration of the wavelength of reflected light according to the temperature. The angle at which the director changes can be made larger, and thus tighten the pitch, by increasing the temperature, hence giving them more thermal energy. Similarly, decreasing the temperature increases the pitch length of the chiral nematic liquid crystal. This makes it possible to build a liquid crystal thermometer that displays the temperature of its environment by the reflected color. Mixtures of various types of these liquid crystals are often used to create sensors with a wide variety of responses to temperature change. Such sensors are used for thermometers often in the form of heat sensitive films to detect flaws
in circuit board connections, fluid flow patterns, condition of batteries, the presence of radiation, or in novelties such as "mood" rings.

Phase changes in LCs

The figure 1.12 below illustrates phase transitions which occur in liquid crystal materials. It is a lattice of liquid crystal molecules that assume different positions and orientations based on temperature. The material begins in the *crystalline* state, and as the temperature increases, it undergoes a phase change. The first liquid crystal phase is the *smectic*, where there is layer-like arrangement as well as translational and rotational motion of the molecules. A further increase in temperature leads to the *nematic* phase, where the molecules rapidly diffuse out of the initial lattice structure and from the layer-like arrangement as well. At the highest temperatures, the material becomes an *isotropic* liquid, where the motion of the molecules changes yet again.



Figure 1.12: Phase changes with temperature⁷.

Chart 1.1 summarises the classification of Liquid Crystals.



Chart 1.1: Classification of Liquid Crystals

1.3 Metal nanoparticles

The prefix nano (from Greek word $v \dot{a} v o \varsigma$ or Latin word *nanus*, both meaning dwarf) was adopted as an official S.I prefix meaning 10^{-9} of an SI base unit at the 11^{th} Conférence Générale des Poids et Measures (CGPM) in 1960 (the status been informal before that time).

Nanoscience is the study of events at 1-100 nm while Nanomaterials are the materials with components structure of at least one dimension less than 100 nm and are defined as follows. Nanoparticles are materials with zero-dimensional nanostructures while nanowires and nanorods are materials with one-dimensional nanostructures. Materials of two-dimensional nanostructures are referred to thin films.

Nanoparticles are structures with nanosize in which at least one of its phases has one or more dimension (length, width or thickness) in the nanometer size range (1 - 100 nm). The existence of metallic nanoparticles in solution was first recognised by Faraday in 1857 while their quantitative explanation of their colour was given by Mie in 1908.

Metal nanoparticles have unique properties due to quantum confinement and very high surface to volume ratio, as well as large surface energy. Other properties are, plasmon excitation, short-range ordering, and large numbers of coordinating sites such as corners and edges, and ability to store excess electrons.

It was belief that the extraction of gold started in the 5th millennium B.C near Varna (Bulgaria) and reached to 10 tons per year in Egypt around 1200-1300 B.C when the marvellous statue of Tutankhamun was constructed (Fig. 1.13 (a)).



Figure 1.13: (a) Marvellous funerary mask of Tutankhamun (b)-(c) The Lycurgus Cup (c) Medieval Stained Glass.

It is probable that 'soluble' gold appeared around the 5th or 4th century in Egypt and China.

The Lycurgus cup (Fig. 1.13 (b-c)) was manufactured in the 5th to 4th century B.C. It is ruby red in transmitted light and green in reflected light due to the presence of gold colloids⁸⁻⁹.

The ancient stain-glass makers produced red and yellow colour found in stained-glasses by adding varying and small amount of gold and silver to the glass.

Today, scientists and engineers also change the materials physical properties by the addition of small amounts of nanoparticles. Examples are given in the Table 1.1¹⁰.

Particles in glass	Size	Colour reflected	Shape
Gold	25 nm	Red	Sphere
Gold	50 nm	Green	Sphere
Gold	100 nm	Yellow	Sphere
Silver	100 nm	Yellow	Sphere
Silver	40 nm	Blue	Sphere
Silver	100 nm	Brown	Prism

Table 1.1: Properties of Nanoparticles¹⁰.

Extensive attention of scientists in various subjects have been drawn to nanometre-size generally termed nanoparticles, basically due to their unusual chemical and physical properties, when compared with those of metal atoms or bulk metal¹¹⁻¹². These properties are due to the quantum size effects and their large surface area and responsible for their applications in optics, electronics, catalysis, and biology.

It was predicted¹³ that NPs in the diameter range of 1-10 nm (intermediate between the size of small molecules and that of bulk metal) would display electronic structures, reflecting the electronic band structure of NPs, owing to quantum-mechanical rules. The resulting physical properties are neither those of bulk metal nor those of molecular compounds, but they strongly depend on the particle size, inter-particle distance, nature of the protecting organic shell, and the shape of the nanoparticles¹⁴.

The properties of metal nanoparticles have generated great interest over the last decade and metals involved are silver^{15,16,17}, platinum^{18,19}, CdSe^{20,21}, copper^{21,22,23,24}, tin^{22,25}, iron^{26,27,28}, gold and others. Among the various metal nanoparticles, gold nanoparticles (AuNPs) have the tremendously high optical absorption in the visible region and also the particle aggregation leads to mutually induced dipoles that depends on inter-particle distance and aggregate size¹².

Metal nanoparticles are prepared by employing either physical or chemical methods. Physical methods use the mechanical subdivision of the metallic aggregates and evaporation of a metal in a vacuum by resistive heating or laser ablation. On the other hand, chemical methods involve the reduction of metal salts in solution and this is considered the most convenient way of controlling the size of the particles and modification of the surface chemical composition¹².

In 1857, Faraday reported the formation of a deep-red solution of colloidal gold by reduction of an aqueous solution of chloroaurate (AuCl₄⁻) using phosphorus in CS₂ (a twophase system) in a well-known work²⁹. He investigated the optical properties of the thin films prepared from dried colloidal solution and observed reversible colour changes of the films upon mechanical compression (from bluish-purple to green upon pressurizing). Self-organisation of nanoparticles in a controlled manner is essential for various applications.



Figure 1.14. NP formation.

Metal nanoparticles tend to irreversibly aggregate over time or when not in a solvent. In order to prevent this agglomeration, metal nanoparticles are protected or capped by various types of organic materials which could be polymeric or monomeric as illustrated in Figure 1.14. Examples of polymer used are poly(vinyl alcohol), poly(vinyl pyrrolidone), and poly(vinyl ether). Although these polymer-stabilised metal nanoparticles are easy to prepare and stable in solution, it requires large amount of polymers which disallows close-pack assembly of the metal cores (close-packed assembly of the metal nanoparticles produce complex electronic and functions based on quantum mechanical coupling of conduction electrons localised in each nanoparticle)¹².

Stabilization of metal nanoparticles by ligands as capping agents give room for further manipulation, controlled solubility, characterization, and facilitate their analysis¹⁰. Common examples of ligands used in stabilizing metal nanoparticles are thiol, amine, bipyridyl, phosphine etc.

1.4 Gold nanoparticles (AuNPs)

Recently, there are more interest on the metal nanoparticles than their corresponding bulk metal due to their diverse size-related properties, such as magnetic, electronic and optical properties. These properties are making them accessible for applications in different fields such as biological, catalysis, material science, electronic, engineering, chemistry and chemical platforms in general.

Based on the understanding of thiol chemistry, organosulfur compounds (alkyl thiols, aromatic thiols and disulfides) form a self-assembled monolayers on the surface of the metal through chemisorbed Au-S bonds (for gold) or Ag-S bonds (for silver) and the understanding of this bond formation has also made the synthesis of stable and functionalized nanoparticles possible³⁰. Among the metal nanoparticles, gold nanoparticles are the most stable with colloidal solutions of a strong colour as characteristic⁸.

The optoelectronic properties of AuNPs are explained based on the collective oscillation of the conduction band electrons on the surface of the nanoparticles and its termed localised surface plasmon resonance $(LSPR)^{31}$.

Many methods have been used for the synthesis of AuNPs which includes the Turkevich method³²⁻³³, the Brust method³⁴ and the corresponding modified methods.

The differences, advantages and disadvantages of Turkevich and Brust methods are given in the table below³⁵.

Method	Principle	Advantages	Disadvantages
Turkevich	Reduction of	-Synthesis is simple and highly	-Unreliable
	chloroauric acid by	reproducible.	synthesis of
	trisodium citrate	-Citrate acts as stabilising and	AuNPs > 35 nm.
		capping agent.	-Moderate
			reducing ability of
			trisodium citrate
			gives AuNPs≥10
			nm.
			-Low stability of
			citrate.
			High temperature
			often required.
Brust	Reduction of	-Synthesis of AuNPs \leq 5 nm	-Synthesis of
	chloroauric acid by	possible.	larger AuNPs not
	sodium borohydride	-Highly reproducible.	possible.
		-High thermal and air stability.	-Separate capping
		-Easy to manipulate by ligand	agent must be used
		exchange/substitution.	to confer stability.
		-Reduction at low temperatures	
		(usually at rt).	

Table 1.2: Comparison between Brust and Turkevich methods

1.5 Properties of materials at nano-level

Nanoparticles are made up of from just few atoms to a few thousand atoms; conversely, the bulk materials contain many billions of atoms. This is why nanomaterials behave differently from their bulk counterparts. For example the large surface area to volume ratio of gold nanoparticles enables them to catalyse the oxidation of CO to CO_2 while bulk gold is inert.

1.5.1 Colour of AuNPs

The colour exhibited by AuNPs depends on the size concerned. Metals generally shine because of reflection of light from their surfaces which is related to the electron clouds at their surfaces. Visible light is absorbed and emitted in tiny 'packets' known as photons. When light falls on metal, the photons cannot penetrate the electron clouds and be absorbed by the electrons bound to atoms in metals. Instead, they are reflected back and will be seeing as a shining object. This is exactly what is observed in the bulk metals. In nanoparticles, the electron cloud at the surface resonates with a certain frequency which depend on the size and the wavelength. Red and yellow end of the colour spectrum is absorbed by AuNPs (~90 nm) thereby making the particle appear blue-green, while AuNPs (~30 nm) will absorb blue-green, resulting in red appearance.



Figure 1.15: Different colours of gold nanoparticles are the result of SPR.

Since colloidal AuNPs produces vibrant colours by their interaction with visible light (Fig. 1.15), these unique optical-electronics are being researched and utilized in high technology applications. The electronic and the optical properties of AuNPs are tuneable by changing the size, shape, surface chemistry or aggregation state.



Figure 1.16: Extinction (the sum of scattering and absorption) spectra of gold nanoparticles with diameters ranging from 10 - 100 nm at mass concentrations of 0.05 mg/mL. ^{nanocomposix.com}

1.5.2 Optical and electronics properties of AuNPs

AuNPs absorb and scatter light with extraordinary efficiency (Fig. 1.16). Their strong interaction with light occurs because the electrons on metal surface undergo a collective oscillation when they are excited by light at specific wavelengths. This oscillation is known as a surface plasmon resonance (SPR) (Fig. 1.17) and it causes the absorption and scattering intensities of AuNPs to be much higher (can be up to 40x) than the identical sized non-plasmonic NPs.



Figure 1.17: SPR of plasmonic materials

Since the AuNPs interaction with light is dictated by the environment, size and physical dimensions, the resonant oscillation of the free electrons on their surfaces can be tuned by varying the size or shape of the NPs, leading to particles with tailored optical properties for different applications. Smaller particles primarily absorb light and have a peak near 520 nm, while larger particles exhibit increase scattering (due to their larger optical cross section) and have peaks that are broaden significantly and shift towards longer wavelengths (red-shifting)³⁶. When excess NaCl is added to the colloidal solution of Au, the surface charge of the AuNP becomes neutral, causing NPs to aggregate (red to blue) and this can be prevented by coating the versatile surface of Au with polymers, small molecules and even biological recognition molecules (properties which enable their uses in chemical,

biological engineering and medical field). Some specific applications are molecular detection, solar energy materials and cancer detection and treatment.

NP optical properties are highly dependent on material composition, size and the medium in which the particles are embedded. NP optical properties are also sensitive to the proximity of other plasmonic materials. When two or more plasmonic NPs are near each other (with edge-to-edge separations of one particle diameter or less) their surface plasmons couple as the conduction electrons on each particles surface collectively oscillate. This effect is in analogy to molecular orbital theory in that plasmon coupling results in the oscillating electrons assuming the lowest energy state, causing the plasmon resonance wavelength of the coupled particles to red-shift to longer wavelengths (lower energies). This explains the colour changes observed when NP in solutions aggregate and also the basis of many different types of plasmonic NP sensors.

1.6 Introduction to liquid crystal-nanoparticle composites

Liquid-crystalline nanoparticles are an exciting class of new materials that combine supramolecular ordering with fluid properties of the liquid crystalline state. They have the ability to organise nanoparticles into addressable 2 dimensional and 3 dimensional arrangements, thereby making them processable, and self-healing, and available for variety of potential applications³⁷. Major researches have focused on the nature/properties of the nanoparticles, the mesogen (organic ligand coating), and their resulting phase behaviour.

The most common nanoparticles are the metallic particles (including alloys and oxides) of at least one dimension lesser than 100 nanometre. These species can exhibit physical and chemical properties that differ tremendously from their bulk counterparts, and which depend not only on their composition but also on their shape and size³⁸. These properties

are already being applied in biology and medicine^{39,40}, optics and electro-optics^{41,42}, catalysis^{40,43}, and environmental remediation⁴⁴.

In order to exploit the exciting properties of NPs, it is necessary to incorporate them into a more complex structure, often through the use of a suitable organic coating, which imparts stability against aggregation, solubility, modularity, and optical and self-organisation properties⁴. The composition of the nanoparticles (surface chemistry, magnetic/electrostatic properties), morphology (size, shape and roughness), and the manipulative ability to be coated with structure-directing agents, are the important factors to be taken into consideration for choice of particle.

The major factor to be considered in the synthesis of NPs is self-assembly⁴⁵. Liquidcrystalline (LC) materials offer unique opportunities in the field of NP organisation due to the intrinsic order and fluid properties that they possess, allowing for complex architectures to be established with high processability and defect tolerance. The properties of LCs can also be influenced by external factors, such as applied magnetic and electric fields and surface effects, all of which lend these materials towards their use in stimuli-responsive advanced materials⁴⁶.

1.6.1 Formulation

Nanoparticles must be coated with suitable material (mesogen) that allows them to exhibit liquid-crystalline phase at relatively moderate temperatures (i.e., ideally <250 °C)³⁷. Different strategies can be used to induce mesogenic properties into the target nanoparticles and this will depends on the morphology of the nanoparticles involved.

Although, it was predicted theoretically⁴⁵⁻⁴⁷ that Au NPs coated with simple linear thiols should exhibit spontaneous asymmetry at low temperatures or in solution, most simple NP-

hybrids of this type do not exhibit LC phases³⁷. Therefore, it is clear that the ligands must impart sufficient anisotropy into the hybrid system to force the pseudospherical particles to form ordered self-assembled structures whilst maintaining a fluid state. Thus, parameters such as the orientational flexibility and mobility of the ligands on the NP surface are just as important as their chemical structure, or in other words, their mesogenic character³⁷.

1.6.2 Synthesis of liquid crystal Nanoparticles

The synthesis of NP LC composite is largely determined by the following:

- (i) nature of the nanoparticles;
- (ii) the synthetic method used to prepare the inorganic species;
- (iii)presence of co-ligands (stabilisers);
- (iv) and the surface chemistry of the particular material under investigation.

Furthermore, the relative ease and flexibility of synthesis of the organic ligand(s) means that their design is tailored to the particular surface chemistry and morphology characteristics of the NP under investigation, ensuring a suitable anchoring group and structure-directing groups are present in the molecular structure.

The most extensively investigated type of metal nanoparticle liquid crystal are gold nanoparticles liquid crystal (AuNP LC). Two main methods are used in the preparation of AuNP LC;

(i) Direct synthesis of the NPs in the presence of the ligand of interest by using a modified Brust–Schiffrin procedure⁴⁸; this method gives a NP surface coated with exclusively (but not necessarily completely) the ligand of interest.

(ii) Two-step process in which the NPs are first synthesised with a protective layer (e.g., a simple alkanethiol), followed by solvent-mediated ligand exchange to give the desired product³⁹. Here, invariable products with mixed ligand coatings are produced³⁷.

Any of the above methods could be used, but the final product must be pure and characterization can be determined using NMR spectroscopy, thermal analysis (Differential Scanning Calorimetry-DSC/Thermo-gravimetric Analysis-TGA), elemental analysis, X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and other spectroscopic techniques (e.g., Ultraviolet–Visible Spectroscopy(UV-Vis)).

1.7 AuNP grafted polymeric composites

Liquid crystalline polymers combine the thermal and orientational properties of liquid crystals, at the same time elasticity of polymers. These properties, in addition to the plasmonic properties of AuNPs, act together to give a lot of physical phenomena which include shape change with a change of temperature, extreme opto-mechanical effect, rotatory-mechanical coupling and opto-electronic properties.

The self-organizing ability of the liquid crystals molecules forming coating around nanoparticles, which act as central scaffolds, is intensely investigated and has been claimed to be the driving force for the self-assembly of NPs into secondary or tertiary hierarchical superstructures with optical properties that could potentially lead to a new class of stable liquid-crystalline metamaterials⁴⁹.

1.8 Gold nanorods

GNR is a cluster of gold atoms in a cylinder shape with two axes - the transverse axis and the longitudinal axis. The transverse axis is the one along the short axis while the longitudinal axis is the one along the long axis. The surface plasmon resonance for AuNRs is split into two basically due to its anisotropical nature (Fig.1.18).



Fig. 1.18 (a) Schematic of plasmon oscillation for a nanosphere. (b) Measured absorbance spectra of a GNR solution. The insets show the schematic of the transverse and longitudinal SPR modes, which correspond to two absorption peaks, respectively. (c) TEM images of as synthesized GNRs with different longitudinal SPR wavelength as noted. (d) Measured absorbance spectra of gold nanospheres (GNSs) and GNRs, whose SEM images are shown in $(c)^{51}$.

The transverse resonance is the same as that for the NPs and usually occurs around 500 nm although this may shift due to surface modification of the NRs with red shift when coating causes an increase in the local refractive index of the medium surrounding the NP. Most often, the magnitude of the shift is commensurate with the thickness of the coating⁴⁹.

The longitudinal surface plasmon resonance is very sensitive the nature (polarization and wavelength) of the incident light and it is tunable between visible and near infrared (NIR)

range of wavelength⁵⁰. Also, longitudinal resonance is aspect ratio dependent and this can be tuned by functionalization or surface modification of the NRs.

AuNRs are synthesised by the reduction of gold salt using week reducing agent in the presence of a surfactant. Common method used is the seed-mediated technique in which gold nanoparticles serving as the seed, are placed in a growing solution containing surfactant, gold ions, silver ions, and week reducing agent. Also, of recent is the non-seeding method in which the reduction occur without the seeds⁵³.

1.9 Liquid crystalline polymers

There are two basic types of liquid crystal polymers;

- (a) Main chain liquid crystalline polymers (MCLCPs)
- (b) Side chain liquid crystalline polymers (SCLCPs)

In MCLCPs, the repeating monomer units are made up of the mesogen which must be anisotropic with functionality to enable polymerisation and mesophase generation. In SCLCPs on the other hand, the mesogenic unit is laterally attached or linked to the polymer backbone either directly through a spacer or through linking units. The general templates of both MCLCPs and SCLCPs are presented figure 1.19.



Figure 1.19: General template of MCLCPs and SCLCPs.

1.10 Polymerisation

Preparative polymer chemistry initially was faced with challenges of synthesising welldefined polymers and copolymers with predetermined molecular weights, low polydispersities, precisely controlled end group functionalities and chain topologies⁵⁴. The advent of living polymerization made the synthesis of such macromolecules possible. Living polymerization (first used by Szwarc⁵⁵) is a chain growth process without chain breaking reactions (transfer and termination) which enables the proper control of end group and synthesis of important architectural macromolecules (like block copolymers) by addition of monomer sequentially. However, polymers with controlled molecular weights and narrow molecular weight distributions may not be formed to this the rate of initiation is at least comparable to that of propagation and that exchange between species of various reactivities and lifetimes is fast in comparison with propagation^{56,57,58,59}. Polymerizations can also be regarded as controlled if side reactions occur but only to an extent which does not considerably disturb the control of the molecular structure of the polymer chain. Many polymerisation mechanisms for the formation of controlled polymer structures have emerged and have been named "living", such as cationic-, ring-opening metathesis-, group transfer-, and radical polymerisations⁵⁴. Living radical polymerisation is an important tool for the synthesis of nanostructural molecules with defined structures possessing a variety of functional groups⁶⁰ and its application to nanocomposites is relatively gaining ground⁶¹. Atom transfer radical polymerisation (ATRP) is classified as one of the living radical polymerisations, in which its application is limitless with respect to monomer types, topology of polymer (linear, branched or others) or composition of the polymeric chains (block or graft copolymers, etc)³⁰ and this is an important goal in synthetic polymer chemistry in addition to gaining control over the molecular weight and polydispersities⁶².

ATRP has its roots in and is mechanistically related to transition metal mediated atom transfer radical addition (ATRA) reactions of organic chemistry and has, among various advantages, its effectiveness for a wide range of monomers (styrene, (meth)acrylates, acrylonitriles, acrylates etc), in variety of solvents (benzene, water, toluene, methanol, etc), at moderate temperature (80-120 °C) and finally using different catalysts (Cu^{63,64}, Fe⁶⁵⁻⁶⁸, Ru⁶⁹⁻⁷⁰, Ni⁷¹⁻⁷², Rh⁷³, Pd⁷⁴, Ti⁷⁵, Mo⁷⁶⁻⁷⁸, Os⁷⁹).

The most efficient catalysts in the ATRP of broad range of monomers in diverse media are found to be Cu complexes⁸⁰. ATRP mechanism can be viewed as a special ATRA process⁸¹⁻⁸² which requires reactivation of the first formed alkyl halide adduct with the unsaturated monomer and further reaction of the intermittently formed radical with additional monomer units (propagation).

Another advantage of ATRP is the readily availability of the necessary reagents such as alkyl halide, ligands and the catalysts (transition metals and their salts). Dry solvent should be used in ATRP so as to avoid dissociation of the halogens from Cu.

Most effective and efficient initiators are formed from most compounds with halogen atoms that are activated by α -carbonyl, phenyl, vinyl or cyano groups.

The realisation of ATRP and the extraordinary control it can provide over polymer topology, composition and functionality has led to intensive developments in material science and the novel properties of the new polymers with precise control architecture (structure-property correlations) are being investigated for many applications⁸⁰.

1.11 Atom Transfer Radical Polymerization (ATRP)

ATRP in term of mechanism is related to the transition metal mediated atom transfer radical addition (ATRA) reactions and indeed can be viewed as a very special case of ATRA. However, in contrast to ATRA reactions, the reactivation of the first formed alkyl

halide adduct with the unsaturated compound (monomer) and the further reaction of the intermittently formed radical with additional monomer units (propagation) is required in ATRP. The polymerization process is living if a linear first-order kinetic plot is obtained and is accompanied by a linear increase in polymer molecular weight with conversion, with the value of the number-average degree of polymerization (DP_n) determined by the ratio of reacting monomer to initially introduced initiator (i.e., DP_n = D[M]/[RX]₀).

The normal schematic of the ATRP equilibrium, which emphasizes the repetitive nature of the activation and deactivation steps and the need to push the equilibrium to the left hand side, thereby forming a low concentration of radicals to reduce radical-radical termination reactions, and ensure a high mole fraction of dormant chains, is shown in Scheme 1.1.



Scheme 1. 1: Mechanism of metal complex-mediated ATRP⁵⁸.

ATRP is based on an inner sphere electron transfer process⁸³. The added initiator, **R-X**, can be a mono functional initiator or a multifunctional initiator; i.e. it can possess more than one functional group capable of providing a site for chain growth. The added initiator can also be used to introduce additional functionality into the α -chain end of a linear copolymer or within the "core" of a multi-armed star or composite material. It can be a macroinitiator

(a polymer containing one or more initiator site(s)) or the initiator(s) can be attached to any type of surface, either a particle, a flat surface, a fibre, or a porous material.

The transition metal catalyst ($\mathbf{M}_t^n/\mathbf{L}$), where \mathbf{M}_t^n is the transition metal in the lower oxidation state *n* complexed with appropriate ligand(s) **L**, reacts reversibly with the added initiator molecule to transfer the radically transferable atom or group from the initiator to generate an oxidized transition metal halide complex ($\mathbf{X}-\mathbf{M}_t^{n+1}/\mathbf{L}$) and a radical (\mathbf{R}^-). This radical propagates, adding monomer (\mathbf{M}), and is rapidly deactivated by reaction with the oxidized transition metal halide complex to reform the lower oxidation state transition metal catalyst and an oligomeric **X**-terminated chain ($\mathbf{R}-\mathbf{P}_{1+}-\mathbf{X}$).

This sequence can repeat itself, until the desired level of consumption of the monomer is reached, resulting in the synthesis of polymers with predetermined molecular weights $(DP_n = D[M]/[RX]_0)$ and low polydispersities $(M_w/M_n < 1.5)$.

The primary advantage of a "normal ATRP initiation" procedure is that it provides great freedom for the choice of both initiator and catalyst complex. The most active catalyst can be selected (provided all reagents are pure and oxygen free) resulting in lower levels of transition metal and other impurities in the final product. Selection of the appropriate initiator, catalyst and reaction conditions are crucial step since activation rate constants k_{act} for a variety of initiators can vary by a factor of one million^{84,85}.

As the reaction progresses radical termination is diminished as a result of the persistent radical effect $(PRE)^{86-87}$ increased chain length, as well as conversion and viscosity⁸⁷. Consequently, the equilibrium is strongly shifted towards the dormant species $(k_{act} \ll k_{deact})^{88}$.

Variables such as temperature, pressure, media/solvent, type of alkyl halide, and catalysts influence the K_{ATRP}.

The initiator is most frequently an alkyl (pseudo)halide which can be either a low or high molar mass.

Copper has proven by far to be the transition metal of choice, as determined by the successful application of a spectrum of copper complexes as catalysts, for the ATRP of a publications broad range of monomers in diverse by many researchers. Polymers prepared by other polymerization processes can be functionalized at the termini or along the backbone and incorporated into an ATRP as a macromonomer or macroinitiator, or simultaneously through use of both a macroinitiator and a macromonomer to improve incorporation of the macromonomer into the polymer⁸⁹ leading to the preparation of well-defined block and graft copolymers. There may be multiple initiating sites in either a small molecule or a macroinitiator, leading to chain growth in several directions. A functional initiator may carry a second non-initiating functionality, in addition to a radically transferable atom or group, to yield telechelic materials⁹⁰.

The transition metal complex has to be at least partially soluble in the reaction medium and reactions can be run under homogeneous or heterogeneous conditions. The former generally provides better control since the concentration of activator and deactivator can be controlled⁹¹.

Reaction temperatures typically range from room temperature to 150 °C, but can be correspondingly altered. Reactions can not only be conducted in the presence of moisture but even in the presence of water under homogeneous⁹².

Oxygen should be removed from the reaction medium, but a limited amount of oxygen can be tolerated particularly in the presence of an added reducing agent e.g. Cu(0), $Sn(EH_2)$, ascorbic acid, reducing sugars or amines⁹³⁻⁹⁹.

The order of addition of reagents may vary but most often the initiator, or catalyst activator, is the last reagent to be added to a preformed solution of the catalyst in the monomer/solvent.

Note however that the addition of a low level of the redox conjugate such as Cu(II) species to the initial reaction medium does provide complete control from the start of the polymerization and increases the amount of added initiator incorporated into the final product, by reducing the fraction of termination reactions between low molecular weight species normally required to form the persistent radical⁹⁹. This is important in industrial scale processes where the cost of a functional initiator may be a major concern.

1.12 Methods for Characterisation of Nanoparticle Liquid Crystals

1.12.1 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a LC sample and reference is measured as a function of temperature. The liquid crystal sample and reference sample are both maintained at nearly the same temperature throughout the experiment.

The basic principle is that when the sample undergoes a physical transformation such as phase transition, more or less heat will needed to flow to it than the reference to maintain both at the same temperature. Either less or more heat must flow to the sample depending on whether the process is exothermic or endothermic. For example, when a sample melts to a liquid it requires more heat flowing to the LC sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the LC sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the LC sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions¹⁰².

DSC is used in the analysis of NP LCs to reveal the presence of mesophases. The instrument detects the enthalpy change associated with a phase transition. Although, it cannot identify the type of LC phase, the level of enthalpy change does give some information about the degree of molecular ordering. The instrument is pre-calibrated with a sample of known enthalpy of transition. Then, the sample (usually 2-10 mg) is weighed into a small aluminium pan, which is cramp-sealed with an aluminium top. The sample pan is then placed into a holder in larger aluminium block to ensure good temperature control. The sample can be cooled using liquid nitrogen and a working temperature range of between -180 and 600°C is possible⁵.

The two figures below¹⁰³ are the DSC traces obtained with a small sample of the liquid crystal material 8 OCB (octyloxy cyanobyphenyl) at a rate of 1 $^{\circ}$ C /min. The lower curve in figure 1.20 (a) corresponds to a heating process followed by a cooling process, represented in the upper curve.

A phase sequence indicator illustrating the heating process is placed just above the temperature axis (at one atmosphere pressure). This includes a crystal to liquid crystal (smectic A) transition at 55 °C followed by a barely detectable smectic A to nematic transition at 67 °C and finally the nematic to isotropic (NI) transition near 80 °C. The upper, cooling, curve shows a slight displacement of the NI transition, partially due to supercooling and partially instrumental hysteresis attributable to the temperature scan rate. The smectic A to crystal transition is depressed strongly due to supercooling of the smectic

A phase. Thus, the phase sequence for the cooling process would not be identical to that for heating.



Figure 1.20 (a): DSC plot with phase sequence of 8OCB.

Figure 1.20 (b) is a repeat of this run, beginning to heat at a temperature above the crystal to smectic A transition so higher resolution could be shown. This makes the smectic A to nematic transition more visible and illustrates the capability of the DSC method is detecting subtle effects.



Figure 1.20 (b): DSC plot of 8OCB.

1.12.2 Optical polarizing microscopy (OPM)

Optical polarizing microscopy is a standard tool in the identification of liquid crystal phases and phase transitions but requires considerable experience, particularly in the study of new and less familiar materials.



The technique involves the identification of different LC phases as a distinct optical texture. Identification usually involves the magnified view of a thin sample of a mesogenic material sandwiched between a glass microscope slide and a glass cover slip. The slide is placed on a stage with accurate temperature control (-20 to 300°C) placed between crossed polarizer⁵.

1.12.3 X-ray diffraction (XRD)

X-ray diffraction is the ultimate technique use for the identification and classification of mesophases as it will map out the positions of the molecules within the phase and hence determine the phase structure. XRD is a powerful technique used in the investigation of nanomaterials as the wavelength of X-rays is on the atomic scale. When a beam of X-ray is incident on the sample, X-rays are scattered by each atom in the sample. Maximum intensity of the constructive interfere is obtained when the scattered beams are in phase at that particular angle. This interference can be studied using Bragg's Law to determine various characteristics of the material.



Figure 1.22: X-ray diffractometer features.

The angle between the transmitted and the diffracted beams is always 2θ and is obtained from the experiment. Using Bragg's law,

2d sin θ = n λ , the interplanar spacing, d, can be easily determined⁵.

1.12.4 Transmission Electron Microscope (TEM)

The average particle size and size distribution of the nanoparticles are determined by thetransmissionelectronmicroscope.



Figure 1.22: Schematic outline of a TEM.

1.13 Earlier works

To induce liquid crystalline properties into nanoparticle, suitably functional mesogen is introduced onto its surface. Thereby, the NP LC retaining the self-assembling and mesogenic ability of the ligand. Below are some of the earlier works on AuNP LC. Ikeda et al¹⁰⁴ reported AuNPs covered with a liquid crystalline ligand, 10-[(trans-(4-pentylcyclohexyl)phenoxy)]decane-1-thiol, with the AuNP LC exhibiting characteristic double-melting behaviour.



=AuNP

Figure 1.23: AuNP covered with mesogen.

Kim et al¹⁰⁵, also described the spontaneous one dimensional arrangement of a spherical AuNPs with liquid crystalline thiol, 4'-(12-marcaptododecyloxy)biphenyl-4-carbonitrile,



Figure 1.24: AuNP covered with mesogen.

They disclosed that AuNPs covered with a LC mesogen unit and alkanethiol unit, spontaneously ordered themselves just by a simple thermal treatment without any template with mesophase between 110 and130°C.

The first AuNP LC system which is stable and exhibits thermotropic nematic phase behaviours at room temperature was reported by Mehl et al¹⁰⁶. They bonded AuNPs capped with hexylthiol with 4'-(undecyloxy)biphenyl-4-yl-2-(11-marcaptoundecyloxy)-4-(octyloxy)benzoate.



=AuNP

Figure 1.26: AuNP covered with mesogen.

In a further investigation¹⁰⁷, AuNPs (capped with dodecythiol or hexythiol chain) was covered with 4'-(4-octyloxybenzoyloxy)biphenyl-4-octyloxy-2-(11marcaptoundecyloxy)-4-(octyloxy)benzoate. They reported that the spherical particles were covered with monolayer of calamitic mesogens and hydrocarbon chains. Also, they said the variation in the particle size and hydrocarbon chain length modifies the onset and the range of the liquid crystal phase thereby making the materials chemically stable and exhibit nematic phase behaviour at room temperature.



Figure 1.26: AuNP covered with mesogen.

It was also shown that the NPs can form more-complex anisotropic lattices with two dimensional and three dimensional long-range order¹⁰⁸⁻¹¹⁰.

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CHAPTER TWO

PROJECT TARGET

The many interesting properties of nano-structural materials have attracted considerable interest over the recent years. The combination of liquid crystal organic groups in conjunction with gold nanoparticles has allowed for the 2D and 3D structuring in the bulk of a low ordered nematic phase.

As is was found that increasing the size of the NPs in such systems leads, as anticipated to improved plasmonic properties, but also enhanced viscosities, the scientific challenge was identified to increase NP size and to control the viscosities.

Moreover, rod-shaped NPs are known to show enhanced plasmonic properties, but they can, so far only be prepared at larger sizes than the liquid crystal- NP system explored so far. Thus the target of the project was identified to synthesise AuNP of a well-defined size functionalised them with liquid crystal group. The schematic representation is given in figure 2.1.

The composites (a) were to be synthesised by ligand exchange between mesogenic thiol and 1-dodecnae thiol-capped AuNPs, while composites (b) were to be synthesised hydrolysis/ condensation reaction between triethoxysilane modified mesogen and 11-mercapto-1-undecanol-capped AuNPs.

In order to increase the liquid crystal content, it was decided to use the NPs as centres for the macroinitiators and to polymerise reactive mesogens using a ATRP polymerisation techniques. The structure of the reactive mesogens was schedule to be very close to that of already explored systems.



Figure 2.1: Summary of the project target.

For that an initiator was developed and thiol could be attached to the NPs via thiol ligand exchange.

The side chain liquid crystalline polymer (SCLCP) composites (c) were to be synthesised by grafting SCLCP thiol to AuNPs. The SCLCP composites (d) were to be obtained by growing the polymer from initiator attached to AuNP surfaces.

The aim was to explore the difference in access to those materials using different routes. The synthesis of rod-shape NPs was developed based on literature report using reduction of Au(III) to Au(I) by ascorbic acid in the presence of CTAB and silver nitrate. Following that, in an exchange reaction thiol ligand was introduced in order to remove charged surface group and in the subsequent step initiator molecules were introduced for ATRP polymerisation of the mesogens.

SCLCP composites (e) were to be obtained by growing the polymer from initiator attached to AuNR surfaces while (f) is the similar to (e) but with a longer length of initiator chain. The materials synthesised were to be characterized by NMR, GPC, POM, UV-vis, TEM, SEM, mass spectrometry and XRD.

Fundamentally, the aim of the project was to extend the knowledge of structure properties relationship for liquid crystal-metal nanoparticles to nanoparticles systems of larger size and anisometric shape.

CHAPTER THREE

SYNTHESIS OF GOLD NANOPARTICLES AND GOLD NANORDS

3.1 Introduction

Researchers are more interested in the nanoscience and nanotechnology nowadays than ever before due to different methods of the production and characterization of the new materials with remarkable properties for diverse applications. The properties of these nanomaterials are different from their counterpart with the bulk size. Among other metals, gold nanoparticles (AuNPs) and gold nanorods (AuNRs) are the most investigated nanoparticles due to their unique properties, ease of synthesis, chemical stability and processability. Au nanostructures have unique and interesting mechanical, magnetic, electrical and optical behaviours which are totally different from their conventional macroor millimetre size materials. Their properties rely hugely on their corresponding sizes, shape, surface chemistry and topology.

Nanomaterials have applications in display (flat panel), magneto-optical discs, computer chips, sensors, non-volatile memories, insulators, catalysts, batteries, colour imaging, printing, photodetectors, solar cells, holography, optoelectronics, transistors and switches, medicine (drug delivery, implant, pharmacy) and cosmetics¹.

Gold is a noble metal of group 1B of the periodic table with atomic number of 79 and atomic mass of 197. Gold can exist in various oxidation states, namely, 5, 4, 3, 2, 1, 0, -1. Among all the states, only 0, 1 and 3 states of gold are stable in aqueous solution. Gold (metallic form- 0 oxidation state) is considered the least chemically reactive metals known to man because it stable in air, even when heated, and inert to strong alkalis and acids,

which makes it occur in elemental form on earth. Conversely, Au(I) and Au(III) are not as stable and inert as Au^0 . Au(III) is a strong oxidizing agent which is reduced to Au(I) in the reaction to synthesise gold nanoparticles². Au(I) preferentially reacts with Sulphur and this is why it is possible to stabilize it with thiolate ligands.

3.2 Synthesis of AuNPs

There are different ways of synthesising AuNPs but all base on the same principle of reducing Au(III) salts to Au(0). The synthesis of gold nanoparticles (AuNPs) was based on the reduction of gold salt (HAuCl₄) by sodium borohydride (NaBH₄) following the modified process described by Brust and Schiffrin³. AuNPs when unprotected/uncoated ('naked') are unstable and tend to irreversibly form larger particles, thus there is need to stabilise them, thereby preventing their aggregation. A lot materials have been reported appropriate for stabilizing the nanoparticles but based on the affinity of gold to sulphur, thiol based-ligand/stabilizer are most appropriate⁴.

$$HAuCl_4 + 4 NaBH_4 \longrightarrow Au^{o} + 5/2 H_2 + 2 B_2H_6 + 4 NaCl_4$$

Here, capping of AuNPs with different molar concentrations of 1-dodecanethiol was investigated and reported. Also, the possible effect of temperature was investigated by preparing the AuNPs at 3 different temperatures. When compared to the previous works^{5,6}, the investigation was not limited to low temperature but higher ones were investigated.

3.3 Synthesis of Gold Nanoparticles

Gold Nanoparticles of various sizes were synthesised^{6,7}.

3.3.1 Preparation of stock solution

Stock solution of gold salt (Stock **A**) was prepared by dissolving HAuCl₄ (0.17 g, 0.5 mmol) in water (5 ml) followed by the addition of conc. HCl (0.032 ml) with brief sonication. This was kept from light by storing in dark colour container or wrapping transparent ones with aluminium foil.

Stock solution **B** was prepared by dissolving NaBH₄ (0.03 g, 0.8 mmol) and NaOH (0.03 g, 0.75 mmol) in water (3.23 ml) with brief sonication.

3.3.2 Synthesis of gold nanoparticles of 2 nm



Figure 3.1: Schematic representation of AuNP preparation

Stock **A** (100 μ l) and 1-dodecanethiol (**DDT**) (20 μ l, 0.084 mmol) were added to THF (5 ml) while sonicating. Stock **B** (30 μ l) was then added to the solution and further sonicated for 10 min. The solvent was reduced *in vacuo* and the residue dispersed in ethanol to remove excess/unreacted DDT and finally centrifuged (5000 rpm, 5 min). The supernatant was removed and the process repeated (x3). The black residue was dried *in vacuo* and analysed.

3.3.3 Synthesis of gold nanoparticles in the 3-6 nm range

5 ml of deionised water (DI) was measured into 25 ml vial on ultrasonic bath. 100 μ l of stock solution **A** was added followed by 30 μ l of **B**. Upon the addition of **B**, the aqueous solution became brown or reddish-brown.

3.3.3.1 AuNPs transfer

Acetone (6.5 ml) and hexane (7.6 ml) was added to the vial followed by the addition of 60 μ l of 1-Dodecanethiol to stabilize the NPs. The vial was further sonicated for 10 min. The colloidal gold NPs was transferred from the bottom layer to the top layer. These layers were separated and the brown/red coloured organic phase was concentrated in vacuo. In order to increase the monodisperse of the gold NPs, 10 ml of toluene was added to the residue refluxed for 3 hours.

3.3.4 Synthesis of gold Nanoparticles in 6 nm

An approach to synthesise AuNPs of 6 nm size was attempted⁸ as follows using the ratio of [Au]: [DDT]: [NaBH₄] = 3.5 : 1 : 11. Gold salt trihydrate (HAuCl₄.3H₂O, 0.2065g, mmol) was dissolved in water (0.5 ml), to this solution was added 1-dodecanethiol (0.03g, 0.15 mmol) and finally, NaBH₄ (0.086 g, 2.27 mmol) in water (0.6 ml) was added and the mixture sonicated for 10 min. The mixture was diluted with ethanol (100 ml) and centrifuged (5000 rpm, 5 min), the supernatant removed and the procedure repeated 3 times. The residue was dried and characterized. ¹H NMR confirmed the capping while the average size determined by TEM was 4 nm.

To investigate the effect of the molar concentration of capping agent on plasmonic property of the gold nanoparticles, the above procedures for synthesising 2 nm AuNPs were repeated for [Au]/[Thiol] = 7:1, 5:1, 3:1, 1:1, 1:3 and 1:5 while keeping the $[Au]/[BH_4] = 3:1$ constant. Also, this investigation was extended to other two ligands, viz 1-decanethiol (**DT**) and 1-hexanethiol (**HT**). Table 3.1 shows the volume requirement for each molar ratio of the ligands considered.

Entry ([Au]/[Thiol])	DDT (Volume, µl)	DT (Volume, µl)	HT (Volume,
			μl)
A (7:1)	0.34	0.30	0.20
B (5:1)	0.45	0.41	0.28
C (3:1)	0.79	0.69	0.46
D (1:1)	2.38	2.07	1.40
E (1:3)	7.14	6.21	4.21
F (1:5)	11.90	10.36	7.02

Table 3.1: Volume requirement for each molar ratio of the ligands.



Figure 3.2: Plasmonic behaviour of entries A, B and C for 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT).



Figure 3.3: Plasmonic behaviour of entries D, E and F for 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT).

Entry	DDT (λ_{max}, nm)	DT (λ_{max} , nm)	HT (λ_{max} , nm)
А	540	560	555
В	550	545	*
С	545	540	545
D	-	540	545, 620
E	-	540	540
F	-	540	540

* = Not clearly defined. - not determined

Table 3.2: Maximum wavelength (nm) for corresponding AuNPs

3.4 1-Docanethiol capped gold nanoparticles

The gold nanoparticles were characterised by ¹H NMR, TEM, TGA, UV-vis and elemental analysis.

Figures 3.4 (a) and (b) show the NMR spectra of free 1-dodecanethiol and gold nanoparticle capped with 1-dodecanethiol respectively.



Figure 3.4 (a): ¹H NMR spectra of free 1-Dodecanethiol



Figure 3.4 (b): ¹H NMR spectra of gold nanoparticle capped with 1-Dodecanethiol The signal peak at δ =2.50 ppm (quartet due to -<u>CH₂SH</u> in free thiol) in (b) is broader than in (a,) and appeared as triplet (due to -<u>CH₂S-Au)</u>, and the peak at δ =1.29 ppm (-SH) presents in free thiol (a) has disappeared in capped AuNPs (b).



Figure 3.5: TEM images of AuNPs

The images confirm the monodispersity of the AuNPs with the size distribution ranging between 1.94 nm and 2.51 nm for particles with average size distribution of 2.4 nm, and Table 3.3 shows the size distribution of the AuNPs as observed on TEM and this is depicted in Figure 3.6.

S/n	AuNPs	AuNPs
	(2 nm)	(3 nm)
1	2.20	3.01
2	2.76	3.33
3	2.48	2.74
4	2.32	2.89
5	2.22	2.79
6	2.53	3.17
7	2.40	3.10
8	2.19	3.38
9	2.23	2.68
10	2.21	2.78
11	2.35	3.10
12	2.57	2.71
13	2.23	2.68
14	2.31	3.46
15	2.13	3.29
16	2.49	3.34
17	2.22	2.75
18	2.23	3.34
19	2.23	2.54
20	2.44	3.33
Min =	2.13	2.54
Max =	2.78	3.46
Average=	2.34 ± 0.16	3.02 ± 0.30

Table 3.4: Size distribution of AuNPs



Figure 3.6: Size distribution of the AuNPs.

The size distributions of AuNPs are shown in Figure 3.6: (a) 2 nm AuNPs and (b) 3 nm AuNPs. The minimum size obtained for 2 nm AuNPs was 2.13 nm while the maximum value was 2.78 and with average value of 2.34 ± 0.16 nm. For 3 nm AuNPs, the minimum value recorded was 2.54 nm and 3.46 nm for maximum while the average was 3.02 ± 0.30 nm. From the small relative values of the standard deviations for both 2 nm and 3 nm AuNPs respectively, it is clearly seen that the particles are monodispersed.

The UV-vis spectrum of the two AuNPs are given in Figure 3.7: (a) 2 nm (b) 3 nm





Figure 3.7: The UV-Vis of AuNPs (a) 2 nm (b) 3 nm

In order to ascertain the effect of the concentration of 1-Dodecanethiol (DDT) and/or temperature on the size and size distribution of the capped AuNPs, the concentration of the DDT and temperature in the synthesis were varied and investigated. The normal procedure for the synthesis of particles of average size was maintained with the exception of the varied variables. Table 3.5 shows the result obtained and are present in Figure 3.15.

	DDT x2	DDT x3	DDTx3,	DDT x4	Seeded	150 °C	210 °C	4-6
/N	(nm)	(nm)	50 °C	(nm)	toluene 120 °C	(nm)	(nm)	(nm)
1	3.36	1.94	2.24	2.35	3.17	2.64	1.91	8.93
2	2.84	2.57	2.89	2.01	3.46	2.92	2.14	7.57
3	3.19	2.16	2.46	2.25	2.47	2.97	2.75	6.31
4	3.31	2.36	2.40	2.15	2.89	3.20	1.94	8.02
5	3.23	2.07	2.96	2.39	2.79	2.92	2.80	6.84
6	3.27	2.75	2.60	2.44	3.01	2.19	2.43	7.31
7	3.00	2.37	2.43	2.44	3.58	2.57	2.19	7.20
8	2.99	2.10	2.64	2.92	3.38	2.60	2.44	7.32
9	3.77	2.44	3.10	2.32	2.68	2.54	2.25	7.09
10	2.75	2.90	3.19	2.29	2.78	2.82	2.62	7.09
11	3.38	2.04	3.00	1.99	3.10	2.34	3.00	5.86
12	3.04	2.36	3.44	2.04	2.71	2.46	1.78	7.61
13	3.31	2.44	2.90	2.14	2.68	3.16	2.19	8.65
14	3.19	2.84	2.96	2.19	3.68	2.32	2.46	7.65
15	3.06	2.05	2.79	2.69	3.29	2.54	2.99	6.56
16	3.14	2.49	2.44	2.39	3.34	1.84	2.19	6.08
17	3.15	2.54	2.72	2.71	2.75	2.25	2.11	5.51
18	2.86	2.09	2.71	1.92	3.64	2.78	2.02	6.84
19	3.38	2.38	2.47	2.01	2.54	2.79	2.00	6.84
20	3.56	2.45	2.69	2.34	3.33	2.90	2.19	6.60
Min =	2.75	1.94	2.24	1.92	2.47	1.84	1.78	5.51
Max =	3.77	2.90	3.44	2.92	3.68	3.20	3.00	8.93
Average=	3.20	2.37	2.76	2.31	3.06	2.63	2.33	7.11

Table 3.5: Changes in concentration of 1-Dodecanethiol and temperature of AuNPs.



Figure 3.8: Size distribution of AuNPs

It was observed that when the DDT concentration was doubled (DDT x2), the average size was 3.20 nm with the smallest particle size of 2.75 nm and largest size 3.77 nm. Increasing the DDT concentration further (DDT x3) leads to further decrease in the size of the nanoparticles to 2.90 nm (23 % decrement) for largest particle and 1.94 nm (29 % decrement) for the smallest particle. The average particle size decreases from 3.20 nm for DDT x 2, to 2.37 nm for DDT x 3 (26 % decrement).

When a temperature of 50 °C was used while maintaining the concentration at DDT x 3, an increment in the particle sizes was observed and eventually increment of the particle size distribution. The smallest particle size increase from 1.94 nm to 2.44 nm (26 %) while the largest particle size increased from 2.90 nm to 3.44 nm (19 %) and the average particle size increased from 2.37 nm to 2.76 nm (16%).

Further decrease in particle sizes was observed with further increase in DDT concentration (DDT x 4). The smallest particle size was 1.92 nm (30 % decreases) while the largest particle size was 2.92 nm (23 % decrease) and the average particle size 2.31 nm (28 % decrease). Also, shown in the table is the result obtained when 2 nm as prepared AuNPs are seed at 120 °C for 3 h. There was observable increase in the particle sizes, with the smallest particle 2.47 nm and the largest particle 3.06 nm.

This work is in agreement with the literature⁹ that the amount of the capping agent and temperature influence the size of the nanoparticles and their size distribution.

3.5 SYNTHESIS OF GOLD NANORODS (AuNRs)

There are many potential sensing applications for Au nanorods due to a tunable localized surface plasmon resonance (LSPR) frequency that changes with aspect ratio. Two different methods were investigated for the synthesis of AuNRs. The first is the seed-mediated or growth method¹⁰ in the reduction of gold salt by weak reducing agent to NRs takes place in the presence of seed NPs, surfactant and silver ions. The second method is non-seeding it also produce NRs with good dimensions¹¹.

3.5.1 Results

Fig. 3.9 shows the concentrated solution of as-prepared AuNRs



Figure 3.9: AuNRs as prepared



Figure 3.10: TEM image of AuNRs

Shown in Fig. 3.10 is the TEM image of the AuNRs. The dimensions of the NRs are given in Table 3.6 below.

Entry	1	2	3	4	5	6	7	8	9	10
L (nm)	29.32	30.42	29.78	23.96	27.62	24.98	25.09	23.65	24.33	26.35
B (nm)	9.77	8.97	10.63	7.87	9.39	8.35	8.11	10.05	8.14	8.11
A/R	3.0	3.4	2.8	3.0	2.9	3.0	3.1	2.4	3.0	3.3

Entry	11	12	13	14	15	16	17	18	19	20
L (nm)	30.44	26.86	22.29	24.69	23.37	29.63	25.61	25.71	24.33	26.32
B (nm)	10.66	7.71	7.04	8.18	8.09	9.18	8.46	8.90	8.18	8.01
A/R	2.9	3.5	3.2	3.0	2.9	3.2	3.0	2.9	3.0	3.3

	Min	Max	Ave
L (nm)	22.29	30.44	26.24
B (nm)	7.04	10.66	8.69
A/R	2.4	3.5	3.03

Table 3.6: Size distribution of AuNRs.

The average length for the AuNRs was 26.24 nm with 22.29 nm as minimum and 30.44 nm as maximum. Also, the average diameter was 8.69 nm with 7.04 nm as minimum and 10.66 nm as maximum. The minimum dimensions gave average aspect ratio of 2.4 while the maximum values gave 3.5 and on average the aspect ratio was 3.03.

Figure 3.11 shows the plasmonic behaviour of AuNRs in UV-vis. Unlike AuNPs, AuNRs exhibits two absorption peaks with the first around 502 nm which is the same as that seen in NPs, while the second peak is at 775 nm is not seen in NPs and the position varies from visible region to near infrared region depending on the aspect ratio.



Figure 3.11: UV-vis spectrum of AuNRs

3.6 Experimental procedures

Two different methods were explored for the synthesis of gold nanorod (AuNRs).

3.6.1 First method (modified seed-mediated growth approach)⁶



 \square = AuNR

This method involves the addition of seed solution to growing solution of AuNRs.

3.6.1.1 Preparation of seed solution

Ice-cold solution of NaBH₄ (0.6 ml, 10 mM) was added to stirred solutions of CTAB (5ml, 0.20 M) and HAuCl₄ (5 ml, 0.5 mM) to obtain a brownish-yellow solution. This solution was vigorously stirred for 2 min and kept at 25 $^{\circ}$ C.

3.6.1.2 Growth of NRs (plasmon band <850 nm)

AgNO₃ solution (0.25 ml, 4 mM) was added to a solution of CTAB (5 ml, 0.20 M) at 25 $^{\circ}$ C, followed by HAuCl₄ solution (5 ml, 1 mM) with gentle mixing. Solution of L-ascorbic acid (70µl, 0.0788 M), was added. Immediately, the dark yellow colour turned colourless due to reduction by the ascorbic acid. Finally, the seed solution (12 µl) was added at 30 $^{\circ}$ C and the colour of the solution gradually changed (10-20 min). The AuNRs are precipitated by centrifugation. The NRs with aspect ratio of 4.7 were obtained.

Note: the amount of AgNO₃ solution can be varied so as to obtain different aspect ratios $(0.05, 0.10, 0.15, 0.20 \text{ ml})^2$.

3.6.1.3 Preparation of Reagents

A. SEED SOLUTION

• CTAB solution (20 ml, 0.20 M)

Water (DI, 20 ml) was added to CTAB (1.4578 g, 4 mmol) to have 20 ml solution since it would still be used in the growth of the NRs.

• HAuCl₄ (5 ml, 0.5 mM)

HAuCl₄ (0.00085 g, 0.0025 mmol) was dissolved in DI water (5 ml).

• NaBH₄ (1 ml, 10 mM)

NaBH₄ (0.00038 g, 0.01 mmol) was dissolved in DI water (1 ml).

B. GROWTH OF NRs WITH PB < 850 nm

• AgNO₃ (2 ml, 4 mM)

AgNO₃ (0.0014g, 0.0082 mmol) was dissolved in DI water (2 ml).

• HAuCl₄ (5 ml, 0.1 mM)

HAuCl₄ (0.0017 g, 0.005 mmol) was dissolved in DI water (5 ml).

• L-ascorbic acid (1 ml, 0.0788 M)

L-ascorbic acid (0.0139 g, 0.079 mmol) was dissolved in DI water (1 ml).

3.6.2 Second method (Non-seeding)¹²

The gold nanorods were prepared by non-seeding and one step method¹. HAuCl₄ (0.1103 g, 0.28 mmol) and CTAB (18.23 g, 0.05 mol) were dissolved in deionised water to form a 200 ml orange aqueous solution by mild stirring at 30 °C. To this was added AgNO₃ (8.5 mg, 0.05 mmol) in water (5 ml) and L-ascorbic acid (0.1 g, 0.6 mmol) in water (5 ml) while gently stirring continued to obtain a colourless solution immediately upon addition. NaBH₄ (1.875 ml, 0.1 mM) was finally added and stirred for 2 min. The deep colour solution was kept undisturbed at 26 °C in water bath for minimum of 12 h to obtain a reddish brown solution. The AuNRs suspension was centrifuged to remove excess CTAB, the supernatant was discarded and the precipitated AuNRs re-dissolved in water (100 ml). The process was repeated to obtain AuNRs capped with CTAB.

3.6.2.1 Preparation of reagents

• 200 ml solution of HAuCl₄ and CTAB

HAuCl₄ (0.1103 g, 0.28 mmol) and CTAB (81.23 g, 0.05 mmol) were dissolved in DI water (200 ml).

• AgNO₃

5 ml of 0.05 mmol = 0.0085 g of AgNO₃ (0.0085 g, 005 mmol) was dissolved in DI water (5 ml).

• L-ascorbic acid

5 ml of 0.5 mol = 0.1 g of L-ascorbic acid, make up to 5 ml with DI water

• NaBH₄

 1.875μ l, $0.1 \text{ mM} = 7.09 \text{ x } 10^{-6} \text{ g in } 1.875 \text{ ml of DI water}$

This was a very small amount of NaBH₄ and measurement was difficult! So, 0.1 M NaBH₄ was prepared from which 0.1 mM was later made by dilution.

3.6.2.2 Preparation of 2 ml of 0.1 M NaBH₄

2 ml of 0.1 M NaBH₄ = 0.00757 g of NaBH₄, make up to 2 ml with DI water

3.6.2.3 Preparation of 1.875 ml of 0.1 mM NaBH₄ from 0.1 M NaBH₄

Using $V_1N_1 = V_2N_2$, the volume of 0.1 M NaBH₄ conc solution needed to prepare 0.1 mM NaBH₄ was obtained.

 $V_1N_1 = V_2N_2$, where $V_1 = 1.875$ ml, $N_1 = 0.1$ mM = 0.0001 M, $N_2 = 0.1$ M, $V_2 =$? (volume of 0.1 M required to make the desired conc).

 $V_2 = 0.001875$ ml of 0.1 M NaBH₄ conc solution. Was made up to 1.875 ml with DI water to have 0.1 mM solution of NaBH₄.

 $1.875 \ \mu l$ of $0.1M \ NaBH_4$ was then made up to $1.875 \ m l$ by DI water to have $0.1 \ m M$ NaBH₄.

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CHAPTER FOUR

COMPOSITES OF GOLD NANOPARTICLES AND ORGANIC MESOGENIC LIGANDS

4.1 Introduction

The attention of scientists is now on the metal nanoparticle liquid crystalline materials due to their potential applications in magnetic, optical, electronic devices and as catalyst. Nanocomposites are of great and interesting properties most especially those made up of gold nanoparticles and liquid crystalline materials. In this report, gold nanoparticle liquid crystalline composites were synthesised and their properties determined. Firstly, the mesogen 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 4-(octyloxy)-2-(pent-4-en-1-yloxy)benzoate (**4.7**) was synthesised followed by functionalising gold nanoparticles (2-3 nm and 3-6 nm) (synthesised by reducing a gold salt and subsequently capped by 1-dodecanethiol) by it through different means. The mesogen, nanoparticles and the composites were characterized.

4.2 Synthesis of the mesogen 4.7

Synthesis of the mesogenic compound $(4.7)^{1-2}$ started by alkylation of methyl-2,4dihydroxybenzoate, **4.1**, in the para-position by 1-bromooctane, followed by alkylation by 5-bromo-1-pentene in the ortho-position (using Williamson etherification) of the aromatic ring to afford compound **4.3** (Scheme 4.1). The deprotection of the carboxylic acid function of compound **4.3** afforded the first intermediated compound **4.4**². The second intermediate compound **4.6** was synthesis from 4'4-biphenol (**4.5**) by alkylation of one of the hydroxyl functional group. Three methods were explored, all giving appreciable yield (>60 %) $^{3-5}$.



Scheme 4.1: (a) K_2CO_3 , KI, 4 Å molecular sieves, butanone, 1-bromooctane, $\triangle T$, 75%; (b) K_2CO_3 , KI, 4Å molecular sieves, butanone, 5-bromo-1-pentene, $\triangle T$, 98%; (c) (i) KOH, H₂O, MeOH, THF (ii) HCl, H₂O, 60%; (d) K_2CO_3 , KI, acetone, 1-bromoundecane, $\triangle T$, 62%; (e) (i) SOCl₂, toluene, $\triangle T$ (ii) pyridine, toluene, $\triangle T$, 69%; (f) AIBN, 1,4-dioxane, CH₃COSH,C₆H₁₂, 76%; (g) TBACN, CH₃Cl, CH₃OH, 92%.

Esterification of the intermediate compounds 4.4 and 4.6 yielded mesogenic compound

4.7 ^{1,2,4,6}.

4.3 Synthesis of 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-mercaptopentyl)oxy)-



4-(octyloxy)benzoate (4.9)

Figure 4.1: Synthesis of the AuNP composite.

In order to attach gold nanoparticles synthesised to the mesogen, there is need to convert the lateral alkene end of compound **4.7** to a thiol. To achieve this, the alkene end was converted to thioacetate **4.8** using AIBN as free radical initiator⁷ and thioacetic acid. Two methods were explored with the amount of thioacetic acid used in the first smaller than with the second effort. Although, the yield obtained in the first method was higher (88%), the reaction took 10 hours. The second method took 2.20 hours with a 66% yield. The reason could be associated with the temperature and solvents used. Earlier studies⁸ show that thermal decomposition of AIBN is complicated; it behaves differently in different conditions.

The deacylation of compound **4.8** to afford the targeted mesogenic thiol compound **4.9** was a challenging step as eight different methods (experiments) were investigated without a

positive result due to the cleavage of fragile and sensitive ester linkage (-COOC) in the compound **4.8**.

To overcome this challenge, a catalyst that would effect the deacylation without cleaving the ester linkage is required. Below are some of those tried.

5% methanolic KOH was used. After 12 hours of reaction, potassium salt of the cleaved product was obtained. Hydrazine (4 hours), Hydrazine acetate (15 hours), Methanolic ammonoia (1 hour), Pyrrolidine with Acetonitrile as solvent (3 hours), Pyrrolidine with *N*, *N*-Dimethylformamide as solvent (3 hours) were other methods used but with the same results: a cleaved ester linkage.

With Pyrrolidine (in *N*, *N*-Dimethylformamide), lowering the amount used from 0.111 ml (1.33 mmol) to 0.042 ml (0.5 mmol) yielded 0.0061 g (5.4%) of the desired product (thiol mesogen). When the amount of pyrrolidine was lowered to less than 0.042 ml, there was no reaction and the starting material was recovered.

In the ninth experiment, Tetrabutyl ammonium cyanide (TBACN)³ was used and it yielded a positive result. With 10 % TBACN, 100 % of compound **4.9** was obtained. Increasing the amount of TBACN to 28 %, also yielded 100 % of thiol. The purity was determined by HPLC (peak area of 88.612 % at 14.39 minutes).

Scaling up the reaction (with magnitude of 10), dropped the yield to 91.3 %. Although, the deacylation of compound **4.8** was a challenging step, with perseverance, it was possible to overcome this challenge.

4.4 Synthesis of AuNP-4'-(Undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-

mercaptopentyl)oxy)-4-(octyloxy) benzoate liquid crystal composite (4.10)

1-Dodecanethiol capped AuNPs was subjected to ligand exchange reaction with compound 4.9 in DCM at 25 °C for 5 days. The composite formed was purified by repeated centrifugation and dried *in vacuo*.

4.5 Synthesis of AuNP-Ethoxysilane composite (4.13)

In order to investigate another material from gold nanoparticles and mesogenic compound **4.7**, gold nanoparticles were functionalized by compound **4.7** via siloxane linkage⁹.



Figure 4.2: Synthesis of composite 4.13.

AuNP surface was also functionalised by the mesogen **4.7** via a siloxane linkage⁹. The silane conjunction approach was carried out by capping AuNP with 11-marcapto-1-

Undecanol¹⁰ while the terminal alkene of mesogen **4.7** was converted to a triethoxysilane end group (**4.11**) by hydrosilylation reaction.

The targeted composite was obtained by the hydrolysis and condensation of the hydroxyl ends of 11-marcapto-1-Undecanol capped-AuNP and the ethoxy groups of the mesogenic silane to afford the composite **4.13** as shown in **scheme 4.2**.



Scheme 4.2: Synthesis of composite **4.13**.

4.6.1 Synthesis of the mesogenic ligand

4.6

The targeted mesogenic ligand **4.9** was systematically synthesised through eight steps synthetic sequence route with each intermediate obtained in, at least, a very good yield. **Table 4.1** presents the yields and the elemental analysis of the compounds.

Compound		Yield (%)	Element	Expected	Found (%)
				(%)	
C ₈ H ₁₇ O			С	68.55	68.70
OCH3 OH	4.2	75	Н	8.63	8.69
			С	72.38	72.37
O C C H ₃ (H ₂ C) ₃	4.3	98	Н	9.26	9.03
C ₈ H ₁₇ O-			С	71.83	72.02
(H ₂ C) ₃	4.4	60	Н	9.04	9.34
HO-	4.6		С	81.13	81.03
		64	Н	9.47	9.70
C ₈ H ₁₇ O	ц		С	78.62	78.32
0 (H ₂ C) ₃ (H ₂ C) ₃	п ₂₃	80	Н	9.21	9.47
	4.7				
C ₈ H ₁₇ O			С	73.73	73.53
(H ₂ C) (H ₂ C)	H ₂₃	88	Н	8.80	8.81
०≼ॅ			S	4.37	4.37



Table 41: Yield and elemental analysis results of compounds

The alkylation of the para and ortho hydroxyl groups involved the formation of intermediate alkoxide which subsequently reacted with the alkyl halide to afford the targeted ether bond of 75 % for the para- and 98 % for the ortho-substitution. The values obtained from elemental analysis for these compounds are in good agreement with the theoretical values (Table 4.1).

Deprotection of the acid functional group in compound **4.3** was achieved by base hydrolysis of the ester group to afford compound **4.4** in a very good yield.

Compound **4.6** was obtained by the alkylation of one hydroxyl group of the compound **4.5**. The mechanism is similar to that used in the synthesis of compound **4.3** and **4.4**.

The targeted mesogenic compound **4.7** was synthesised by the esterification of intermediate compounds **4.4** and **4.6** in quantitative yield. The details of which involving first the conversion of carboxylic intermediate compound **4.4** to an acyl chloride using thionyl chloride followed by the in situ esterification with hydroxyl intermediate compound **4.6**. The conversion of the terminal alkene of the mesogenic compound **4.7** to the thioacetyl group was confirmed by NMR (Figure 4.3) where the signal due to methylene protons (d = 5.0 ppm) and the methine proton (d = 5.7 ppm) observed in (a) have completely disappeared in the thioacetate **4.8** (b).



Figure 4.3: ¹H NMR of (a) **4.7**, (b) **4.8** and (c) **4.9**.

Also, the signal due to the methylene protons adjacent to the double bond in **4.7** (d = 2.3 ppm in (a)) has disappeared in **4.8** (b). The appearance of a singlet peak (d = 2.28 ppm, due to methyl protons of thioacetyl group) and triplet peak (d = 2.84 ppm, due to methylene protons bonded to S) in **4.8** (b), further confirmed the conversion.

The deacylation of compound **4.8** to obtain the targeted mesogenic ligand **4.9** was confirmed by the disappearance of the signal at d = 2.28 ppm (due to acetyl methyl protons in (b)) and the appearance of the methylene protons adjacent to S upfield and as a quartet (d = 2.50 ppm) in **4.9** (c).

The mesophase characterisation of compounds **4.7**, **4.8** and **4.9** were determined by polarising optical microscope (POM) and Differential Scanning Calorimetry. The mesophase properties are summarised in Table 4.2.

Compound	Melting Point	Transition	Enthalpy Change
	(°C)	Temperature (°C) N	(Jg ⁻¹)
		to I	
$C_8H_{17}O \longrightarrow O O O O O O O O O O O O O O O O O O$	53.3	71.7	1.59
4.7			
$C_8H_{17}O \xrightarrow{O} O O \longrightarrow{O} O \longrightarrow{O} O $	57.0	57.9	1.48

4.8


Table 4.2: Thermal behaviour of compounds 4.7, 4.8, 4.9.

CompoundTransition temperature/ °C (Enthalpy J g⁻¹)4.7Cr 53.3 (71.9)N 71.7 (1.59)4.8Cr 57.0 (117.9)N 57.9 (1.48)4.9Cr 42.2 (56.4)N 54.6 (0.60)Cr = crystalline,N = Nematic, Iso = Isotropic

Table 4.3. Transition temperature (°C) as determined by DSC (10 °C/min)

The melting transition energy from crystalline solid to nematic phase for compounds **4.7**, **4.8**, and **4.9** are 71.92, 117.98 and 56.42 Jg⁻¹ respectively, and as Table 4.3 shows, their corresponding temperatures are 53.3 °C, 57.0 °C and 42.2°C. The transition enthalpy from the nematic phase to isotropic phase is usually small (1.59, 1.48 and 0.60 J/g respectively)¹¹ and the values obtained above conform to this range. Data obtained from heating and cooling cycle of compound **4.7**, **4.8** and **4.9** is respectively shown in figure 4.4, 4.5 and 4.6.



Figure 4.4: DSC heating and cooling curve of compound **4.7**.



Figure 4.5: DSC heating and cooling curve of compound **4.8**.



Figure 4.6: DSC heating and cooling curve of compound **4.9**.

The textures observed from OPM for compounds **4.7**, **4.8**, and **4.9**, are as shown in figure 4.7.



Figure 4.7: Textures of compounds as observed under POM (a) Crystalline phase of compound **4.2** (x 100) at 25 °C (b) Crystalline phase of compound **4.4** (x 100) at 25 °C. (c) Compound **4.7** (x 400) at 25 °C (d) Compound **4.7** (x 400) at 70.9 °C (e) Compound **4.8** (x 400) at 25 °C (f) Compound **4.8** (x 400) at 52 °C (g) Compound **4.9** (x 400) at 25 °C (h) Compound **4.9** (x 400) at 48 °C (i) Coupled AuNP (3 nm)-mesogen liquid crystal (x 100).

Compounds **4.7**, **4.8**, and **4.9** are nematic as evidenced by their schlieren textures, and their respective clearing points are at 71.2 °C, 57.9 °C and 54.6 °C.

Compounds **4.2** and compound **4.4** were also observed under OPM and their respective crystalline textures are as shown in figures 4.7 (a) and 4.7 (b).

4.7 Gold nanoparticle-4'-(Undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-

mercaptopentyl)oxy)-4-(octyloxy) benzoate liquid crystal

Figures 4.8, 4.9, 4.10 and 4.11 show the ¹H NMR spectra of pure mesogen (compound **4.9**), coupled AuNP (2-3 nm)-mesogen, coupled AuNP (3-6 nm)-mesogen and direct mesogen-capped AuNP liquid crystals.



Figure 4.8: ¹H NMR of compound **4.9**.



Figure 4.9: ¹H NMR of composite **4.10** (2 nm).



Figure 4.10: ¹H NMR of composite **4.10** (3 nm)..



Figure 4.11: ¹H NMR of direct mesogen-capped AuNP LC.

As can be seen from figures 4.9, 4.10 and 4.11, there is evidence of bonding of gold to the sulphur atom of the mesogen. The signal at 2.2 ppm in the mesogen is not seen in coupled AuNP-mesogen liquid crystals (figure 4.9 and 4.10), but it is still visible on direct mesogen-capped AuNP liquid crystal (Figure 4.11). This can be explained as the total substitution of all the hydrogen bonded to sulphur by gold in composite **4.10**. However, in the direct mesogen-capped there are possibly free mesogen present. This might be explain based on the time allowed for the reaction- more in coupled (5 days) than in the direct capped methods (ten minutes).

Also, when all the AuNP/mesogen liquid crystals are compared with the mesogen, there is transformation of quartet signal at $\delta = 2.4-2.5$ (CH₂CH₂SH) to triplet (CH₂CH₂S-Au). This is evidence that there is -S-Au bonding throughout the samples. Although, this is almost invisible in figure 4.8 due to the smaller size of the gold nanoparticles (2-3nm).

It was also noted that the peaks were not sharp but blurred in all the AuNP/mesogen liquid crystals even at a high scanning rate (64). This is attributed to the polymer-like structure of the system with reduced mobility of the organic groups, when compared to small molecules.

Table 4.4 presents the size distributions of composites as measured from TEM while figure 4.12 shows the distribution.

Sample	4.10 (2 nm)	4.10 (3 nm)
1	2.41	2.74
2	2.04	2.57
3	2.36	2.68
4	2.40	2.54
5	2.43	2.64
6	1.94	2.47
7	2.42	3.14
8	2.06	2.89
9	2.25	2.91
10	2.18	2.52
11	2.07	3.41
12	2.24	3.14
13	2.14	2.91
14	2.14	3.07
15	2.27	3.21
16	2.09	2.80
17	2.51	2.99
18	2.26	3.21
19	2.37	2.64
20	2.31	3.27
Min =	1.94	2.47
Max =	2.51	3.41
Average =	2.24 ± 0.16	2.89 ± 0.28

Table 4.4: Size distribution of composite **4.10**.



Figure 4.12a: TEM image of composite **4.10**.



Figure 4.12b: Size distribution of composite **4.10**.

When observed by OPM, only the composite 4.10 (3 nm)-mesogen shows liquid crystalline phase behaviour although the textures are not well formed as figure 4.13 shows the observed texture by OPM.



Figure 4.13: OPM image of composite **4.10** (3 nm) (x100) at 25°C.



Figure 4.14: SEM images of **4.10**: (a) Back Scattered Detector image (b) SecondaryElectron imaging.

Figure 4.14 shows the SEM images of composite **4.10**. (a) is the BSD images which shows the presence of AuNPs in the homogenous composites (the white spots; bigger regions shows lots of Au closer to the surface). (b) is the SEI image of the composite and it shows the topography of the area scanned. Also, this confirms the homogeneity of the composite and the presence of the ligand on Au.

The data obtained from heating and cooling cycle of coupled AuNP (2 nm)-mesogen and coupled AuNP (3 nm)-mesogen liquid crystal respectively is shown in figure 4.15 and 4.16.



Figure 4.15: DSC heating and cooling curve of coupled **4.10** (2 nm).



Figure 4.16: DSC heating and cooling curve of composite **4.10** (3 nm).

The phase transition is difficult to detect as can be seen from figures 4.15 and 4.16 for nanoparticle composites, this result is not unexpected and is attributed to the fact that the transition are broad because of the nanoparticles. This behaviour is similar to the one observed for some polymers.

Also, figure 4.17(a) and (b), shows the results of the thermogravimetry analysis of composite **4.10** (3 nm) and **4.10** (2 nm) respectively.



Figure 4.17 (a): TGA thermogram of **4.10** (3 nm).



Figure 4.17 (b): TGA thermogram of 4.10 (2 nm)

The mass losses exhibited by the composites were single, well defined steps of approximately 200 °C width beginning at 240 °C for the two composites. The mass losses were 42.48 % and 50.16 % which correspond to quantitative loss of the mesogenic thiolated ligands from **4.10** (3 nm) and **4.10** (2 nm) respectively. The residue which is gold is 57.50 % and 49.77 % respectively.

Elements	4.10 (2 nm)	4.10 (3 nm)
	(%)	(%)
С	58.45	27.82
Н	6.85	4.61
S	3.84	5.40

The composition elemental analysis (C, H, and S) are presented in Table 4.5.

Table 4.5: Elemental analysis of AuNPLC

The plasmonic properties of the composites are shown in figure 4.18.



Figure 4.18: UV-vis of **4.10** (a) 2 nm (b) 3 nm

There is absorption in the wavelength of 530 nm although this was more pronounced in **4.10** (3 nm) than in **4.10** (2 nm) as the increase in size of the nanoparticles enhances the properties of the resulted composites.

4.8 AuNP-ES Nanocomposite (composite 4.13)

4.8.1 11-Mercapto-1-undecanol capped AuNPs (4.12)

The ¹H NMR confirmed the capping of AuNPs by 11-Mercapto-1-undecanol (compound **4.12**) as shown in figure 4.19 where all the signals on the free 11-mercapto-1-undecanol (a) were seen on the capped AuNPs (**4.12**).



Figure 4.19: ¹H NMR of (a) Free 11-mercapto-1-undecanol ; (b) compound **4.12**.

The TEM image of **4.12** is as shown in figure 4.19 in which the monodispersity of the particles was observed and the smallest size observed was 2.52 nm while the largest was 3.98 nm with average particle size of 3.2 nm (Table 4.6 & Figure 4.20).



Figure 4.19: TEM of **4.12**.

S/n	Compound 4.12
1	2.62
2	2.52
3	3.42
4	3.98
5	3.38
6	3.41
7	3.23
8	3.28
9	3.30
10	3.34
11	3.16
12	3.28
13	3.56
14	2.66
15	2.52
16	3.45
17	3.19
18	3.50
19	2.88
20	3.30
Min =	2.52
Max =	3.98
Average=	3.20 ± 0.38

Table 4.6: Sizes of compound 4.12.



Figure 4.20: Compound 4.12 size distribution

The compositional elemental analysis (C, H, and S) found for compound **4.12** are presented in Table 4.7.

Element	Composition			
	(%)			
С	9.96			
Н	1.61			
S	2.37			

Table 4.7: Elemental analysis of compound **4.12**

The thermal behaviour of compound **4.12** is presented in the TGA thermogram, figure 4.21.



Figure 4.21: TGA thermogram of compound **4.12**.

The UV-Vis spectrum of compound **4.12** shows absorption at about 540 nm as shown in Figure 4.22.



Figure 4.22: UV-vis of compound **4.12**.

4.9 Ethoxysilane mesogen (compound 4.11)

The synthetic yield for the ethoxy silane mesogen (compound **4.11**) was good but it was observed that the only side product was the one in which the double bond of compound **7** migrated to position 2. Compound **4.11** was reacted with compound **4.12** to obtain the targeted composite **4.13**.

4.9.1 Nanocomposite 4.13

¹H NMR confirmed the success of the reaction. Figure 4.23 compares the spectrum of ethoxysilane mesogen compound **4.11** (a) with that of the nanocomposite **4.13** (b) in which all the signals due to the mesogen are clearly seen.



Figure 4.23: ¹H NMR of (a) mesogen **4.11**; (b) nanocomposite **4.13**.

The TEM image of the composite **4.13** is shown in figure 4.24 while Table 4.8 shows the size distribution of the particles.



Figure 4.24: TEM of **4.13**.

Sample	Composite 4.13
1	3.06
2	4.24
3	3.28
4	3.73
5	3.34
6	3.15
7	3.17
8	3.16
9	3.90
10	4.27
11	3.71
12	3.36
13	3.60
14	3.80
15	3.90
16	3.34
17	3.34
18	3.17
19	4.10
20	4.14
Min = 3.06	
Max = 4.27	
Average =	3.59 ± 0.4

Table 4.8: Sizes of composite **4.13**.

From TEM data, the average size of composite **4.13** was 3.60 nm and the thermal behaviour from DSC experiment is shown in figure 4.25. The DSC curve shows a broad absorption between 50 °C and 110 °C which is peculiar to composites and polymeric materials.

The optical texture observed by POM with slightly uncrossed polarizers, is as shown in figure 4.26. Composite **4.13** shows birefringence after been sheared, although there was no observable phase transition under POM. This type of birefringence is common to composites with high metal content.



Figure 4.25: DSC of composite **4.13**.



Figure 4.26: POM texture of composite 4.13 (x 400).

Figure 4.27 shows the XRD for composite **4.13** while Table 4.9 shows the 2θ angle, their corresponding lattice spacing and intensity.

20	2.49	5.0	7.6
(°)			
d	35.5	17.7	11.8
(Å)			

Table 4.9: XRD data of composite **4.13**.



Figure 4.27: XRD of composite 4.13.

The results obtained here are very new and need confirmation. The data with reflection of composite **4.13** associated with 001, 002, 003 reflections fit to a smectic layering of 35.5 Å. This is the first example of such a laterally allocated mesogen not showing columnar but smectic organisation of the gold nanoparticles in layers. Also, the size of the NP is confirmed by XRD to be 3.6 nm which is in agreement with that obtained from TEM data.





Figure 4.28: TGA thermogram of composite 4.13.

The mass losses exhibited by the composites occurred in two steps, the first is the mass loss of 2.64 % between 50-110 °C and the second loss 12.17 % between 110-150 °C. The moiety responsible for the mass loss of 11.38 % observed between 210- 410 °C is not too clear at moment and possibly due to further oxidation of silanes/silicates. The first mass loss is probably due to the water and condensation by-products of organic alkoxy silane compounds, while the second is due to loss of the ligand. The gold residue is 84.76 % which means that the organic content is 14.81 %. Which is in agreement with the compositional elemental analysis (C, H, and S) for composite **4.13** presented in Table 4.10.

Element	Composition			
	(%)			
С	12.67			
Н	1.91			
S	1.95			

Table 4.10. Elemental analysis of composite **4.13**.

The UV-Vis spectrum of composite **4.13** shows absorption at approximately 560 nm as shown in figure 4.29.



Figure 4.29: UV-Vis spectrum of composite 4.13.

This is evidence that there is change in the environment of the Au surfaces and this can be attributed to the presence of the mesogenic units which further confirms the success of the reaction.

4.10 Conclusion

Mesogenic ligand was synthesised using a seven steps synthetic route with the last step presenting a challenge of deacylating thioacetate without cleaving the sensitive ester linkage in the compound. With perseverance the challenge was overcome by using TBACN to obtain the targeted ligand in quantitative yield. Also, 1-dodecanethiol capped AuNPs were synthesised and characterised and later coupled to the ligand through ligand exchange to obtain the targeted composites.

It was observed that the mass loss in TGA and percent (C + H + S) from the composition elemental analysis is in close agreement although for AuNPLC (2 nm), the difference may be attributed to the small amount of sample available for the analysis. This is show in the Table 4.11.

4.10 (2 m	.10 (2 nm)		4.10 (3 nm)		4.12		te 4.13
EA	TGA	EA	TGA	EA	TGA	EA	TGA
value	value	value	value	value	value	value	value
(70)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
69.14	50.16	37.83	42.50	13.94	16.21	16.53	14.81

EA: Elemental analysis (values are for organic components)

Table 4.11: Elemental analysis and TGA results for the composites

All nanocomposites show Bragg reflections corresponding to the (001), (002) and (003) reflections at $2\theta = \sim 2.5^{\circ}$, 5.0° and 7.5° respectively, with the (003) signal more pronounced in nanocomposite **4.13** than others possibly due to the smaller size of the ligand when compared to the polymeric nanocomposites (**25/28**, **AuNP-MCP**). The size

of the corresponding AuNP was estimated from the strong (001) Bragg reflection in the XRD pattern at $2\theta = \sim 2.5^{\circ}$ and indicates that gold particles possess a highly oriented crystalline character.

From XRD, TEM and TGA data, the average number of gold atoms (N_{Au}), the number of ligands/polymers per nanoparticles (N_L or N_P) and the average molecular weight of the composites (M_W) were estimated using the equation (1), (2) and (3) respectively¹⁴⁻¹⁵.

Where $Vg(volume \ of \ gold \ atom) = 17 \ \text{\AA}, r = radius \ of \ AuNP(\text{\AA})$

or

 $N_{Au} = \frac{\pi \rho d^3}{6Au} N \qquad (1b)$

Where ρ = density of fcc gold (19.3 g/cm³ = 1.93 x 10⁻²¹ g/ nm³), Au = atomic weight of gold = 197 g/mol and d = average diameter of the nanoparticles (nm) and N = number of atoms per mole (6.02 x 10²³).

The number of ligand/polymer per nanoparticle (NL) was calculated using,

$$N_{L} = \frac{(N_{Au})(Au)(wt\%L)}{(M_{wL})(wt\%Au)} \qquad(2)$$

Where wt%L = weight percent of ligand/polymer (obtained from TGA), wt%Au = weight percent of gold (obtained from TGA), M_{wL} = average molecular weight of the ligand (for polymeric composites, it is obtained either from Mass spec or GPC for free polymers). Finally, the average molecular weights of the composite were obtained using equation (3). $M_w = (N_{Au})(Au) + (N_L)(M_{wL})$ Table 4.12 presents the results obtained for different AuNP surface-modified and the composites.

Table 4.12 presents the results obtained for different AuNP surface-modified and the composites.

Material/Composite	Wt%Au	Wt%L	d (nm)	r	M _{wL}	N _{Au}	NL	Mw
	(TGA)	(TGA)	(TEM)	(nm)				
4.10 (2 nm)	49.77	50.16	2.24	1.12	691	346	99	137562
4.10 (3 nm)	57.50	42.48	2.89	1.45	691	751	158	257104
4.12	60.31	39.69	3.20	1.60	203	1009	643	329510
4.13	71.58	28.42	3.60	1.80	1012	1437	49	332628

Table 4.12: N_{Au} , N_L and M_w for the nanocomposites.

4.11 Experimental Procedure

4.11.1 Methyl 2,4-dihydroxybenzoate (4.1)



Pending the availability of the compound **1** from Aldrich, it was synthesised from 2,4dihydroxybenzoic acid as follows.

Concentrated sulphuric acid (6.5 ml) was slowly added to a solution of 2,4dihydroxybenzoic (5.0 g, 32mmol) in methanol (300 ml). The reaction mixture was reflux with stirring for 4 h. The solvent was evaporated and water (50 ml) added. The precipitate was filtered off, washed with water and re-crystallized from ethanol (96%) to give a white powder.

Yield: 4.12 g (84%)

Melting point: 118.5 °C

 R_{f} (EtOAc/Hexane, 1:1) = 0.61.

¹**H-NMP** (**400** MHζ, ΨΔΨλ₃): δ = 3.89 (σ, 3H), 5.35 (σ, 1H), 6.33-6.39 (μ, 2H), 7.70 (δ, Ξ = 8.7 Hζ, 1H), 10.94 (σ, 1H).

4.11.2 Methyl 2-hydroxy-4-octyloxybenzoate (4.2)





A solution of 1-bromooctane (31.5 ml, 0.18 mol) in dry butanone (100 ml) was added under reflux to a suspension of methyl 2,4-dihydroxybenzoate (25.5g, 0.15 mol), K_2CO_3 (103.5g, 0.75 mol) and powdered 4 Å molecular sieves (30 g) in dry butanone (500 ml) over a period of 7 h. The reaction mixture was heated under reflux for an additional 18 h until the reaction completed (confirmed by TLC). The reaction mixture was filtered and the butanone distilled off followed by recrystallization of the residue three times from methanol (50 ml) to yield white crystals.

Yield: 32.0 g (75%)

Melting point: 46°C

 $R_{f}(CH_{2}Cl_{2}) = 0.72$

Elemental Analysis: Calculated values for $C_{16}H_{24}O_4$ (MW=280.36): C 68.55%, H 8.63%; Found values: C 68.70%, H 8.69%

¹**H NMR (400 MHz, CDCl₃):** δ = 0.89 (t, 3H, CH₃), 1.22-1.47 (m, 10H, CH₂), 1.74-1.81 (m, 2H, OCH₂CH₂), 3.91 (s, 3H, OCH₃), 3.98 (t, 2H, OCH₂), 6.41-6.44 (m, 2H, CH _{arom}), 7.72 (m, 1H, CH _{arom}), 10.90 (s, 1H, OH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 22.6, 25.9, 28.9, 29.2, 31.7, 51.9, 68.2, 76.6, 101.1, 105.0, 107.9, 131.1, 163.7, 165.2, 170.5.

Mass Spectrometry: m/z(abundance): 281(2), 280(18), 169(5), 168(45), 151(2), 149(8), 137(25), 136(100), 120(2), 108(20), 107(15), 95(8), 79(8), 71(9), 69(18), 63(5), 57(22), 55(30), 43(48), 41(60).

4.11.3 Methyl 4-octyloxy-2-(pent-4-en-1-yloxy) benzoate (4.3)





5-Bromo-1-pentene (22.35 g, 0.15 mol) was added to a suspension of compound **4.2** (33.05 g, 0.118 ml), K_2CO_3 (103.5 g, 0.75 mol), KI (2.5g, 15 mmol) and powdered 4 Å molecular sieves (25 g) in dry butanone (350 ml) and the reaction mixture was heated under reflux until the reaction completed (confirm by TLC) (8 days). The reaction mixture was filtered and the butanone distilled off. The residue was dried in vacuum to leave slightly yellow oil.

Yield: 40.35 g (98%)

 $R_f(CH_2Cl_2) = 0.51$

¹**H NMR (400 MHz, CDCl₃):** δ = 0.89-0.92 (m, 3H, CH₃), 1.04-1.48 (m, 10H, CH₂), 1.74-1.81 (m, 2H, OCH₂), 1.90-1.97 (m, 2H, OCH₂), 2.26-2.32 (m, 2H, CH₂CH-CH₂), 3.85 (s, 3H, OCH₃), 3.96-4.03 (m, 4H, OCH₂), 4.97-5.09 (m, 2H, CH-CH₂), 5.81-5.91 (m, 1H, CH-CH₂), 6.45-6.48 (m, 2H, CH arom), 7.83 (m, 1H, CH arom). ¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 22.5, 25.9-26.1, 28.1, 29.0-29.9, 31.7, 32.3, 34.1-34.5, 37.7, 50.4, 51.4, 67.8, 68.1, 76.6, 100.2, 105.0, 112.2-115.8, 133.7-137.7, 160.6, 163.6, 166.2.

4.11.4 4-Octyloxy 2-(pent-4-en-1-yloxy)benzoic acid (4.4)



Compound **4.3** (38.75 g, 0.111 mol) was dissolved in THF (125 ml) and methanol (700 ml). A solution of KOH (33.3 g, 0.59 mol) in water (100 ml) was added. After stirring for 2 days at room temperature, the reaction was completed by heating at reflux for 2 h and the solvents distilled off. Ice/water (450 ml) was added and acidification by concentrated HCl (55 ml). The mixture was extracted with CH_2Cl_2 (6 x 125 ml) and dried with MgSO₄ after which the solvent was distilled off. Recrystallization was then carried out with hexane (150 ml) to obtain off-white crystals.

Yield: 21.94 g (60%)

Melting point: 67°C

 $R_{\rm f}(\rm CH_2\rm Cl_2) = 0.63$

Elemental Analysis:

Calculated values for C₂₀H₃₀O₄ (MW=334.45): C 71.83%, H 9.04%; Found values: C 72.02%, H 9.34%

¹**H NMR (400 MHz, CDCl₃):** δ = 0.89 (t, 3H, CH₃), 1.25-1.49 (m, 10H, CH₂), 1.76-1.83 (m, 2H, OCH₂), 1.99-2.05 (m, 2H, OCH₂), 2.24-2.29 (m, 2H, CH₂CH-CH₂), 4.01 (m, 2H, Page | 111

OCH₂), 4.21-4.24 (t, 2H, OCH₂), 5.05-5.12 (m, 2H, CH-CH₂), 5.78-5.88 (m, 1H, CH-CH₂), 6.51 (d, 1H, CH _{arom}), 6.63 (dd, 1H, CH _{arom}), 8.12 (d, 1H, CH _{arom}), 10.72 (br, 1H, COOH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 22.5, 25.9, 27.8, 29.0-29.8, 31.7, 68.5, 69.2, 76.6, 99.8, 107.0, 110.2-11.3, 135.4, 136.4, 158.8, 164.6, 165.2.

Mass Spectrometry: m/z(abundance): 335(2), 334(10), 267(3), 266(15), 249(8), 207(15), 177(3), 155(9), 154(55), 136(98), 110(5), 108(12), 83(2), 81(5), 71(12), 69(38), 55(25), 43(42), 41(100).

4.11.5 4-Hydroxy 4'-undecycloxybiphenyl (4.6)



Two different procedures were used to synthesis compound **4.6**. The two gave the same yield of the product.

(i) To 4,4'-dihydroxy biphenyl (compound **4.5**) (5.00 g, 27.0 mmol), K_2CO_3 (3.70 g, 27.0 mmol), KI (0.45 g, 2.71 mmol) in a 1000 ml three necked round bottom flask equip with condenser and a CaCl₂ tube was added acetone (150 ml). The solution was refluxed with stirring and 1-Bromoundecane (6.35 ml, 28.5 mmol) was added dropwise. The solution was refluxed for 24 h with stirring. After cooling, ethyl acetate (500 ml) was added and the solution washed with water (500 ml x 3). The organic solution was dried over anhydrous MgSO₄, filtered and concentrated *in vacuo* to give white crystals. The product was purified by recrystallization from ethyl acetate-hexane, 1:1.

Yield: 5.72 g (63%)

Melting point: 148-149 °C

 R_f (EtOAc/Hexane, 1:1) = 0.67

Elemental Analysis:

Calculated values for $C_{23}H_{33}O_2$ (MW=340.50): C 81.13%, H 9.47%; Found values: C 81.03%, H 9.70%.

¹**H NMR (400 MHz, CDCl₃):** $\delta = 0.89$ (t, 3H, CH₃), 1.24-1.50 (m, 16H, CH₂), 1.74-1.81 (m, 2H, OCH₂CH₂), 3.97 (t, 2H, OCH₂), 6.85-6.87 (m, 2H, CH_{arom}), 6.89-6.92 (m, 2H, CH_{arom}), 7.34-7.37 (m, 2H, CH_{arom}), 7.40-7.44 (m, 2H, CH_{arom}), 9.00 (s, 1H, OH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 23.0, 29.3, 29.6, 76.6, 77.0, 114.7, 115.5, 127.6, 127.9, 154.0.

Mass Spectrometry: m/z(abundance): 341(5), 340(23), 187(12), 186(100), 157(11), 128(5), 115(3), 71(2), 69(4), 57(5), 55(18), 43(25).

(ii) 4,4'-biphenol (compound 4.5) (10 g, 53.7 mmol) was dissolved in a solution of KOH (6 g, 107 mmol), water (25 ml), ethanol (75 ml) and KI (0.8 g, 4.82 mmol). After refluxing for 1 h, 1-Bromooctane (16.75 ml, 53.7 mmol) was added dropwise. The solution was refluxed for 24 h. After filtration and evaporation of the solvent, the product was isolated by column chromatography on silica gel using THF/Hexane, 1:5 as solvent.

Yield: 11.76 g (64%)

Other properties are as given in (i) above.





Scheme 4	.8
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Compound **4.4** (10.6 g, 31.7 mmol) was dissolved in dry toluene (130 ml) under nitrogen; thionyl chloride (50 ml, 0.68 mol) was added and the solution heated to 80°C for 3 hour, the reaction being completed after heating for 45 minutes at reflux. The thionyl chloride and toluene was distilled off under nitrogen. A solution of compound **4.6** (10.8 g, 31.7 mmol) and pyridine (50 ml, 0.62 mmol) was added to the residue. This reaction mixture was heated at 80°C for 18 hour and the reaction completed after reflux for 1 hour. Ice-water (400 ml) and 1/1 ether/hexane (400 ml) was then added; the phases were separated and the aqueous layer extracted with CHCl₃ (2 x 250 ml). The combine organic layers were dried with MgSO₄ and the solvent distilled off. The residue was purified by column chromatography using CH₂Cl₂/hexane, 4/1 as the eluent. Recrystallization from hexane yielded a white product.

Yield: 16.6 g (80%) Melting point: 53°C Clearing point (N to I): 71.5°C $R_f(CH_2Cl_2/Hexane,4:1) = 0.67$ Elemental Analysis: Calculated values for C₄₃H₆₀O₅ (MW=656.95): C 78.62%, H 9.21%; Found values: C 78.32%, H 9.47% ¹H NMR (400 MHz, CDCl₃): δ = 0.87- 0.91 (m, 6H, CH₃), 1.23-1.46 (m, 26H, CH₂), 1.76-1.84 (m, 4H, OCH₂CH₂), 1.91-1.98 (m, 2H, OCH₂), 2.26-2.32 (m, 2H, CH₂CH-CH₂), 3.97-4.07 (m, 6H, OCH₂), 4.94-5.05 (m, 2H, CH₂CH-CH₂), 5.77-5.87 (m, 1H, CH₂CH-CH₂), 6.48-6.56 (m, 2H, CH arom), 6.94-6.98 (m, 2H, CH arom), 7.20-7.25 (m, 2H, CH arom), 7.48-7.58 (m, 4H, CH arom), 8.04 (d, 1H, CH arom).

¹³C NMR (100 MHz, CDCl₃): δ = 14.0-14.1, 22.6, 25.9, 26.0, 28.2, 29.1-29.9, 31.7-31.8, 67.9-68.3, 76.6, 77.0, 100.2, 105.2, 111.2, 114.7, 115.2, 122.1, 127.6, 128.0, 132.9, 134.4, 137.7, 138.2, 150.0, 158.6, 161.5, 164.1, 164.39.

Mass Spectrometry: m/z(abundance): 657(100), 317(14), 249(3).

4.11.7 4'-(undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-acetylthio)pentyl)oxy)-4-(octyloxy) benzoate (4.8)



Scheme 4.9

Two methods were used to synthesis compound **4.8**.

Method i:

Thioacetic acid (98%, 0.56 ml, 1 mmol) was introduced to a stirred mixture of compound **4.7** (0.84 g, 0.5 mmol) and AIBN (from Aldrich, 0.21 g, 0.5 mmol) in dry THF (19.0 ml) under nitrogen. This final mixture was heated at 60°C for 10 hours. The reaction was monitored by TLC until the disappearance of the starting materials. The solvent was distilled off and column chromatography carried out on the residue using Ethyl acetate/hexane,1:2, as the eluent. Recrystallization from propan-1-ol yielded a white crystal.

Yield: 1.29 g (88%)

Melting point: 57°C

Clearing point (N to I): 58°C

 R_f (EtOAc/Hexane, 1:2) = 0.67

Elemental Analysis:

Calculated values for C₄₅H₆₄O₆S (MW=733.05): C 73.73%, H 8.80%, O 13.10%, S 4.37%; Found values: C 73.53%, H 8.81%, O %, S4.37 % ¹H NMR (400 MHz, CDCl₃): δ = 0.82-0.89 (m, 6H, CH₃), 1.27-1.32 (m, 12H, CH₂), 1.56-1.61 (m, 2H, CH₂), 1.85-1.92 (m, 2H, OCH₂), 2.28-2.30 (s, 1H, CH₃), 2.80-2.90 (m, 2H, CH₂S), 3.93-4.08 (m, 6H, OCH₂), 6.45-6.60 (ddd, 2H, CH _{arom}), 6.92-6.97 (m, 2H, CH arom), 7.19-7.29 (d, 2H, CH arom), 7.45-7.61 (dd, 4H, CH arom), 8.01-8.08 (d, 1H, CH arom).
¹³C NMR (100 MHz, CDCl₃): δ = 14.0-14.1, 22.6-22.7, 25.2, 25.8, 25.9, 26.0, 28.6, 28.9, 29.1-29.6, 30.6, 31.7, 31.8, 68.1-68.5, 76.6, 100.0, 105.0, 111.0, 114.0, 122.0, 127.0, 128, 132.0, 134.0, 138.0, 150.0-150.1, 158.6, 161.4, 164.1-164.4, 195.9.

Mass Spectrometry: m/z(abundance): 733(58), 395(25), 393(100), 371(5), 351(3).

Method ii

A solution of compound **4.7** (0.56 g, 0.17 mmol) in 1,4- dioxane (20 ml) was purged with nitrogen for 20 minutes. Thioacetic acid (7 ml, 2.55 mmol, 15 equivalents) was added, followed by AIBN (24.63 mg, 0.03 mmol). The reaction was left to stir under nitrogen atmosphere at 75°C until no starting material could be detected by TLC (approximately 2 hours and 10 minutes). The reaction was quenched with cyclohexene (0.5 ml) and the co-evaporated with toluene (few drops). Flash column chromatography on silica gel with dichloromethane/hexane, 3:1, gave a yellow residue. Recrystallization from propan-1-ol yielded off-white crystals.

Yield: 0.41 g (66%)

Melting point: 58.6°C

 $R_f(EtOAc/Hexane, 1:2) = 0.67$

Elemental Analysis: As given above

4.11.8 4'-(undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5-mercaptopentyl)oxy)-4-(octyloxy) benzoate (4.9)

$$C_{8}H_{17}O \longrightarrow O \\ O \longrightarrow O \\ (H_{2}C)_{5}' \\ O \longrightarrow (4.8) \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{17}O \longrightarrow O \\ C_{8}H_{17}O \longrightarrow O \\ O \longrightarrow O$$

Scheme 4.10

Nine different methods were tried for the synthesis of compound **4.9** but only one gave the desired product and in appreciable yield. The details of the methods are given below.

<u>Method i</u>

5% methanolic KOH (0.0321 g of KOH in 2.5 ml methanol) (2.1 mol of KOH per acetylthio group) was added to compound **4.8** (0.22 g, 0.30 mmol) under nitrogen and the reaction mixture stirred at room temperature for 12 hours. The reaction was monitored by TLC. A few drops of 0.1 HCl was added with cooling over ice. Methanol was then removed under reduced pressure and the product isolated by ether extraction.

The product was not soluble in organic solvent. This implies that there is cleavage of –O-O- with potassium salt being formed.

Method ii

Hydrazine solution (1M in THF, anhydrous, 7.5 ml, 30 mmol) was added, at 0°C, to a solution of compound **4.8** (0.533 g, 2.90 mmol) in freshly distilled CH_2Cl_2 (5 ml) and the reaction mixture stirred for 4 hours at 23°C. The solvent was concentrated in vacuo and the
residue dissolved in CH_2Cl_2 (12.5 ml). The resulting solution was washed with a saturated NH₄Cl solution (12.5 ml) and water (12.5 ml). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography, eluted with ethyl acetate/ hexane, 1:4, yielded a pure white crystal.

The target compound was not obtained as the thiol of the cleavage product was formed.

<u>Method iii</u>

Hydrazinium acetate (0.75 g, 43.2 mmol) was added to a solution of compound **4.8** (0.69 g, 4.32 mmol) in N, N-Dimethylformamide (10.4 ml). The reaction flask was purged with nitrogen and the reaction mixture stirred at room temperature for 15 hours. The reaction was monitored by TLC. The reaction mixture was diluted with CH_2Cl_2 (10.4 ml) and washed with water (20.8 ml). The organic phase was dried over Na_2SO_4 and the solvent evaporated in vacuo. The crude product was purified by column chromatography (cyclohexene/ ethyl acetate, 1:2).

Cleavage also occurred and the target compound was not obtained.

Method iv

Compound **4.8** (80 mg, 0.12 mmol) was dissolved in methanol (5 ml) followed by the addition of methanolic ammonia (25 ml). The solution was stirred at room temperature. After 1 hour, there was no evidence of reaction therefore; additional methanolic ammonia (15 ml) was added while the stirring continued for 12 hours.

There was no evidence of a reaction.

<u>Method v</u>

Compound **4.8** (0.12 g, 0.16 mmol) was measured into 10 ml 2-necked flask and flushed with nitrogen gas. Acetonitrile (1.0 ml) was added followed by the addition of pyrrolidine (0.111 ml, 1.33 mmol) via syringe. The solution was stirred at room temperature and

monitored by TLC. At the completion of the reaction, distilled water (50 ml) was added. The organic layer was separated and the aqueous layer extracted with chloroform (2 x 50 ml). The combined organic layers were washed with ammonium chloride (5 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified using column chromatography (ethyl acetate/hexane, 1:4) and the product precipitated by 1-propanol (few drops).

The reaction took 3 hours but there was cleavage and the desired product was not obtained.

<u>Method vi</u>

The above procedure was carried out except that N, N-Dimethylformamide was used as the solvent.

The reaction took 3 hours but there was cleavage of the ester group and the desired product was not obtained.

<u>Method vii</u>

The same conditions as for method ii were used but with less amount of pyrrolidine (0.042 ml, 0.5 mmol). This yielded the same result as above, although with a very minute (0.0061 g, 5.4%) amount of compound **4.9**.

Method viii

Repeating the above procedure with a smaller amount of pyrrolidine less than 0.042 ml (0.5 mmol) did not yield any product and the starting material was recovered.

<u>Method ix</u>

Tetrabutyl ammonium cyanide (18.3 mg, 0.068 mmol, 0.1 equiv.) was added to chloroform (10 ml), compound **4.8** (0.5 g, 0.68 mmol) and methanol (10 ml) under nitrogen. The reaction was stirred at room temperature for 76 hours (monitored by TLC). After the completion of the reaction, water (50 ml) and chloroform (50 ml) was added. The organic layer was separated and the aqueous layer extracted with chloroform (50 ml). The

combined organic layers were washed with MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (dichloromethane/hexane, 1:4 or Ethyl acetate/hexane, 1:4) yielded a white crystal (precipitated by adding few drops of 1-propanol).

Yield: 0.47 g (100%)

Melting point: 42.4°C

Clearing point (N to I): 54.6 °C

 $R_{\rm f}({\rm Ethyl\ acetate}) = 0.87$

Elemental Analysis:

Calculated values for C₄₃H₆₂O₅S (MW=691.01): C 74.74%, H 9.04%, S 4.64%;

Found values: C 74.51%, H 9.29%, S 4.64%

¹**H** NMR (400 MHz, CDCl₃): $\delta = 0.83 - 0.94$ (q, 6H, CH₃), 1.21-1.54 (m, 28H, CH₂), 1.55-1.69 (m, 1H, C<u>H₂</u>CH₂-SH), 1.72-1.90 (m, 3H, OCH₂C<u>H₂</u>), 2.04 (s, 1H, SH), 2.26-2.29 (s, 3H, CH₃), 2.44-2.53 (q, 2H, CH₂SH), 2.81-2.86 (t, 2H, CH₂CH-CH₂), 3.56-3.64 (q, 2H, CH₂SH), 3.8 (s,), 3.94-4.07 (m, 6H, OCH₂), 6.43-6.57 (ddd, 2H, CH arom), 6.91-6.99 (d, 2H, CH arom), 7.19-7.26 (m, 2H, CH arom), 7.45-7.60 (dd, 4H, CH arom), 8.02-8.08 (d, 1H, CH arom).

¹³C NMR (100 MHz, CDCl₃): δ = 14.0-14.1, 22.6-22.7, 24.4, 24.8, 25.1, 25.9, 26.0, 28.6, 28.9, 29.1-29.6, 30.6, 31.7, 31.8, 33.6, 68.0-68.4, 76.6, 100.0, 105.0, 111.0, 114.0, 122.0, 127.0, 128, 132.0, 134.0, 138.0, 150.0, 158.6, 161.0, 164.1, 164.4.

Mass Spectrometry: m/z(abundance): 691(100), 589(2), 425(3), 393(22), 351(13), 281(4).

Note:

(i)The reaction time was reduced to 8 hours when the TBACN (50.8 mg, 0.19 mmol) and compound **4.8** (0.1 g, 0.13 mmol) was used. The yield was 0.09 g (100%).

(ii) When scaled up, TBACN (0.7133 g) and compound **4.8** (0.98 g), the yield was 0.84 g (91.3%).

Method X

A new method was discovered that uses sodium thiomethoxide (NaSMe) as the deacylation agent¹².



Scheme 4.11

To a mixture of compound **4.8** (0.5 g, 0.68 mmol) in methanol (10 ml) and DCM (5 ml) under nitrogen and at -20 °C was added NaSMe (72 mg, 1.02 mmol). The mixture was stirred at this temperature for 3 h (monitored by TLC), after which the reaction was quenched by adding water (20 ml) and DCM (40 ml) was also added. The organic layer was separated, dried over MgSO4 and concentrated *in vacuo*. Column chromatography was used for purification with DCM as solvent to obtain compound **4.9**, 0.30 g (64 %).

4.11.9 Synthesis of gold nanoparticle-4'-(Undecycloxy)-[1,1'-biphenyl]-4-yl 2-((5mercaptopentyl)oxy)-4-(octyloxy) benzoate liquid crystal (4.10)

Two methods were used to synthesis the composite **4.10**.

4.11.9.1 Coupling of gold nanoparticles and mesogen (compound 4.9)

To a solution of dodecanethiol capped gold nanoparticles (26.5 mg, in freshly distilled 18 ml CH₂Cl₂) was added a solution of the mesogen (compound **4.9**) (106 mg in 4 ml CH₂Cl₂) and the mixture was stirred at 25°C for 5 days. The solution was then concentrated to 2 ml at temperature below 30°C. Ethanol (12 ml) was added and briefly sonicated. The solution was the centrifuged at 5000 rpm for 10 minutes after which the clear ethanol is pipetted out. The centrifugation process was repeated three times to ensure removal of free mesogen. The black residue was dispersed in hexane and centrifuged. The composite was then dried in vacuo for 12 hours.

¹**H NMR (400 MHz, CDCl₃):** δ = 0.83- 0.94 (q, 6H, CH₃), 1.21-1.54 (m, 28H, CH₂), 1.72-1.90 (m, 3H, OCH₂C<u>H₂</u>), 3.94-4.07 (m, 6H, OCH₂), 6.43-6.57 (ddd, 2H, CH _{arom}), 6.91-6.99 (d, 2H, CH _{arom}), 7.19-7.26 (m, 2H, CH _{arom}), 7.45-7.60 (dd, 4H, CH _{arom}), 8.02-8.08 (d, 1H, CH _{arom}).

4.11.9.2 Direct capping of gold nanoparticles with the mesogen (compound 4.9)

The method for synthesising gold nanoparticles capped with dodecanethiol was employed with the replacement of compound **4.9** for dodecanethiol. The detail is as contained in 4.1.2 and 4.1.3.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.83 - 0.94$ (q, 6H, CH₃), 1.21-1.54 (m, 28H, CH₂), 1.55-1.69 (m, 1H, C<u>H₂</u>CH₂-S), 1.72-1.90 (m, 3H, OCH₂C<u>H₂</u>), 2.1 (s, 1H, SH), 2.5-2.6 (t, 2H, CH₂CH-CH₂), 3.94-4.07 (m, 6H, OCH₂), 6.43-6.57 (ddd, 2H, CH _{arom}), 6.91-6.99 (d, 2H, CH _{arom}), 7.19-7.26 (m, 2H, CH _{arom}), 7.45-7.60 (dd, 4H, CH _{arom}), 8.02-8.08 (d, 1H, CH arom).

4.11.10 Synthesis of AuNPs capped with 11-Mercapto-1-Undecanol (4.12)^{10,13}



The method used for the synthesis of **4.12** is a modified method used for the synthesis of 4 nm AuNPs.

To a solution of HAuCl₄.3H₂O (0.2065 g in 0.5 ml H₂O) was added 11-mercapto-1undecanol (0.03 g, 0.1 mmol) in THF (5 ml) and sonicated for 5 min. NaBH₄ (0.086 g in 0.6 ml H₂O) was added while sonication continued for 10 min. The black mixture was precipitated in ethanol (50 ml) and centrifuged (5000 rpm, 5 min) to have a black residue which was re-dispersed in ethanol. Centrifugation process was repeated three times to ensure complete removal of the excess and unreacted 11-mercapto-1-undecanol. AuNPMUD was dried under vacuum and sample taken for TEM, ¹H NMR, TGA and UV.

4.11.11 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 4-(octyloxy)-2-((5-





Scheme 4.12

Compound **4.7** (0.33 g, 0.5 mmol) was dissolved in dry toluene (10 ml) and triethoxysilane (0.43 ml, 2.5 mmol) added under argon atmosphere and stirred for 30 min followed by the addition of 1,1,3,3-tetramethydidloxane Pt-complex (Karstedt's catalyst, 0.1 M) in xylene (50 μ l, 0.01 eq.). Stirring was continued for 18 h. The solvent and excess triethoxysilane was removed under vacuum to give a brown residue which was purified by PTLC using DCM as solvent to yield 0.26 g (63 % yield).

¹**H** NMR (400 MHz, CDCl₃): $\delta = 0.57$ (t, 2 H, CH₂Si), 0.82 (t, 6 H, CH₃), 1.11 (m, 9 H, SiOCH₂CH₃), 1.12-1.14 (m, 26 H, CH₂CH₂), 1.49 (t, 4 H,CH₂CH₂), 1.78 (m, 6 H, OCH₂CH₂), 3.7 (q, 6 H, SiOCH₂), 3.9 (t, 4 H, OCH₂), 6.43 (d, 2 H, CH_{arom}), 6.90 (d, 2 H, CH_{arom}), 7.19 (d, 2 H, CH_{arom}), 7.41 (d, 2 H, CH_{arom}), 7.50 (d, 2 H, CH_{arom}), 7.97 (d, 1 H, CH_{arom}).

4.11.12 Reacting AuNPMUD with 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 4-(octyloxy)-2-((5-(triethoxysilyl)pentyl)oxy)benzoate (AuNP-7ES)



Scheme 4.13

To **4.12** (45.7 mg) in ethanol (0.5 ml) was added **4.11** (0.14 g, ~ 4 eq. w/w) in chloroform (2 ml) and 1M NaOH (40 μ l). The mixture was stirred at room temperature for 12 h to ensure completeness of the reaction. The nanocomposite **4.13** was obtained by centrifuging the mixture (5000 rpm, 5 min), removing the supernatant, re-dissolving the residue in toluene and centrifuging. The process was repeated three times to ensure complete removal of unreacted **4.11**. The composite **4.13** obtained was dried in vacuo and sample taken for ¹H NMR, TEM, UV and TGA. The experimental results have been discussed in section **4.9**.

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CHAPTER FIVE

SIDE-CHAIN LIQIUD CRYRALLINE POLYMERS

5.1

Introduction

The advancement of electronic liquid crystals displays and non-linear optical systems has led many areas of chemistry/material science to intense research into the introduction of liquid crystal/mesogenic units onto polymers and this in turn has led to the advent of materials of high performance and interestingly unique properties.

Liquid crystalline polymer (LCP) are polymeric materials that exist as a liquid crystal (LC) mesophase under suitable conditions of temperature, pressure and concentration¹. They exibit solid like behaviour while still retaining the liquid state behaviour and conversely. LCP can either be main-chain liquid-crystalline polymer (MCLCP) whose molecules have mesogenic unit only in their main chain, or side-chain liquid-crystalline polymer (SCLCP) whose molecules have mesogenic units only in the side-group's side chains¹. They have global attention since the 1980s basically due to their applications as electro-optical or non-linear optical materials, engineering plastics, high modulus and strength fibre, gas separation membranes and stationary phases². In most of the applications, the LC materials should have broad operating temperature range, high anisotropic dielectric and optical properties³. SCLCP materials combine the anisotropy of liquid crystalline mesogens with the mechanical properties of polymer and decoupling the motions of a polymer main chain from the mesogen would allow the side-chain moieties to build up long range ordering⁴.

5.2 Side chain liquid crystal polymers

Three types of side-chain liquid crystalline polymers were investigated. The polymers **5.7**, **5.10**, and **5.15** were respectively synthesised from monomer **5.6**, **5.9** and **5.14**. The synthetic approach used for the synthesis of the first monomer **5.6** is shown in scheme 5.1. The details of the systematic synthesis of each monomer, their polymerization and their

corresponding properties with those of the polymers are hereby described.



Scheme 1: synthesis of 20. (a)Triethyl amine, THF, 0 °C, 9 h, 84 %(b) 1,1,3,3-Tetramethyldisiloxane, Toluene, Pt cat., 30 °C, 12 h, 92 %(c)Toluene, Pt cat., 12 h, 86 %.

The hydroxyl group of 3-Buten-1-ol, **5.1**, was esterified by methacryloyl chloride, **5.2**, to obtained the first intermediate, **5.3**, in a very good yield, 84 %. From ¹H NMR spetrum, the signals at 5.5 ppm and 6.1 ppm due to the two methylene protons of the methyl methacrylic end of **5.3** confirm the reaction. The second intermediate, **5.5**, was synthesised by the hydrosilylation of the mesogen **4.7** using 1,1,3,3-tereamethyldisiloxane in the presence of platinum catalyst, in a quantitative yield, 92 %.

The attachment of the disiloxane to the mesogen was confirmed from ¹H NMR spetrum as the signals due to lateral alkene end at 4.9 ppm and 5.8 ppm have completely disappeared in **5.5**. The target monomer was obtained from the second hydrosilylation reaction between **5.3** and **5.5** in a very good yield, 86 %. Also, from the ¹H NMR spetrum the eminent of signals at 5.5 ppm and 6.1 ppm due to the methylene of methyl methacrylic end in **5.6** confirm the success of the hydrosilylation reaction.

Monomer **5.6** was subjected to free radical polymerization under nitrogen using AIBN as the radical initiator in toluene and at 70 °C for 24 h (Scheme 5.2).



Scheme 5.2: Polymerization of **5.6**.

The polymer **5.7** was precipitated in cold methanol, redisolved in minimum amount of THF, re-precipitated in cold methanol again and finally dried *in vacuo*.

The synthetic approach used for the synthesis of the second monomer was based on the hydroboration/ oxidation sequence being a powerful technique to generate region- and stereoselective alcohols followed by the esterification of the resulted hydroxyl group (Scheme 5.3).

$$(4.7) \xrightarrow{(a)}_{C_8H_{17}O} \xrightarrow{(b)}_{O} \xrightarrow{(c)}_{O} \xrightarrow{(c)} \xrightarrow{(c)}_{O} \xrightarrow{(c)}_{O} \xrightarrow{(c)}_{O$$

Scheme 5.3: Synthesis of **5.9**: (a)(i) 9-BBN, THF, 40 °C, 12 h; or BH₃.THF,0 °C, 2 h (ii) NaOH/H₂O₂, 0 °C, 2 h, 44 %; or NaBO₃.4H₂O, rt, 2 h, 54 % (b) methacryloyl chloride, triethyl amine, rt, 9 h, 98 %.

The lateral alkene end of the mesogen was subjected to hydroboration by 9-BBN and subsequently oxidised by sodium perborate to afford hydroxyl intermediate compound **5.8**, 54 %. Hydroboration by BH₃.THF followed by NaOH/H₂O₂ oxidation was also investigated and gave **5.8** in yield of 44%. The disappearance of the signals due to methylene protons at 4.9 ppm and 5.7 ppm in ¹H NMR spectrum of **5.8** confirm the reaction. The hydroxyl functional end of **5.8** was modified by esterification with methacryloyl chloride to yield the target polymerizable monomer **5.9** almost quantitavely, 98 %.

Monomer **5.9** was subjected to radical polymerization under nitrogen using AIBN as the radical initiator in toluene and at 70 °C for 24 h (Scheme 5.4).



Scheme 5.4: Polymerization of 5.9.

The polymer **5.10** was precipitated in cold methanol, redisolved in minimum amount of THF, re-precipitated in cold methanol and finally dried *in vacuo*.

For the third monomer, **5.14**, the systematic approach used in the synthesis is as shown in Scheme 5.5.



Scheme 5.5: Synthesis of 5.14: (a) Methacrylic acid, hydroquinone, H_2SO_4 , reflux, 3 h, 58 % (b) Chlorodimethylsilane, Pt catalyst, Toluene, rt 12 h (c) Imidazole, DCM, rt, 24 h, 67 %.

One hydroxyl group of 1,4-butanediol was esterified with methacrylic acid to obtain the first intermediate, **5.12**, in 58 % yield. ¹H NMR confirm the conversion in which there was eminent of signals due to methylene of methyl methacrylic end at 5.5 ppm and 6.0 ppm. The second intermediate was synthesised by silylation of the mesogen by chlorodimethylsilane in the presence of platinum catalyst. Form the ¹H NMR spectrum, the disappearance of the signals due to methylene protons at 4.9 ppm and 5.7 ppm in compound **5.13** confirm the product. The condensation of **5.12** and **5.13** using imidazole yielded the target monomer, **5.14**, in 67 % yield.

Monomers **5.14** was subjected to free radical polymerization under nitrogen using AIBN as the radical initiator in toluene and at 70 °C for 24 h (Scheme 5.6).



Scheme 5.6: Polymerization of 5.14.

Generally, polymers were precipitated in cold methanol, redisolved in minimum amount of THF, re-precipitated in cold methanol and finally dried *in vacuo*. The comparative data of polymer **5.7**, **5.10** and **5.15** are given in Table 5.1.

Polymer	Mn	Mw	PD	DP
5.7	3556	4030	1.13	4
5.10	8279	10861	1.31	11
5.15	3197	3671	1.14	4

Table 5.1: Comparative data of **5.7**, **5.10** and **5.15**.

The number average molecular weight (Mn) of the polymers in Table 1 are in agreement with those obtained from mass spectrometer, 3650 g/mol, 6000 g,mol, and 3927 g/mol respectively for polymer **5.7**, **5.10** and **5.15**.

The polymers LC beviours are dependent on the nature of the mesogen, spacer's length and the flexibility of the polymer skeleton⁴. The last factor being affected by the molecular weight (Mn) and the polydispersity (Mw/Mn) of the polymer. The polydispersity of the three polymers are low 1.13, 1.31 and 1.14 respectively for **25.7**, **5.10** and **5.15** which shows that the polymer molecules are well distributed.

5.2.1 Liquid crystals properties

The liquid crystal properties were investigated using polarizing optical microscope and differential scanning calorimeter. The textures were obtained from POM while the transistion properties were confirmed by DSC. Table 5.2 shows the liquid crystalline properties of the intermediates, monomer and polymers.

Entry	Phase transition temperature, °C (Enthalpy, J/g)		
4.7	Cr 53.3 (71.9) N 71.7 (1.59) I		
5.8	Cr 51.3 (1.3) N 71.7 (1.06) I		
5.9	Cr -12.5 (1.93) N 68.8 (0.44) I		
5.5	Cr -12.3 (17.9) N 18.5 (3.06) I		
5.6	Cr -8.07 (0.2) N 18.6 (0.009) I		
5.14	N 10.28 (0.15) I		
5.7	g -24.1 (1.14) N 16.1 (0.24) I		
5.10	g 47.2 (1.28) N 77.9 (3.16) I		
5.15	g 28.4 (1.88) N 51.7 (0.38) I		

Table 5.2: Liquid crystalline properties of the intermediates, monomer and polymers.

The textures of the intermediates, monomers and those of the polymers are as show in figure 5.1.



Figure 5.1: Textures of compounds as observed under POM (x 400)(a) compound **4.7** at 70.9 °C (b) compound **5.8** at 53°C (c) compound **5.9** while cooling 65 °C (d) compound **5.5** when cooled with cardice (e) compound **5.5** at rt (f) polymer **5.7** when cooled with cardice (g) polymer **5.10** while cooling from isotropic phase (h) polymer **5.15** at 48 °C (i) polymer **5.15** at 50 °C..

The mesogen **4.7** and the corresponding intermediates **5.8**, shows nematic texture (Fig 5.1. (a)(b)) from the melting poin (53 °C and 51 °C respectively) to the clearing point (~72°C). The monomer **5.9** also shows nematic texture (Fig. 5.1 (c)). A threaded texture of nematic is observed for compound **5.5** at room temperature (Fig. 5.1(e)) in which lines showup and smim with thermal motion. All polymers exibit mesophases as shown in Fig. 5.1 (f-h). Polymer **5.7** exhibits nematic mable texture when cooled by placing the slide (quickly) on

cardice (f). for polymer **5.10**, it has nematic texture (g). The schliren textures of **5.15** are shown in (h-i).

5.2.2 Thermal properties

The thermal behaviour of the the intermediates, monomers and the polymers were investigated using DSC and in addition, thermogravimetric analysis (both in air and in nitrogen) for the polymers. The heating and cooling curves as obtained from DSC are shown in figure 5.2 while the details of the transitions is as contained in table 5.2.



Figure 52: DSC curves of (a) compound **5.5** at 20 °C/min (b) compound **5.6** at 5 °C/min (c) compound **5.6** at 20 °C/min (d) compound **5.8** at 10 °C/min (e) monomer **5.9** at 10 °C/min (f) monomer **5.14** at 10 °C/min



Figure 53: DSC heating and cooling curves for **5.7.**

Polymer 5.7 has a wide nematic range from its glass transition temperature, -24 °C with enthalpy of 1.14 J/g to the clearing point, 16 °C, with isotropization energy of 0.24 J/g as shown in Fig. 53.



Figure 54: DSC heating and cooling curves for **5.10**.

The glass transition temperature of polymer **5.10** is 47 $^{\circ}$ C with energy of transition 1.28 J/g giving nematic phase upto the clearing point at 78 $^{\circ}$ C with isotropization energy of 3.16 J/g (Fig. 54).



Figure 55: DSC heating and cooling curves for 5.15.

The glass transition of polymer **5.15** is 28 °C with glass transition enthalpy of 1.88 J/g and exhibits nematic phase to 51 °C where it cleared into isotropic state with energy of 0.38 J/g. Comparing the Tg for the three polymer, **5.10** > **5.15** >**5.7**. This comfirms the relationship between the length of the siloxane and Tg of side-chain liquid crystal polymer, the longer the length of the siloxane linker the lower the Tg.

Common to the three polymers is the backbone and the mesogenic unit with differences on the point of linkages. As seem in Table 1, polymer **5.10** has the highest Tg (47.2 °C) followed by **5.15** (28.4 °C) and poymer **5.7** with the least (-24.1 °C). This can be explained based steric hinderance parameter⁵ which is very high in polymer **5.10**, least in **5.7** and subsequently affected the chain segment mobility in these polymers.

In addition to DSC curves, the thermal properties of the polymers were investigated using thermogravimetric analysis techniques in which the polymers were subjected to heat (combustion temperature between 0 °C and 950 °C) both in air and in nitrogen gas. Figure 56 (a), (b) and (c) shows the TGA thermograph of the combustion of **5.7**, **5.10** and **5.15** respectively in nitrogen.



Figure 56: TGA (in nitrogen) thermograph of (a) **5.7** (b) **5.10** (c) **5.15**.

The TGA thermographs for the combustion of the polymers in air are given in figure 57 (a), (b) and (c).



Figure 57: TGA (in air) thermograph of (a) **5.7** (b) **5.10** (c) **5.15**.

Table 5.3 (a) and (b) show the summary of the thermal behaviour of polymers **5.7**, **5.10**, and **5.15** when subjected to combustion from 50 °C to 950 °C under nitrogen and in air respectively.

Polymer	Temperature of mass loss,°C	% mass loss (%)
5.7	260–	14
	260-520	82
		(1.63) Residue
5.10	140 - 170	20
	320 - 520	77
		(3.4) Residue
5.15	250 - 500	92
		(8) Residue

Table 5.3 (a): Thermal behaviours of polymers under nitrogen.

Polymer	Temperature of mass loss,°C	% mass loss (%)
5.7	260-510	94
	Broad/Not clearly defined	0.5
		(4) Residue
5.10	150	2
	190 – 360	20
	370 - 490	70
	510 - 600	7
		(1.7) Residue
5.15	270 - 520	86
	580 - 780	9
		(5.5) Residue

Table 5.3 (b): Thermal behaviours of polymers in air.

The the thermal decomposition of **5.7** and **5.15** began at about 260 °C while that of **5.10** began at 150 °C. This implies that the presence of siloxane in **5.7** and **5.15** has effect on the stability of these polymers at temperature ≤ 260 °C, in addition to lowering the transition

temperatures. Polymer **5.10**, without siloxane linkage to the polymer back bone, is stable at temperatures below 150 °C despite it having the highest transition temperatures. The residues left after the combustion of the polymers might be due to SiO and/or SiC formed. It was observed that the percentages of residue left after the combustion of the three polymers in nitogen are higher than those carried out in air. This is not unexpected as combustion in air might aid the formation of volatile products as compared with that in nitrogen⁶.

5.3 Synthesis of side chain thiol polymer

The synthesis of side chain thiol polymer **5.19** was investigated. The details of the synthetic routes are shown in scheme 5.7.



Scheme 5.7: synthesis of polymer **5.17** (a) Hydroquinone, H_2SO_4 , Toluene. (b) Cu(I)Br, Dry toluene, compound **5.18**, Bpy. (c) (CH₃)₂HSiCl, Pt catalyst, toluene. (d) Toluene or THF, Et₃N. (e) TCEP, THF/H₂O.

One hydroxyl end of 1,4-butanediol was esterified by methacrylic acid to obtain methacrylate monomer¹³, **5.12**, which was then polymerized by atom transfer radical polymerization with monomer/initiator/catalyst/ ligand ratio of 100: 1: 1: 2. The polymerization was first carried out in toluene at 90 °C for 6 h but as the reaction proceeded, the polymer formed, **5.16**, was not soluble in the solvent. The polymerization was later carried out in methanol at 50 °C for 24 h.

In order to functionalised the polymer with the mesogen, the terminal alkene end of compound **4.7** was converted to chlorosilane end by hydrosilylation reaction to obtain compound **5.13**. Efforts were made to link **5.13** to polymer **5.16** but from ¹H NMR integrations, almost 50 % of the hydroxyl group on **5.16** reacted even in the presence of excess **5.13**.



Figure 58: ¹H NMR of monomer **5.12**.



Figure 59: ¹H NMR of polymer **5.16**.



Figure 61: ¹H NMR of monomer **5.19**.



Polymer	Solvent	Temperature	Time (h)	Mn _(GPC)	Mw/Mn
		(°C)		g/mol	
5.16	Toluene	90	6	2956	1.34
5.16	Methanol	50	24	5397	1.13
5.17	-	-	-	3000 - 4000	1.08 - 1.33

Table 5.4: Properties of polymer **5.16** and and **5.17**.

The thermal behaviour of **5.17** as observed on POM is shown in figure 62.



Figure 62: POM texture of **5.17** (x 100) (a) Nematic texture at 40 °C (b) Isotropic at 49 °C

Polymer 5.17 exhibited nematic texture till it turned isotropic at 49 °C.

The DSC heating and cooling curves for **5.17** is shown in figure **62**.



5.4 Conclusion

Three mesogenic monomers, with different linking units between the mesogenic unit and the polymerizable methyl methacrylate end, were successfully synthesised and characterized. The polymerization of the monomers and the properties of their corresponding polymers were investigated. All the polymers have narrow polymer distribution and are liquid crystalline with nematic mesophase. The thermal behaviour of the polymers reveals that those with siloxane and silane linker are stable at temperature up to 260 °C while the one with ester linker exhibits lower stability.

Also, ATRP was used to obtain functionalized polymer which was liquid crystalline upto 49 °C where it turned isotropic.

5.5 Experimental procedures

5.5.1 But-3-en-lyl methacrylate (5.3)⁷⁻⁸



Scheme 5.8

Two different methods were explored for the synthesis of compound 5.3.

Method i

3-Buten-1-ol (**5.1**) (0.114 ml, 0.094 g, 1.3 mmol) and triethylamine (0.362 ml, 2.6 mmol) were dissolved in dichloromethane (30 ml) and the solution cooled to 0 °C under nitrogen atmosphere. Methacryloyl chloride (0.25 ml, 0.272 g, 2.6 mmol) in DCM (10 ml) was added dropwise to the solution. The resulting mixture was stirred for 9 h, poured into cold water (30 ml) and extracted with CH_2Cl_2 (3 x 30 ml).

The combined organic layer was dried over Na_2SO_4 , filtered, solvent removed and the residue purified by silica gel column chromatography using ether as solvent. Further purification was achieved by alumina chromatography using DCM as solvent to yield 1.03 g (55.5 %).

Method ii

Methacryloyl chloride (2.5 ml, 2.6 mmol) was added dropwise to 0 °C solution of triethylamine (3.6 ml, 1.3 mmol), 3-buten-1-ol (1.14 ml, 1.3 mmol) in THF (188 ml) under Page | 152

nitrogen atmosphere. The mixture was then allowed to warm to room temperature and stirred for 9 h. The reaction mixture was partitioned between diethyl ether (200 ml) and 10 % HCl (200 ml). The aqueous layer was separated and extracted with ether (2 x 100 ml). The organic layers were combined, washed with brine (200 ml), dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography using ether as solvent but there was still impurity. Further purification by alumina column chromatography using DCM removed any methacrylic acid by-product and gave pure compound, 1.55 g (83.5 %).

 $R_{\rm f}({\rm ether}) = 0.76$

Elemental analysis: Analytical calculated values for C₈H₁₂O₂ (MW = 140.18): C, 68.55; H, 8.63; O, 22.83 %. Found: C, 58.62; H, 6.17 %.

¹**H NMR (400 MHz, CDCl₃):** δ = 1.99 (s, 3H, CH₃), 2.44 (t, 2H, CH₂CH₂), 4.20 (t, 2H, OCH₂), 5.10-5.15 (dd, 2H, CHCH₂), 5.55 (s, 1H, CHCH₂), 5.82 (m, 1H, CHCH₂), 6.10 (s, 1H, CHCH₂).

¹³C NMR (100 MHz, CDCl₃): $\delta = 167, 136, 133, 125, 117, 63.5, 32.9, 18.1.$

Improved purification method developed

In order to reduce time and materials (including solvents) used in the purification of compound **5.3**, a method was developed in which the column was filled with silica gel and finally top up with small layer of basic alumina. Ether was used as the solvent. This method gave pure compound; reduced time spent on purification and also increased the yield to 83.8 %.

5.5.2 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 4-(octyloxy)-2-((5-(1,1,3,3-

tetramethyldisiloxanyl)pentyl)oxy)benzoate (5.5)



Two different methods were used to synthesise compound 5.5.

Method i

Compound **4.7** (0.5 g, 0.76 mmol) was dissolved in dry toluene (20 ml). 10 μ l of Pt catalyst was added and sealed with rubber septum. The catalyst in the reactant was activated using oxygen (air) through syringe.

1,1,3,3-tetramethyldisiloxane (6 ml, 30.5 mmol) in dry toluene (5 ml) was added dropwise into the solution of compound **4.7** while keeping the temperature at 30 °C. After 18 h of reaction, excess disiloxane and solvent were distilled off at low temperature under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate, 10:1) yielding golden yellow oily compound, 0.54 g (92%).

Method ii

Compound **4.7** (0.5 g, 0.76 mmol) was dissolved in dry toluene (10 ml). 30 μ l of Pt catalyst was added. In another flask 1,1,3,3-tetramethyldisiloxane (2.99 ml, 25.2 mmol) was mixed
with dry toluene (5 ml) under nitrogen gas. Compound **4.7** in dry toluene was added dropwise into the flask containing disiloxane over 1 h and the entire mixture stirred for 24 h, at room temperature (its better done in the dark-wrapped with aluminium foil to disallow the other double bond from reacting). Solvent was removed under vacuum and the green oily residue was purified by column chromatography using toluene as eluent (after trying many solvents mixture including hexane/ethyl acetate, 9:1, given in the earlier reports). This method is similar to (ii) above, only that few solvent and disiloxane were used but more catalyst.

 $R_f(CH_2Cl_2/hexane = 1/1) = 0.44$

Elemental analysis: Analytical calculated values for $C_{47}H_{74}O_6 Si_2$ (MW = 791.27): C, 71.34; H, 9.43; O, 12.13; Si, 7.10 %. Found: C, 71.10; H, 9.70 %.

¹**H** NMR (400 MHz, CDCl₃): δ = 0.09 (s, 6 H, SiC*H*₃), 0.10 (s, 6 H, SiC*H*₃), 0.48 (t, 2 H, SiC*H*₂), 0.84 (t, 6 H, C*H*₃), 1.23-1.32 (m, 26 H, C*H*₂), 1.34 (t, 4 H, C*H*₂), 1.75-1.78 (m, 6 H, C*H*₂), 3.96 (t, 6 H, OC*H*₂), 4.6 (m, 1 H, Si*H*), 6.50 (d, 1 H, C*H*_{arom}), 6.90 (d, 1 H, C*H*_{arom}), 7.10 (d, 2 H, C*H*_{arom}), 7.21 (d, 2 H, C*H*_{arom}), 7.46 (d, 2 H, C*H*_{arom}), 7.50 (d, 2 H, C*H*_{arom}), 8.01 (d, 1 H, C*H*_{arom}).

¹³C NMR (400 MHz, CDCl₃): δ = 164.4, 164.1, 161.6, 158, 150, 138, 137, 134, 132, 129, 128.2, 127.5, 125, 122, 114, 111, 105, 100, 68.8, 68.3, 31.9, 30.9, 29.6, 29.3, 26.0, 22.6, 21.4, 17.9, 14.1, 0.97, 0.13.

5.5.3 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-(3-(4-(methacryloyloxy)butyl)-



1,1,3,3-tetramethyldisiloxanyl)pentyl)oxy)-4-(octyloxy)benzoate (5.6)

Scheme 5.10

To compound **5.3** (0.26 g, 2.5 mmol) was added dry toluene (5 ml) and Pt catalyst (30 μ l). This mixture was added to a flask containing compound **5.5** (0.96 g, 1.21 mmol) in dry toluene (10 ml) over 1 h and wrapped in aluminium foil (equivalent to doing the reaction in the dark) with stirring for 12 h.

The solvent was removed *in vacuo* and the brown residue purified by column chromatography (toluene) to yield golden- light oily compound, 0.99 g (86 %).

Elemental analysis: Analytical calculated values for C₅₅H₈₆O₈ Si₂ (MW = 931.45): C, 70.92; H, 9.31; O, 31.74; Si, 6.03 %. Found: C, 71.0; H, 9.60 %.

¹**H NMR (400 MHz, CDCl₃):** δ = 0.03 (s, 12 H, SiC*H*₃), 0.50 (q, 4 H, SiC*H*₂), 0.89 (t, 6 H, C*H*₃), 1.20-1.34 (m, 28 H, C*H*₂), 1.43 (m, 4 H, C*H*₂), 1.64 (m, 2 H, C*H*₂), 1.74-1.80 (m,

6 H, CH₂), 1.90 (s, 3 H, CH₃), 4.10 (t, 2 H, COOCH₂), 4.19 (t, 6 H, OCH₂), 5.50 (d, 1 H, =CH₂), 6.0 (d, 1 H, =CH₂), 6.50 (d, 1 H, CH_{arom}), 6.95 (d, 1 H, CH_{arom}), 7.16 (d, 1 H, CH_{arom}), 7.23 (d, 2 H, CH_{arom}), 7.48 (d, 2 H, CH_{arom}), 7.54 (d, 2 H, CH_{arom}), 8.03 (d, 1 H, CH_{arom}).

¹³C NMR (400 MHz, CDCl₃): δ = 0.1, 13.8, 22.3, 25.6, 25.7, 29.0, 29.2, 31.4, 64.1, 67.9, 99.8, 104.9, 110.9, 114.4, 121.8, 124.8, 127.2, 127.7, 132.6, 134.1, 137.9, 149.8, 158.3, 161.3, 163.8, 164.0, 167.



5.5.4 Polymerization of compound 20 using AIBN (5.7)

Scheme 5.11

Compound **5.6** (0.99 g, 1.06 mmol), AIBN (17 mg, 0.106 mmol) were dissolved in dry toluene (10 ml) and was purged with nitrogen gas for 20 min. It was then placed in oil bath preheated to 70 °C and stirred for 24 h. The reaction was quenched by removal from oil bath and cooled with ice-water mixture.

The polymer was precipitated in cold methanol drop wisely and stirring. It was kept in fridge overnight followed by removal of methanol. The polymer was dried and samples taken for GPC and NMR analysis.

¹**H NMR (400 MHz, CDCl₃):** δ = 0.06 (s, 48 H, SiC*H*₃), 0.49 (t, 16 H, SiC*H*₂), 0.88 (t, 24 H, C*H*₃), 1.28 (m, 112 H, C*H*₂), 1.47 (m, 16 H, C*H*₂), 1.56 (s, 24 H, C*H*₃), 1.83 (m, 48 H, C*H*₂), 3.99 (m, 32 H, OC*H*₂), 6.50 (d, 1 H, C*H*_{arom}), 6.95 (d, 1 H, C*H*_{arom}), 7.24 (d, 1 H, C*H*_{arom}), 7.26 (d, 2 H, C*H*_{arom}), 7.50 (d, 2 H, C*H*_{arom}), 7.54 (d, 2 H, C*H*_{arom}), 8.05 (d, 1 H, C*H*_{arom}).

5.5.5 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-hydroxypentyl)oxy)-4-

(octyloxy)benzoate (5.8)⁹⁻¹²



Scheme 5.12

Both 9-Borabicyclo [3.3.1] nonane (9-BBN) and Borane tetrahydrofuran complex solution were used in the hydroboration **4.7** to afford **5.8**.

(i) Hydroboration using 9-BBN

9-BBN (0.5 M solution in THF, 1.5 ml, 0.76 mmol) was added to a solution of compound 4.7 (0.5 g, 0.76 mmol) in THF (10 ml) at 40 °C and stirred for 12 h. 3 M NaOH (0.25 ml) was added, stirred for 1 h and cooled to 0 °C. 0.25 ml of 30% H_2O_2 was slowly added and stirred for additional 1 h. The product was extracted by diethyl ether, washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Further purification was obtained by column chromatography (ether, second layer). The yield was 0.23 g (54 %).

(ii) Hydroboration using BH₃.THF

All glass wares were cleaned, dried and flash-flushed with nitrogen prior this experiment. To compound 4.7 (0.2 g, 0.304 mmol) in dry THF (5 ml) at 0 °C, was added BH₃.THF solution (0.95M BH₃.THF solution, 0.16 ml, 0.152 mmol) dropwise. The solution was stirred for 2 h and water (10 ml) was added dropwise followed by NaBO₃.4H₂O (0.03034 g, 0.304 mmol) while the stirring continued for additional 2 h. The mixture was poured into ice cold water (15 ml) and extracted with ether (3 x 25 ml). The organic layer was washed with water (2 x 5 ml), brine (5 ml), dried over MgSO4, filtered and the solvent removed *in vacuo*. Further purification was obtained by column chromatography (ethyl acetate/Hexane 1:5 was used to remove the first two layers, and ethyl acetate used to flush the third layer which is the desired product). The yield was 0.09 g (44 %).

Rf (Ether) = 0.81.

Elemental analysis: Analytical calculated values for C₄₃H₆₂O₆ (MW = 674.96): C, 76.52; H, 9.26. Found: C, 76.44; H, 9.01 %.

¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 6 H, CH₃), 1.26-1.30 (m, 22 H, CH₂), 1.30 (t, 4 H, CH₂), 1.60 (t, 4 H, CH₂), 1.80 (m, 6 H, CH₂), 3.60 (t, 2 H, CH₂OH), 4.10 (t, 6 H, OCH₂), 5.50 (s, 1 H, OH), 6.50 (d, 1 H, CH_{arom}), 6.95 (d, 1 H, CH_{arom}), 7.2 (d, 1 H, CH_{arom}), 7.24 (d, 2 H, CH_{arom}), 7.49 (d, 2 H, CH_{arom}), 7.55 (d, 2 H, CH_{arom}), 8.03 (d, 1 H, CH_{arom}).

5.5.6 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl

2-((5-(methacryloyloxy)pentyl)oxy)-4-



(octyloxy)benzoate (5.9)¹⁴

Scheme 5.11

Methacryloyl chloride (0.2 ml, 0.21 mmol) was added dropwise to 0 °C solution of triethylamine (3.6 ml, 1.3 mmol), **5.8** (0.07 g, 0.1 mmol) in THF (15 ml) under nitrogen atmosphere. The mixture was then allowed to warm to room temperature and stirred for 9 h. The reaction mixture was partitioned between diethyl ether (50 ml) and 10 % HCl (50 ml). The aqueous layer was separated and extracted with ether (2 x 100 ml). The organic layers were combined, washed with brine (20 ml), dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography using ether as solvent. The second layer, with the 0.075 g (98 %) yield was the desired product. Rf (Ether) = 0.67.

Elemental analysis: Analytical calculated values for $C_{43}H_{62}O_6$ (MW = $C_{47}H_{66}O_7$): C, 75.97; H, 8.95. Found: C, 75.89; H, 8.67 %.

¹**H NMR (400 MHz, CDCl₃):** $\delta = 0.89$ (t, 6 H, *CH*₃), 1.20 (t, 4 H, *CH*₂), 1.22 (m, 22 H, *CH*₂), 1.28 (m, 4 H, *CH*₂), 1.95 (m, 4 H, *CH*₂), 2.0 (s, 3 H, *CH*₃), 4.05 (m, 6 H, *OCH*₂), 5.68 (s, 1 H, =*CH*₂), 6.23 (s, 1 H, =*CH*₂), 6.50 (d, 1 H, *CH*_{arom}), 6.96 (d, 1 H, *CH*_{arom}), 7.2

3(d, 1 H, CH_{arom}), 7.25 (d, 2 H, CH_{arom}), 7.51 (d, 2 H, CH_{arom}), 7.55 (d, 2 H, CH_{arom}), 8.06 (d, 1 H, CH_{arom}).

5.5.7 Free radical polymerization of AM-7MC (5.10)



Scheme 5.14

Monomer **5.9** (1.99 g, 2.7 mmol) was dissolved in dry toluene (5 ml) and AIBN (0.4 g, 0.27 mmol) was added. The mixture was degassed by nitrogen purging 5 times and placed in a pre-heated oil bath (70 °C) with stirring for 20 h. the solvent was removed and the polymer re-dissolved in minimum amount of THF and precipitated in cold methanol. The process was repeated twice and the polymer dried in vacuo.

¹**H NMR (400 MHz, CDCl₃):** δ = 0.89 (t, 6 H, CH₃), 1.20 (t, 4 H, CH₂), 1.22 (m, 22 H, CH₂), 1.28 (m, 4 H, CH₂), 1.95 (m, 4 H, CH₂), 2.0 (s, 3 H, CH₃), 4.05 (m, 6 H, OCH₂), 6.50 (d, 1 H, CH_{arom}), 6.96 (d, 1 H, CH_{arom}), 7.2 3(d, 1 H, CH_{arom}), 7.25 (d, 2 H, CH_{arom}), 7.51 (d, 2 H, CH_{arom}), 7.55 (d, 2 H, CH_{arom}), 8.06 (d, 1 H, CH_{arom}).

5.5.8 4-Hydroxylbutyl methacrylate (5.12)¹³





Method (i)

Methacrylic acid (10 g, 0.12 mol), 1,4-butanediol (15.7 g, 0.17 mol), hydroquinone (10 mg, 0.091 mmol) and toluene (100 ml) were stirred at room temperature. H_2SO_4 (0.16 g, 1.62 mmol) was added to the mixture and stirred for 3 h under reflux. The mixture was cooled to room temperature and solvent distilled off. Hexane (150 ml) was added to the mixture and the mixture extracted with distilled water (4 x 100 ml). The aqueous layer was extracted with ethyl acetate (3 x 100 ml). The combine organic layer was washed with saturated Na_2CO_3 solution (3 x 50 ml), saturated NaCl (50 ml) and the solvent removed to give a light/ faint golden oil which was purified by silica column chromatography (ether) to yield a faint golden coloured oil (10.8 g, 58%). L2

Method (ii)

Methacryloyl chloride (5.86 ml, 60 mmol) was added drop wise to a cooled (0 °C) solution of 1,4-butanediol (5.33 ml, 60 mmol) and pyridine (30 ml) in dichloromethane (30 ml). The reaction was stirred at room temperature for 2 h, quenched with 1M HCl (50 ml) and extracted with DCM (3 x 100 ml). The combined organic layers was washed with 3M HCl (3 x 100 ml), dried over MgSO4 and solvent removed to obtain an oil. Further purification by column chromatography (ether or Ethyl acetate/Hexane-3/2) gave a clear oil (4.73 g, 51%). L2

¹**H NMR (400 MHz, CDCl₂):** d = 1.49 (m, 2 H, CH₂CH₂), 1.60 (m, 2 H, CH₂), 1.76 (s, 3 H, CH₃), 3.48 (t, 2 H, CH₂), 4.00 (t, 2 H, CH₂), 4.27 (br s, 1 H, OH), 5.39 (s, 1 H, =CH₂), 5.96 (s, 1 H, =CH₂).

¹³C NMR (100 MHz, CDCl₂): d = 17.8, 24.8, 28.7, 61.9, 64.2, 125, 136, 167.

5.5.9 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-(chlorodimethylsilyl)pentyl)oxy)-4-(octyloxy)benzoate (5.13)



Scheme 5.16

Method (i)

Compound **4.7** (0.5 g, 0.76 mmol) was dissolved in dry toluene (5 ml) and chlorodimethylsilane (0.72 g, 7.61 mmol) was added under nitrogen and stirred for 20 min followed by the addition of Karstedt's catalyst (5 μ l, 2 % Pt in xylene). The solution was stirred for 12 h and the solvent with excess chlorodimethylsilane was removed under vacuum.

Method (ii)

A mixture of compound **4.7** (3 g, 4.56 mmol), toluene (20 ml), chlorodimethylsilane (0.51 g, 5.4 mmol) and Karstedt's catalyst (30 μ l) was stirred under argon at 60 °C for 24 h. The solvent was removed to leave a golden oil product.

¹**H NMR (400 MHz, CDCl₃):** $\delta = 0.20$ (s, 6 H, SiCH₃), 0.70 (t, 2 H, SiCH₂), 1.00 (s, 6 H, CH₂CH₃), 1.40 (m, 26 H, CH₂CH₂), 1.90 (m, 4 H, CH₂CH₃), 2.40 (m, 6 H, OCH₂CH₂), 4.20 (m, 6 H, OCH₂), 6.60 (m, 2H, CH arom), 7.10 (m, 2 H, CH arom), 7.60 (m, 2 H, CH arom), 7.70 (m, 4 H, CH arom), 8.04 (d, 1 H, CH arom).

¹³C NMR (100 MHz, CDCl₃): δ = 1.27, 14.3, 21.7, 22.9, 26.3, 29.4, 29.6, 29.8, 32.2, 68.5, 100, 106, 115, 122, 126, 127, 128, 129, 135, 138, 149, 159, 162, 164, 166.

4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-((4-

(methacryloyloxy)butyl)dimethylsilyl)pentyl)oxy)-4-(octyloxy)benzoate (5.14)



Scheme 5.17

A mixture of compound **5.13** (0.4820 g, 0.64 mmol), compound **5.12** (0.1012 g, 0.64 mmol) and imidazole (0.47 g, 6.9 mmol) in DCM (10 ml) was stirred at rt for 24 h. Saturated NH₄Cl aqueous solution (10 ml) and DCM (10 ml) were added to the mixture. The organic layer was washed with water (2 x 10 ml) and concentrated followed by drying. Column chromatography (Ethyl acetate as eluent) monitored by permanganate dip, was use to obtain a pure golden light oil, 67 %.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.0$ (s, 6 H, SiCH₃), 0.37 (t, 2 H, SiCH₂), 0.81 (t, 8 H, CH₂), 1.23 (m, 27 H, CH₂), 1.39 (m, 6 H, CH₂), 1.73 (m, 7 H, CH₂), 1.96 (s, 3 H, CH₃), 3.61 (t, 2 H, SiOCH₂), 3.90 (m, 6 H, CH₂OCH₂), 4.01 (t, 2 H, CH₂CO), 5.47 (s, 1 H, =CH₂), 6.02 (s, 1 H, =CH₂), 6.42 (m, 2H, CH arom), 6.89 (m, 2 H, CH arom), 7.15 (m, 2 H, CH arom), 7.46 (m, 4 H, CH arom), 8.08 (d, 1 H, CH arom).

5.5.10 Polymerization of monomer 5.14 (5.15)



Scheme 5.18

Monomer **5.14** (0.3 g, 0.34 mmol) and AIBN (5.7 g, 0.034 mmol) were dissolved in dry toluene (5 ml) and purged with nitrogen for 10 min. the solution was then place in oil bath ore-heated to 70 $^{\circ}$ C and stirred for 24 h. The polymer was precipitated in cold methanol. The process was repeated twice and the polymer dried in vacuo.

 $Mn_{GPC} = 4016 \text{ g/mol}, Mw = 4629 \text{ g/mol}, Mw/Mn = 1.15, n~5.$

¹**H NMR (400 MHz, CDCl₃):** δ = 0.04 (s, 6n H, SiCH₃), 0.50 (t, 2n H, SiCH₂), 0.89 (t, 9n H, CH₂CH₃), 1.32 (s, 2n H, CH₂), 1.46 (s, 3n H, CH₃), 1.60 (s, 3 H, CH₃), 1.80 (m, 2n H, CH₂), 2.0 (m, 2n H, CH₂), 2.29 (q, 2n H, CH₂), 3.47 (s, 2n H, CH₂O), 3.60 (m, 2n H,

CH₂OCO), 4.00 (t, 2n H, CH₂O), 6.52 (m, 2n H, CH _{arom}), 6.96 (m, 2n H, CH _{arom}), 7.23 (m, 2n H, CH _{arom}), 7.54 (m, 4n H, CH _{arom}), 8.05 (d, 1n H, CH _{arom}).

5.5.11 4-Hydroxylbutyl methacrylate (5.12)



Scheme 5.19

Method (i)

Methacrylic acid (10 g, 0.12 mol), 1,4-butanediol (15.7 g, 0.17 mol), hydroquinone (10 mg, 0.091 mmol) and toluene (100 ml) were stirred at room temperature. H₂SO₄ (0.16 g, 1.62 mmol) was added to the mixture and stirred for 3 h under reflux. The mixture was cooled to room temperature and solvent distilled off. Hexane (150 ml) was added to the mixture and the mixture extracted with distilled water (4 x 100 ml). The aqueous layer was extracted with ethyl acetate (3 x 100 ml). The combine organic layer was washed with saturated Na₂CO₃ solution (3 x 50 ml), saturated NaCl (50 ml) and the solvent removed to give a light/ faint golden oil which was purified by silica column chromatography (ether) to yield a faint golden colour oil (10.8 g, 58%). L2

Method (ii)

Methacryloyl chloride (5.86 ml, 60 mmol) was added drop wise to a cooled (0 °C) solution of 1,4-butanediol (5.33 ml, 60 mmol) and pyridine (30 ml) in dichloromethane (30 ml). The reaction was stirred at room temperature for 2 h, quenched with 1M HCl (50 ml) and

extracted with DCM (3 x 100 ml). The combined organic layers was washed with 3M HCl (3 x 100 ml), dried over MgSO4 and solvent removed to obtain an oil. Further purification by column chromatography (ether or Ethyl acetate/Hexane-3/2) gave a clear oil (4.73 g, 51%). L2

 $R_{\rm f}$ (Ether) = 0.46

¹H NMR (400 MHz, CDCl₂): d = 1.49 (m, 2 H, CH₂CH₂), 1.60 (m, 2 H, CH₂), 1.76 (s, 3 H, CH₃), 3.48 (t, 2 H, CH₂), 4.00 (t, 2 H, CH₂), 4.27 (br s, 1 H, OH), 5.39 (s, 1 H, =CH₂), 5.96 (s, 1 H, =CH₂).

¹³C NMR (100 MHz, CDCl₂): d = 17.8, 24.8, 28.7, 61.9, 64.2, 125, 136, 167.

5.5.12 Polymerization of 4-Hydroxylbutyl methacrylate (5.16)



Scheme 5.20

Method (i)

Compound **5.18** (50 mg, $1.11 \ge 10^{-4}$ mol), Cu(I)Br (16 mg, $1.11 \ge 10^{-4}$ mol) and compound **5.12**(1.80 g, $1.13 \ge 10^{-2}$ mol) were dissolved in 5 ml of dry toluene. The solution was

degassed three times by evacuation with nitrogen. Finally, 2, 2'-bipyridine (35 mg, 2.22 x 10^{-4} mol) was added and the mixture degassed twice.

The mixture was then place in pre-heated oil bath at 90 °C for 6h. Although the monomer was soluble in toluene, the polymer was not. The reaction was quenched by removing it from the oil bath and different methods were used to remove the catalysts which include reacting the polymer with Zinc dust and filtering through alumina column.

The polymer was dissolved in methanol before filtering through alumina column.

The polymer was re-dissolved in minimum amount of THF and precipitated in cold hexane.

 $Mn_{GPC} = 2956 \text{ g/mol}, Mw/Mn = 1.34.$

Method (ii)

Compound **5.18** (50 mg, $1.11 \ge 10^{-4}$ mol), Cu(I)Br (16 mg, $1.11 \ge 10^{-4}$ mol) and compound **5.12** (1.80 g, $1.13 \ge 10^{-2}$ mol) were dissolved in 5 ml of methanol. The solution was degassed three times by evacuation with nitrogen. Finally, 2, 2'-bipyridine (35 mg, 2.22 $\ge 10^{-4}$ mol) was added and the mixture degassed twice.

The mixture was then place in pre-heated oil bath at 50 °C for 24 h. The reaction was quenched by removing it from the oil bath and the catalyst was removed by filtering through alumina column.

The polymer was re-dissolved in minimum amount of methanol and precipitated in cold diethyl ether. Mn $_{GPC} = 5397$ g/ mol, n = 34.

¹**H NMR (400 MHz, CDCl₂):** d = 1.16 (s, 12 H, CH₃), 1.64 (t, 4n H, CH₂CH₂), 2.10 (s, 3n H, CH₃), 2.90 (t, 2 H, SCH₂), 3.50 (t, 2n H, CH₂OH), 3.70 (t, 2n H, OCOCH₂), 4.00 (m, 2 H, COOCH₂), 5.30 (s, n H, OH).

¹³C NMR (100 MHz, CDCl₂): d = 14, 17, 24, 25, 26, 39, 44, 52, 59, 60, 65, 68, 168, 175.



5.5.13 Functionalization of compound 5.16 with compound 5.13 (5.17)



Method (i)

Polymer **5.16** (0.2731 g, 0.05 mmol) was dissolved in dry THF (10 ml), triethyl amine (3 ml) was added and stirred followed by compound **5.13** (1.3 g, 1.73 mmol). The mixture was stirred for 3 days at room temperature. The solvent and triethyl amine were removed in vacuo and the polymer re-dissolved in minimum amount of THF, precipitated in cold methanol. The process was repeated twice.

Method (ii)

A mixture of polymer **5.16** (0.1984 g, 0.05 mmol, $Mn_{GPC} = 4000$ g/mol), imidazole (8.5 mg, 0.125 mmol, ca. 2.5 equiv of -OH), and compound **5.13** (0.95 g, 1.27 mmol) in DMF

(7 ml) was stirred at room temperature for 24 h. The polymer was precipitated in cold methanol. The process was repeated twice to obtain a white polymer.

¹**H NMR** (**400 MHz, CDCl₃**): $\delta = 0.0$ (s, 6n H, SiCH₃), 0.40 (t, 2n H, SiCH₂), 0.83 (s, 6n H, CH₃), 1.20 (s, 6n H, CH₃), 1.48 (m, 38n H, CH₂), 1.73 (m, 6n H, CH₂), 2.01 (s, 3n H, CH₃), 2.10 (s, 2n H, CH₂), 2.23 (t, 2 H, SCH₂), 3.50 (t, 2n H, SiOCH₂), 3.70 (t, 2 H, CH₂OCH₂), 4.01 (m, 8n H, OCH₂), 6.50 (m, 2H, CH _{arom}), 6.90 (m, 2n H, CH _{arom}), 7.20 (m, 2n H, CH _{arom}), 7.59 (m, 4n H, CH _{arom}), 8.04 (d, 1n H, CH _{arom}).

¹³C NMR (100 MHz, CDCl₃): δ = 1.3, 14, 17, 22, 23, 24, 25, 26, 29, 29.6, 30, 32, 39, 44, 52, 59, 60, 65, 68, 69, 100, 106, 115, 122, 126, 127, 128, 129, 135, 138, 149, 159, 162, 164, 166, 168, 175.

5.5.14 Free radical polymerization of 49 (54)



Scheme 5.23

AM-49 (1.5054 g, 9.51 mmol) and AIBN (0.1560 g, 0.951 mmol, 0.1 equiv) was dissolved in dry toluene (10 ml). The solution was degassed by purging with nitrogen 5 times and placed in oil bath (70 $^{\circ}$ C) with stirring for 24 h. the solvent was removed and the polymer

dissolved in minimum amount of THF and precipitated in cold hexane. The process was repeated 5 times and the polymer dried in vacuo.

Mn _{GPC} = 1962 g/mol, Mw = 3173 g/mol, Mw/Mn = 1.617

¹H NMR (400 MHz, CDCl₃): δ = 0.87 (s, 3 H, CH₂CH₃), 1.25 (s, 3n H, CH₃), 1.40 (m, 2 H, CH₂CH₃), 1.61 (m, 2n H, CH₂), 1.70 (m, 2n H, CH₂), 1.84 (t, 2n H, CH₂OH), 2.18 (s, 2n H, CH₂), 2.10 (s, 2n H, CH₂), 3.74 (t, 2n H, CH₂OCO₂), 4.01 (bs, 1n H, OH).
¹³C NMR (100 MHz, CDCl₃): δ = 18, 25, 63, 68, 125, 136, 167.

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CHAPTER SIX

COMPOSITES OF GOLD NANOPARTICLES AND SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS

6.1 Synthesis of AuNP-polymer liquid crystalline composites

This chapter describes the synthesis of gold nanoparticle-side chain liquid crystalline polymers by atom transfer radical polymerization (ATRP) in which Cu(I)Br, bipyridine and disulfanediylbis(ethane-2, 1-diyl) bis(2-bromo-2-methylpropanoate) (compound **6.3**) serves as catalyst, ligand and initiator in the reaction, while toluene or methanol was employed as solvent for the reaction.

The liquid crystal polymers investigated are side chain liquid crystal polymers (SCLCP) and the general template for the composites is given below (Fig. 6.1).



Figure 6.1: The general template of the composites

Many routes were investigated for the synthesis of the AuNP-polymer composites.

Common to all the polymer are the polymer backbone and the mesogen but disiloxane linkage was investigated in the first synthesis (scheme 6.1) while no linkage was used in the second synthesis (scheme 6.2).

From scheme 6.1, two routes were investigated to synthesise the composite. The first route involved the synthesis of methacrylate monomer, but-3-en-lyl methacrylate (6.6), polymerization and subsequently functionalizing the resulting polymer with mesogenic siloxane compound (5.5) (obtained by transforming the terminal alkene end of mesogenic compound 7 to siloxane end by 1,1,3,3-tetramethyl disiloxane).

The second route involved the conversion of mesogenic siloxane compound **5.5** to polymerizable mesogenic monomer **5.6** by reacting it with but-3-en-lyl methacrylate (**6.6**). The composites were purified by repeated precipitation and centrifugation while the purity and the characters of the materials are determined by NMR spectroscopy, thermal analysis (DSC and TGA), elemental analysis, UV-vis spectroscopy, TEM and XRD.

6.1.1 Synthesis of the monomer

Methacrylate monomer, but-3-en-lyl methacrylate (**6.6**), was synthesised by acylation of 3-buten-1-ol (**6.4**), by methacryloyl chloride (**6.5**) in a very good yield as compared with the literature value¹⁻².

6.1.2 Synthesis of the initiator

The initiator used for the polymerization, disulfanediylbis(ethane-2,1-diyl) bis(2-bromo-2methylpropanoate) (6.3), was synthesised by the esterification of 2, 2'-dithioldiethanol (6.1) by 2-bromoisobutyryl bromide $(6.2)^3$ in a quantitative yield.

6.1.3 Purification of the catalyst

The Cu(I)Br was purified by washing it with glacial acetic acid, followed by ethanol and finally ether. It was then dried *in vacuo* overnight⁴.

6.1.4 Purification of the ligand

Bipyridine was purified by recrystallization from acetone and dried in vacuo.

The synthesis of the methacrylate mesogenic monomer containing disiloxane as linking unit was carried out by hydrosilylation⁵⁻⁷ of the alkene terminal of compound **7** using 1,1,3,3-tetramethyldisiloxane to obtain compound **5.5**, in an excellent yield (>90%), which was subsequently linked to the But-3-en-lyl methacrylate (**6.6**) by second hydrosilylation to yield the target monomer (**5.6**) in a very good yield (> 80%).

6.2 Synthesis of AuNP-polymer liquid crystalline composites

In synthesising AuNP-polymer crystalline composites, both grafting to and grafting from the surface of the AuNPs were investigated and is summarised in scheme 6.1.



Scheme 6.1: Synthetic routes for composites

6.2.1 POLYMERIZATION

ATRP of the But-3-en-lyl methacrylate (**6.6**) was first investigated in toluene using Cu(I)Br as catalyst and 2, 2'-bipyridine as ligand with monomer to initiator ratio of 100:1 and the reaction allowed for 4 h at 90 °C ³. The monomer conversion was monitored by gel permeable chromatography (GPC), quenched after 4 h, catalyst removed and the polymer **6.7** precipitated in cold methanol. In order to completely remove any monomer precipitating along with the polymer, the polymer was re-dissolved in minimum amount of THF and re-precipitated in cold methanol while stirring very fast. The methanol was decanted and the polymer **6.7** dried in vacuo and finally analysed.

Attempt was made to introduce the hydrosilylated mesogen, **5.5**, to the polymer **6.7**, but from NMR analysis it was found that about 50% of the unsaturated terminal end of polymer reacted even in the presence of excess compound **5.5** probably due to its bulkiness.

The methacrylate mesogenic monomer (5.6) was polymerised using the same principle used for the 6.7 above only that the reaction time was extended to 24 h to yield polymer 6.8 containing S-S disulfide bond. The S-S bond was cleaved using Tris(2-carboxyethyl)phosphine (TCEP)⁸ to afford thiol polymer 24 which was coupled to gold nanoparticles to obtain the composite 6.9.

The 'grafting-from' method was also investigated in which the initiator disulfanediylbis(ethane-2, 1-diyl) bis(2-bromo-2-methylpropanoate) (6.13) was cleaved and coupled with AuNP to form initiator coupled AuNP (6.11). This was used as the macroinitiator in the polymerization of the monomer (5.6) with the same reaction condition given above but at room temperature after the reaction at 90 °C caused the detachment of the initiator from the surface of AuNP-initiator and increment of the NP sizes. The composite obtain, 6.12, was analysed.

Page | 177

6.3 Synthesis of composite (6.15)



The scheme for the synthesis of composite without disiloxane linage is shown below.

Scheme 6.2: Synthesis of composite 6.15.

The terminal alkene of the mesogen **4.7**, was converted to hydroxyl end group 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-hydroxypentyl)oxy)-4-(octyloxy)benzoate (**5.8**) by hydroboration using 9-borabicyclo[3.3.1]nonane (9-BBN) or borane tetrahydrofuran complex solution (BH₃.THF) followed by oxidation by either sodium perborate (NaBO₃.4H₂O) or sodium hydroxide/hydrogen peroxide solution (NaOH/H₂O₂)⁹⁻¹³.

The hydroxyl end group of compound **5.8** was directly acylated by methacryloyl chloride to afford the targeted methacrylate mesogenic monomer, 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-(methacryloyloxy)pentyl)oxy)-4-(octyloxy)benzoate (**5.9**). The monomer **5.9** was polymerised using similar condition of ATRP describe above to obtain polymer **6.13** containing S-S disulfide bond. The S-S bond was cleaved to yield active thiol polymer, **6.14** which was coupled with AuNP through ligand exchange to give the target composite **6.15**.

'Grafting-from' method was, also, used to investigate the synthesis of composite **6.15**. The AuNP-coupled-initiator, **6.11**, was used as the macroinitiator for the polymerization of methacrylate mesogenic monomer (**5.9**) at room temperature.

6.4 Synthesis of composite 6.18

Composite 61 is a nanomaterial synthesised by coupling thiol side-chain hydroxyl polymer, **6.16**, to AuNPs and subsequently functionalizing with mesogenic chlorosilane **5.13** (Scheme 6.3).



Scheme 6.3: Synthesis of composite **6.18** (a) Hydroquinone, H_2SO_4 , Toluene. (b) Cu(I)Br, methanol, 50 °C, 24 h. (c) AuNP, THF, rt, 3-5 days (d) (CH₃)₂HSiCl, Pt catalyst, toluene, 12 h. (e) Toluene or THF, Et₃N. (e) (i) DMF, imidazole, 24 or (ii) TEA, THF, 24 h.

Thee monomer **5.12** was synthesised by esterification of one of the hydroxyl group on butan-1,4-diol by methacrylic acid ¹⁴ in about 60 % yield. This was followed by the ATRP of the monomer using compound **6.10** as the initiator to obtain polymer **6.16** which was

coupled to AuNPs through ligand exchange reaction to obtain composite **6.17** which was eventually functionalized by compound **5.13** to have the targeted composite **6.18**¹⁵⁻¹⁶.

6.5 Synthesis of composite 6.20

The approach used for the synthesis of composite **6.20** was based on the conventional knowledge of alkoxy-hydroxyl reactions in which ethoxyl functional mesogenic siloxane, **4.11**, was reacted with the hydroxyl polymeric-AuNP composites (Scheme 6.4). Different approaches were exploited to ensured complete reaction (attachment)¹⁷.

Synthesis of composite 6.20



Scheme 6.4: Synthesis of composite 6.20

6.6 Synthesis of 6.21

Polymerization of monomer **5.14** was investigated using 2-mercaptoethyl 2-bromo-2methylpropanoate modified AuNPs as macroinitiator, **6.11** (Scheme 6.5). The reaction was carried out in toluene at 35 °C for 24 h.

Scheme 6.5: Synthesis of composite 6.21

6.7 Synthesis of composite 6.27

The synthesis of triazolium monomer (6.26) began by mesylation of compound 5.8 using methylsulfonyl chloride followed by reaction with NaN₃ to obtain the first intermediate compound 6.23. The second intermediate, 6.25, was synthesised by esterification of the hydroxyl end group of 3-butyn-1-ol, 6.24, to methacryloyl chloride. The targeted monomer was finally synthesised by click reaction between 6.23 and 6.25. Polymerization of the triazole monomer, 6.26, using 2-mercaptoethyl 2-bromo-2-methylpropanoate modified AuNPs as macroinitiator, 6.11 gave the targeted composite (6.27) (Scheme 6.6).





Scheme 6.6: Synthesis of composite 6.27.

6.8 Results and Discussion

6.8.1 Polymerization

6.8.1.1 Methacrylate monomer

The results obtained for the polymerization of But-3-en-lyl methacrylate (**6.6**) using $[M]_0:[I]_0=100:1$ and $[Cu(I)]_0:[I]_0=1$ to obtain polymer **6.7** are shown in Table 6.1.

The crude polymer solution was green in colour and therefore it was necessary to remove the catalyst (Cu(I)Br) which was associated with the colouration. The catalyst was removed by filtration through alumina column using THF as eluent (Fig. 6.2)



Figure 6.2: Removal of catalyst (Cu(I)Br) from polymer 6.7.

After the removal of the catalyst, the brownish solution of the polymer was precipitated in cold methanol, filtered and dried in vacuo to give a white polymer (Fig. 6.3).



Figure 6.3: (a) Crude polymer solution (b) Precipitated polymer after purification (c) Dry purified polymer (d) Spent Cu(I)Br (green) on column

Time				Conversion	[M]=(1-		
(min)	Mn	Mw	M _w /M _n	(%)	Conversion)[M ₀]	[M ₀]/[M]	ln([M ₀]/[M])
2	0	0	0	0	1.13 x 10 ⁻²	1.00	0
15	1235	2407	1.95	24	8.59 x 10 ⁻³	1.32	0.27
30	1882	4018	2.14	36	7.23 x 10 ⁻³	1.56	0.45
60	2462	5157	2.10	48	5.88 x 10 ⁻³	1.92	0.65
75	2674	5195	1.94	52	5.42 x 10 ⁻³	2.08	0.73
90	2985	5757	1.93	58	4.75 x 10 ⁻³	2.38	0.87
120	3158	6012	1.90	62	4.29 x 10 ⁻³	2.63	0.97
135	3221	5176	1.61	63	4.18 x 10 ⁻³	2.70	0.99
165	3755	6128	1.63	73	3.05 x 10 ⁻³	3.70	1.31
195	4281	6543	1.53	83	1.92 x 10 ⁻³	5.89	1.77
225	4758	6582	1.38	93	0.79 x 10 ⁻³	14.29	2.66
240	5130	6887	1.34	100	0.00	0	0

6.8.1.2 POLYMERIZATION

Table 6.1: Results of polymerization monitored by GPC

The polymer is a white rubbery solid after isolation from precipitation in methanol. The molecular weights increased linearly with the conversion (Figure 6.3) while the molecular weight distribution decreased as the reaction proceeded, becoming very narrow, $M_w/M_n < 1.5$ (Table 6.1).



Figure 6.3: Increase in Mn with (a) reaction time (min); (b) conversion (%).

The final polymer has number average molecular weight, M_n =5130 and M_w/M_n =1.3. It was noticed that in subsequent reactions, polydispersity of as low as 1.1 were obtained. The relative low polydispersities indicate that the reaction is a well-controlled polymerization process¹⁸.

A linear plot is observed in a molecular weight range of 3.2×10^3 to 5.1×10^3 (Figure 6.3 (a) above). The slope is of a straight line and is 0.30 indicating a high initiator efficiency¹⁹. The degree of polymerization, i.e the number average molecular weight, M_n is a linear function of monomer conversion and this is indicated by the straight line graph obtained for the plot of M_n vs conversion (Figure 6.3 (b) above).

The semi-logarithmic plot (Figure 6.4) shows the sensitivity of changes of concentration of the active propagating species.



Figure 3.38: ln([M]₀/[M]) vs time (min)

A constant propagating species were formed in the first 30 min of the reaction but decrease between 40 min and 60 min of the reaction. This is possibly due to termination reaction which increased the concentration of the resistant radicals or catalytic system being poisoned (O_2 getting into the system during the process of taking sample for analysis). There was increase in the propagating species between 60 min and 90 min, decrease between 120 min and 135 min before maintaining a constant concentration increment to the end of the reaction.

Figure 6.5 shows the rate of monomer consumption.



Figure 6.5: Rate of monomer consumption.

The rate of radical polymerization for any given monomer is directly proportional to the concentration of the radicals in the system¹⁹ and this means that rate of polymerization is given as

$$R_p = -d[M]/dt = k_p[M][R']$$

From Figure 6.5,

$$R_p = -d[M]/dt = -[(2-8) \times 10^{-3} \text{ mol}]/[(195-18)/60 \text{ sec}] = 2.03 \times 10^{-3} \text{ mol Sec}^{-1}$$
.

Also, using the expression,

 M_n , theory = ([M]₀/[I]₀) x (M_w)₀ x conversion¹⁹ it is possible to calculate the theoretical value of the number average molecular mass. Although, using the expression gave higher values than the experimental (obtained) values which confirm higher initiator efficiency.

6.9 Compounds 5.5 and 5.6

Figure 6.6 shows the ¹H NMR of compound **4.7**, **5.5** and **5.6** ((a), (b) and (c) respectively).




The disappearance of the proton (d = 4.95 ppm, 5.80 ppm) due to lateral terminal alkene (a) in **5.5** (b) and the appearance of SiH proton (d = 4.70 ppm) confirmed the attachment of the disiloxane to the mesogen.

In compound **5.6** (c), the disappearance of disiloxane proton (d = 4.70 ppm in (b)), appearance of protons due to unsaturation in methacrylate (d = 5.50 ppm, 6.20 ppm in (c)) provide the evidence for its attachment to **5.5**.

The texture observed from POM for **5.5** and **5.6** are shown in figure 6.7.



Figure 6.7: Texture observed from POM for (a) **5.5** and (b) **5.6** after cooled by cardice.

Compound **5.5** shows threaded nematic texture between -4 $^{\circ}$ C to 21 $^{\circ}$ C where it cleared into isotropic phase while compound **5.6** shows schlieren nematic texture between -5 $^{\circ}$ C and 20 $^{\circ}$ C.



Figure 6.8: Transition of compound **5.5** to isotropic after cooled by liquid N_2 .

These thermal behaviour are well pronounce in the DCS curves of these compounds as shown in figure 6.9 below.



Figure 6.9: DSC for (a) **5.5** (b) **5.6**.

The summary of the thermal behaviours of **5.5** and **5.6** as determined by DSC and POM are shown in Table 6.2.

Compound	Melting Point (°C)	Transition Temperature	Enthalpy Change
		(°C) N to I	(Jg ⁻¹)
5.5	-4.6	21.2	0.37
5.6	-5.5	20.4	0.54

Table 6.2: Thermal properties of **5.5** and **5.6**.

6.9.1 Polymer 6.8

The molecular weight of polymer **6.8** as determined by GPC was found to be between 1,700 and 2,200 with molecular weight distribution of 1.13. ¹H NMR confirmed the polymerization (Fig. 6.10).



Figure 6.10: ¹H NMR of **6.8**.

The transition of **6.8** from nematic phase to isotropic phase when cooled by liquid nitrogen (as observed under POM), is as shown in figure 6.11.



Figure 6.11: Transition of compound **6.8** to isotropic after cooled by liquid N_2

The thermal behaviour of **6.8** is show in figure 6.12 which is the DSC heating and cooling curves.



Figure 6.12: DSC heating and cooling curves of **6.8**.

The ¹H NMR of cleaved functional thiol **24** is shown in Figure 6.13 (a) while (b) shows that of the nanocomposite **6.9**, formed from coupling **24** with **AuNPs** through ligand exchange. From ¹H NMR of **6.9**, it is evidence that **24** was successfully coupled with AuNPs.



Figure 6.13: ¹H NMR of (a) **24** (b) **6.9**.

The signals due to polymer were present in the composite.

Also, the SEM images for composite 6.9 is shown in figure 6.14.



Figure 6.14:SEM images of 6.9: (a) Back Scattered detector image (b) Secondary electron imaging.

Fig. 6.14 (a) is the back scattered detector image of **6.9** while (b) shows the secondary electron image. From the images, it is evidenced that the composite is made up of the polymer and Au (glittering spots) and is on the scale of the SEM homogeneous. Also, the spectra obtained for the energy dispersive X-ray analysis of the corresponding area is shown in figure 6.15, which confirmed the elements present in the composite to be Au, Si, C, O.



Figure 6.15: EDS of **6.9**.

The monodispersity of the AuNPs and their size stability is confirmed by the image obtained from TEM (Fig. 6.16). The size distribution of the NPs is shown on table 6.3, in which the average particle size was 2.33 and 3.07 nm respectively for 2 nm and 3 nm AuNPs respectively.



Figure 6.16: TEM image of **6.9**.

Sample	6.9 i (2 nm)	6.9 a (3 nm)	
1	2.60	3.15	
2	2.16	2.49	
3	2.29	3.65	
4	2.49	2.99	
5	2.21	3.19	
6	1.98	2.90	
7	2.04	2.97	
8	2.81	3.67	
9	2.16	2.37	
10	2.45	2.69	
11	2.23	2.90	
12	2.69	3.42	
13	2.28	3.15	
14	2.44	3.16	
15	2.23	3.15	
16	2.20	2.99	
17	2.44	3.19	
18	2.44	2.99	
19	2.37	3.15	
20	2.16	3.19	
Min=	1.98	2.37	
Max=	2.81	3.67	
Average=	2.33 ± 0.21	3.07 ± 0.32	
Table 6.3: Size distribution of 6.9.			

The texture of **6.9** when observed on POM is as shown in fig. 6.17. There was no observable transition but this type of texture is typical to composites of this type.



Figure 6.17: POM image of **6.9** (x 400).

When observed on UV-vis, **6.9** has a maximum absorption at 553 nm wavelength which indicated the presence of the polymer on Au surface (Fig. 6.18).



Figure 6.18: UV-Vis spectrum of 6.9.

The XRD data for composite **6.9** is shown in fig. 6.19 and table 6.4. The signal due to small angle is at 2.3 20 which correspond to a lattice spacing (d) of 38. 4 Å. This value also confirmed that there was no remarkable change in the size of the NPs as confirmed by TEM. The second signal which is closed to the first harmonic is at 4.9 20 corresponding to a spacing of 18 Å. This could be associated with the formation of SmA structure being present too.



Figure 6.19: XRD of composite 6.9.

2θ (°)	2.3	4.9
d (Å)	38.4	18.0

Table 6.4: XRD data of composite **6.9**.

6.9.2 Polymer grafting from AuNP macroinitiator surface

For the 'grafting from' method, the macroinitiator **6.11** was synthesised by firstly, the cleavage of compound **6.3** to afford thiol **6.10** followed by coupling to AuNPs. The signal due to HS (d=1.49) in the ¹H NMR of **6.10** shows that **6.3** was successful cleaved. The coupling of **6.10** to AuNPs in ligand exchange reaction is seen in ¹H NMR of **6.11** (fig. 6.20) in which signal due to HS has completely disappeared.



Figure 6.20: ¹H NMR of (a) **6.3**, (b) **6.10** and (c) **6.11**.

The UV-Vis spectrum of **6.11** is shown in figure 6.21.



Figure 6.21: UV-vis of **6.11**.

There is absorption at the wavelength of 545 nm in **6.11** which is not present in the UV-Vis spectrum of AuNPs. This confirmed that **6.10** was successfully coupled to the AuNPs. The same absorption was observed for UV-Vis of **6.11** prepared directly from **6.3** using excess NaBH₄.

The thermal property of **6.11** as investigated by thermogravimetry analysis (TGA) is presented in figure 6.22.



Figure 6.22: TGA thermogram of 6.11.

The thermogram showed the mass loss involves one step which started at 160 °C and ended at about 330 °C. This accounted for 18.34 % mass loss which was attributed to the organic moiety of the macro initiator. The second mass loss of 13.97 % at 800 °C was not well understood. This might be a systematic error because it was noted that the experiments at that time showed the feature.

The grafting of polymer from **6.11** can be seen in the NMR of composite **6.12** shown in figure 6.23.



Figure 6.23: ¹H NMR of **6.12**.

The image of **6.12** as observed on TEM is shown in figure 6.24. There was no appreciable change in the size on particle and they are monodispersed.



Figure 6.24: TEM of **6.12**.

The plasmonic property gave maximum absorption at wavelength of 558 nm which also indicated change in the property of the NP surface due to the attachment of polymer (fig. 6.25).



Figure 6.25: ¹H NMR of **6.12**.

Figure 6.26 shows the texture of **6.12** as observed on POM.



Figure 6.26: Texture of **6.12**.

This type of texture is common to this types of composite although there was no observable transition on POM.

The DSC heating and cooling curves are shown in fig. 6.27.



Figure 6.27: DSC heating and cooling curves for **6.12**.

The heating and cooling curves are broad and there was no sharp transition observed. Once again, this is peculiar to metal composite material of this kind.

The XRD for **6.12** is shown in fig. 6.28 and it shows the smallest angle signal is at 2.3 2θ (corresponding to d = 38.8 Å) and the second signal, which is the first harmonic, is at 4.9 2θ (corresponding to d = 18.0 Å) as shown in Table 6.5.



Figure 6.28: XRD of **6.12**.

2θ (°)	2.3	4.9	
d (Å)	38.8	18.0	

Table 6.5: XRD data of **6.12**.

The size of the NPs is further confirmed by the first signal as 3.88 nm.

Finally, there is no observable change in the particle sizes in composites **6.9** and **6.12** and as seen above, the particles are still monodispersed.

For the plasmonic properties of composite **6.9** and **28**, the absorption at 540 nm in both composites clearly confirmed that they are the same. Although, it was observed that the absorption of **6.9** is higher than that in **6.12**. This could be attributed to the amount of polymers attached to the surface of AuNPs, as the synthesis of **6.9** through 'grafting from' method took only 24 h while the synthesis of **6.12** through 'grafting to' method took 5 days. In other words, there are more polymers attached to AuNP surface in **6.12** than in **6.9** due to reaction time allowed.

6.10 Composite 6.15

The conversion of the terminal alkene of the mesogenic compound **4.7** to hydroxyl group (**5.8**) was confirmed by ¹H NMR (Figure 6.29) and also the attachment of the methyl methacrylate to afford methacrylate mesogenic monomer (**5.9**) was very successful and in quantitative yield (98 %).





Figure 6.29: 1H NMR of (a) 4.7, (b) 5.8 and (c) 5.9.

The polymerization of monomer **5.9** using compound **6.11** by 'grafting from' method was investigated and the properties are given below.



Figure 6.30:SEM images of **6.15**: (a) Back Scattered detector image (b) Secondary electron imaging. The above is the SEM image of composite **6.15**. The glittering spots are the AuNPs and as seen in (a) and (b) the NPs are entangled in the polymer. This is expected as the polymer chains are grown from the surface of the NPs. And structure is depicted is diagram below

which shows AuNRs (black) embedded in the polymer chains (green and white strands) that grew from their surfaces.



Figure 6.31: Schematic representation of the composites

The POM textures for **6.15** after sheared are as given in Figure 6.32.



Figure 6.32: POM image of 6.15.

The observed birefringence is common to AuNP-polymer composites of this type and most often, it is often difficult to observe transition with this type of nanosystem.



The thermal behaviour of composite **6.15**, as investigated on DSC, is shown in figure 6.33.

Figure 6.33: DSC curves of composite 6.15.

From the heating curve there is broad absorption between 80 °C and 110 °C, which is peculiar to polymers and nanocomposites.

The plasmonic property of composite 6.15 is as shown in figure 6.34.



Figure 6.34: UV-vis of composite 6.15.

When compared to the macroinitiator (**6.11**), there is a red shift of the plasmonic peak from 530 nm to 575 in composite **6.15**. This shows that there are changes on the gold surface due to the polymerization of the initially bonded initiator.

The thermal property of composite **6.15** was carried out by TGA analysis which involved heating the composite from 50 °C to 950 °C and the thermogram is shown in figure 6.35.



Figure 6.35: TGA thermogram of 6.15.

The thermogram shows two steps mass losses, the first mass loss between 100 $^{\circ}$ C and 150 $^{\circ}$ C was the thermal degradation of the polymer on the composites. This accounted for 2.07 % mass loss. The combustion of the polymer commenced at 210 $^{\circ}$ C and ended at 410 $^{\circ}$ C leaving a gold residue of 64.88 %.

Element	Found (%)
С	22.74
Н	3.47
S	4.26

Table 6.6: Elemental analysis of **6.15**.



Figure 6.36: XRD of 6.15.

Figure 6.36 shows the XRD for **6.15** while the 2θ angle and the corresponding lattice spacing are presented in table 6.7.

2θ (°)	2.5	4.9	7.5
d (Å)	35.5	17.7	11.8

Table 6.7: XRD data of **6.15**.

The results obtained here are very new and in need of confirmation. The data with reflection of **6.15** associated with 001, 002, 003 reflections fit to a smectic layering of 35.5 Å. The particles are organised in a 1-D array pointing to a smectic phase. This is the first example of such a laterally allocated mesogen not showing columnar but smectic organisation of layer. There is no indication of 2-D or 3-D structures. The diffraction at 2.5 20 further confirmed the size of the AuNP to be 3.55 nm, which shows that there is no noticeable change in the size of the NPs after the polymerization.

6.11 Composite 6.18

The polymerization of monomer **5.12** was successful in methanol and the properties of the polymer **6.16** as determined by GPC are as shown in table 6.8.

Polymer	Mn	Mw	Mw/Mn	n
6.16	8460	12736	1.50	54

Table 6.8:	properties	of 6.16 .

As shown in the table above, the polymerization reaction was well controlled as the molecular weight distribution of the polymer is small (1.50). The degree of polymerization was also found to be 54.

The coupling (attachment) of polymer **6.16** with AuNPs through ligand exchange reaction was also successful when the reaction was allowed for 5 days. This was confirmed by ¹H NMR (fig. 6.37) which shows all the signals due to the polymer **6.16** in composite **6.18**.



Figure 6.37: ¹H NMR of (a) Polymer **6.16** (b) **6.17**.

Also, the wavelength of maximum absorption on the UV-vis absorption of the composite **60** shows a red shift of 25 nm, from 535 nm to 560 nm, when compared to that of the AuNPs (Fig.6.38 (a) and (b))



The red shift of 25 nm was due to the attachment of the polymer **6.16** to the AuNPs which shows that there is increment of inter-particle distances and also there are changes in the refractive indexes of the NPs surfaces.

6.11.1 Thermal behaviour of composite 6.17

The thermal behaviour of the composite 6.17 was investigated using TGA (Fig. 6.39).



Figure 6.39: TGA thermogram for 6.17.

As shown in the thermograph, the composite was subjected to combustion in air upto 950 $^{\circ}$ C and it shows a single step depth loss between 175 $^{\circ}$ C and 325 $^{\circ}$ C accounting for 30 $^{\circ}$ mass loss. This is the amount of the polymer attached to the gold that the composite **6.17** is made of 70 $^{\circ}$ Au.

The functionalising the composite **6.17** with mesogenic silane **5.13** which supposedly considered a simple and straight forward step posed challenges as conventional conditions like the use of imidazole in DMF for 24 h, use of THF instead of DMF, use of TEA instead of imidazole, and increasing the time to 3 days did not show signals due to the mesogenic silane **5.13** in composite **6.18** (Fig. 6.40).



Figure 6.40: ¹H NMR of **6.18**.

It was observed that although there was no prominent signals due to mesogenic silane on 1 H NMR spectrum, there was a red shift of about 25 nm of the wavelength at which maximum absorption occurred on the UV-vis when compared to that composite **6.17** (560 nm to 585 nm) as shown in fig.6.41 and this in an indication that reaction occur to certain extent.



Figure 6.41: UV-vis for **6.18**.

6.11.2 Thermal behaviour of composite 6.18

The thermal behaviour of composite **6.18** on POM is shown in figure 6.42 although there was no prominent phase transition observed, images of **6.18** at the recorded temperature are as shown in fig. 6.42.



Figure 6.42:POM of composite 6.18 (a) Crystalline texture at rt (b) Texture at 35 °C (c) Texture above 100 °C

Composite **6.18** showed a broad transition on DSC between 30 °C and 40 °C while heating as shown below (Fig. 6.43).



Figure 6.43: DSC heating and cooling curves for **6.18**.

The thermal behaviour of composite **6.18** was further investigated by TGA by subjecting it to combustion in air from 0 - 950 °C. The decomposition of the composite starts almost immediately at about 100 °C and ended at 375 °C in a single step accounting for a loss of 45 % (organic moiety) with 55 % Au residue (Fig.6.44).



Figure 6.44: TGA thermogram of 6.18.

6.12 Composite 6.19

The synthesis of composite **6.19** by hydrolysis/condensation reactions between mesogenic triethoxysilane and the hydroxyl groups on the composite **6.17** was really challenging as the reaction did not proceed as expected even when subjected to more reaction time. There was weak signals due to ethoxysilane on the ¹H NMR spectrum as shown below (Fig. 6.45).



Fig. 6.45: ¹H NMR of **6.19**.

The SEM photograph is as shown in fig. 6.46 (a) and (b). This shows that the polymer is

attached to Au.



Figure 6.46: SEM images of 62: (a) Back Scattered detector image (b) Secondary electron imaging.

Also, EDS (fig. 6.47) shows some of the elements made up of the composite.



Figure 6.47: EDS of **6.19**.

When observed on POM with partly uncrossed polarizers (fig. 6. 48), **6.19** did not show any distinct transition but gave the characteristic texture similar to other composite.



Figure 6.48 (x 400):POM image of **6.19**.

6.13 Composite 6.20

Polymerization of monomer **5.14** using macroinitiator **6.11** was very successful as confirmed by NMR (fig. 6.49) which shows all the due to the mesogen.



Figure 6.49: ¹H NMR of **6.20**.

The SEM images of the composite is shown in fig. 6.50. The picture (a) is the back scattered image of the composite which confirmed the presence of Au (the glittering spots) entangled in the polymer.



Figure 6.50: SEM images of 6.20: (a) Back Scattered detector image (b) Secondary electron imaging.

Also, (b) is the secondary electron image of composite **6.20** and it shows the topography of the composite which is peculiar to polymeric composite (the glittering spots are AuNPs). EDS (fig. 6.51) shows the elemental composition of the composite as Au, Si, O, C, Br and S.



Figure 6.51: EDS of **6.20**.

The TEM image of **6.20** shows the monodispersity of the NPs and also that there was no changes in their sizes (fig. 6.52).



Figure 6.52: TEM image of 6.20.
Compositional	%
elements	
С	39.27
Н	6.22
S	4.18

The elemental composition of composite 6.20 is as shown in table 6.9.

Table 6.9: Elemental composition of 6.20.

From the elemental analysis, the total organic moiety is 49.67 % which implies the Au component is 50.33 %.

The plasmonic property of the composite **6.20** as investigated by UV-Vis shows that it has the maximum absorption at 560 nm. This indicates a red shift of about 20 nm when compared to that of macroinitiator **6.11**, (Fig. 6.53).





Figure 6.53: UV-vis of **6.20**.

The difference in the plasmonic properties indicates there is surface modification of the NPs, in this case, by the polymer.

6.13.1 Thermal behaviour of composite 6.20

Figure 6.54 shows the thermal behaviour of composite 6.20 when observed on POM.



Figure 6.54: POM textures of **6.20** (x 100) (a) at rt (b) sheared at rt (c) after annealed at 46 °C for 1 h (d)-(e) sheared after annealed at 46 °C.

(a) and (b) are the images of the composite at room temperature (about 20 °C) before and after sheared respectively. The composite shows a characteristic colourful birefringence and this was made prominent when annealed at 46 °C for 1 h (c-e).

The heating and the cooling curves obtained on DSC for the composite is as shown if figure 6.55.



Figure 6.55: DSC curves of 6.20.

There was a broad absorption between 20 °C and 30 °C with enthalpy of 1.01 J/g.



The thermal behaviour of **6.20** as investigated by TGA is shown in figure 6.56.

Figure 6.56: TGA thermogram of 6.20.

The combustion of **6.20** showed a two conjoined depth starting at 250 $^{\circ}$ C to around 350 $^{\circ}$ C and immediately started to end at 500 $^{\circ}$ C. The composite was made up of 42 $^{\circ}$ Au, which means the polymer content was 58 $^{\circ}$.

Finally, composite **6.20** was investigated on XRD and the result is as shown in figure 6.57 while 6.10 shows the 2θ angle, their corresponding lattice spacing and intensity.



Figure 6.57: XRD data of composite 6.20.

20 (°)	2.5	5.0	7.5
d (Å)	35	17	11

Table 6.10: XRD data of composite 6.20.

Although these results are new and may need further confirmation, the data shows three reflections associated with 001, 002 and 003 reflections. Also, the size of the NP is confirmed by XRD to be 3.5 nm which is in agreement with that obtained from TEM.

6.14 Composite 6.26

The first intermediate compound **6.24** was successfully synthesised in 94 % yield and ¹H NMR shows the signals due to methyl methacrylate methene protons at 5.3 ppm and 6.4 ppm respectively.

Also, the second intermediate **6.22** was successfully synthesised and confirmed by NMR and the thermal properties as observed by POM is as show in figure 6.58.



Figure 6.58: POM textures of **6.22** (x 400) (a) Crystalline texture (b) Nematic texture at 57 $^{\circ}$ C (c) Nematic to Isotropic phase at 62 $^{\circ}$ C

Monomer 6.25

Monomer **6.25** was synthesised by click reaction between **6.22** and **6.25** and the ¹H NMR confirmed the success of the reaction. The textures of **6.25** as observed on POM are given in figure 6.59.



Figure 6.59: POM textures of **6.25** (a) Crystalline texture (b) Nematic texture

Monomer **6.25** exhibits nematic texture and the heating and cooling curves obtained on DSC are shown if figure 6.60.



Figure 6.60: DSC curves of 6.25.

Composite **6.26** was synthesised by ATRP of monomer **6.25** using **6.11** as the macroinitiator. The success of the reaction was confirmed by the ¹H NMR (fig. 6.61), in which all the signals due to the monomer are seen in the composite.



Figure 6.61: ¹H NMR of **6.25** and composite **6.26**.

The SEM images of the composite is shown in figure 6.62. The picture (a) is the back scattered image of the composite which confirmed the presence of Au (glittering spots) entangled in the polymer composite.



Figure 6.62: SEM images of composite **6.26**: (a) Back scattered detector image (b) Secondary electron imaging.

The second image, (b), is the secondary electron image of composite **6.26** and it shows the topography of the composite which is peculiar to polymeric composite (the glittering spots are AuNPs and most of which are those located close to the surface of the composite). The elemental composition (EDS) of the corresponding scanned area is shown in figure 6.63 and the elements identified are Au, C, O, N and Br.



Figure 6.63: EDS of **6.26**.

The particle sizes were not affected by the polymerization process as confirmed by TEM (fig. 6.64).



Figure 6.64: TEM image of **6.26**.

The elemental composition of composite 6.26 is shown in table 6.11 below.

Elemental	%
composition	
С	26.43
Н	3.36
N	1.40
S	3.26

Table 6.11: Elemental composition of **6.26**.

The plasmonic property of the composite was determined by UV-vis and it shows the maximum absorption at 560 nm.



Figure 6.65: UV-vis of **6.26**.

This account for a red shift of 20 nm when compared to that of macroinitiator **27** which indicated the change in surface functionalization of the Au due to the polymer formation. The different textures of composite **6.26**, after sheared, as observed on POM is as shown in figure 6.66.



Figure 6.66: Different textures of composite 6.26 as viewed on POM (x 100).

This type of textures are peculiar to composites of the nature of composite **6.26**. Although, there was no observable transition occurred on POM, DSC heating and cooling curves shows transition at 23 $^{\circ}$ C with corresponding enthalpy of 0.28 J/g (fig. 6.67).



Figure 6.67: DSC curves of **6.26**.

When subjected to combustion, composite **6.26** shows a single step mass loss of 44 %, which commenced at 150 °C and ended at 425 °C (fig. 6.68). This mass loss was attributed to the polymeric unit of the composite. The Au content was 56 % and this remains as residue. The large Au content justifies why it was difficult to observe any noticeable transition on POM.



Figure 6.68: TGA thermogram of **6.26**.

The XRD of composite **6.26** is shown in figure 6.69.



Figure 6.69: XRD data of composite 6.26.

Table 6.12 shows the 2θ angle, their corresponding lattice spacing and intensity for the composite **6.26**.

20 (°)	2.5	5.0	7.5
d (Å)	35	17	11

Table 6.12: XRD data of composite 6.26.

Again, these results are new and may need further confirmation, the data shows three reflections associated with 001, 002 and 003 reflections. The size of the NP is confirmed by XRD to be 3.5 nm which is in agreement with that obtained from TEM.

6.15 General discussion

It was observed that the mass loss in TGA and percent (C + H + S) from the composition elemental analysis is in close agreement although for AuNPLC (2 nm), the difference may be attributed to the small amount of sample available for the analysis. This is show in the Table 6.13.

6.15		6.18		6.20		6.26		6.11	
Elemental	TGA								
analysis	value								
value (%)	(%)								
30.47	35.08	36.82	45.49	49.67	57.58	34.45	44.18	17.61	18.34

Table 6.13: Elemental analysis and TGA results for the composites.

All nanocomposites show Bragg reflections corresponding to the (001), (002) and (003) reflections at $2\theta = \sim 2.5^{\circ}$, 5.0° and 7.5° respectively, with (003) well pronounced in nanocomposite **6.18** than others possibly due to the smaller size of the ligand when compared to the polymeric nanocomposites (**6.9/6.12**, **6.15**). The size of the corresponding AuNP was estimated from the strong (001) Bragg reflection in the XRD pattern at $2\theta = \sim 2.5^{\circ}$ and indicates that gold particles possess a highly oriented crystalline character. From XRD, TEM and TGA data, the average number of gold atoms (N_{Au}), the number of ligands/polymers per nanoparticles (N_L or N_P) and the average molecular weight of the composites (M_w) were estimated using the equation (1), (2) and (3) respectively²⁰⁻²¹.

Where Vg = 17 Å, r = radius of AuNP (Å)

or

$$N_{Au} = \frac{\pi \rho d^3}{6Au} N \qquad (1b)$$

Where ρ = density of fcc gold (19.3 g/cm³ = 1.93 x 10⁻²¹ g/ nm³), Au = atomic weight of gold = 197 g/mol and d = average diameter of the nanoparticles (nm) and N = number of atoms per mole (6.02 x 10²³).

The number of ligand/polymer per nanoparticle (NL) was calculated using,

$$N_{L} = \frac{(N_{Au})(Au)(wt\%L)}{(M_{wL})(wt\%Au)} \qquad(2)$$

Where wt%L = weight percent of ligand/polymer (obtained from TGA), wt%Au = weight percent of gold (obtained from TGA), M_{wL} = average molecular weight of the ligand (for polymeric composites, it is obtained either from Mass spec or GPC for free polymers). Finally, the average molecular weights of the composite were obtained using equation (3). $M_w = (N_{Au})(Au) + (N_L)(M_{wL})$

Table 6.14 presents the results obtained for different AuNP surface-modified and the composites.

Material/Composite	Wt%Au	Wt%L	d (nm)	M _{wL}	N _{Au}	NL	Mw
	(TGA)	(TGA)	(TEM)				
6.11	81.65	18.34	3.07	226	900	176	217070
6.9/6.12	74.00*	26.00*	3.07	1750#	900	36	240300
6.15	64.88	35.12	3.55**	5130#	1390	29	422558

* Obtained from Elemental analysis, ** obtained from XRD, # value for free polymer obtained from GPC.

Table 6.14: N_{Au}, N_L and M_w for the nanocomposites.

6.16 Conclusion

A nematic liquid crystalline mesogen was synthesised. The conversion of a terminal alkene group into a thiol function was explored extensively and the yield of this reaction was improved significantly. Yields of more than 91% and of almost 100% are now achievable, which is a significant improvement and achievement, especially as this is the last step in an eight step synthetic sequence.

The synthesis of AuNPs was explored and related to earlier work. A series of NPs in the size regime of 2-3 nm, 3-6 nm and 4 nm were synthesised. The effects of the capping agent concentration and temperature on the nanoparticle sizes were also investigated.

The syntheses of the AuNP-liquid crystalline composites were investigated in which different ways of linking the NPs to the mesogen and their properties were determined. Further syntheses were investigated on liquid crystalline polymeric composites, using both 'grafting from' and 'grafting to' methods. 'Grafting from' was systematically performed by coating the surface of AuNPs with ATRP initiator and eventually polymerising a methacrylate mesogenic monomer. Also, the 'grafting to' method was strategically carried out by polymerizing the mesogenic monomer by ATRP using a disulfide initiator to obtain polymer with disulfide bond which was eventually cleaved and through ligand exchange bonded to the AuNPs. The attachments of the polymer to the NPs were confirmed by NMR and their sizes were not affected as confirmed by TEM and XRD. The composites showed birefringence after sheared under OPM and gave a broad absorption for composite **6.18** and composite **6.15** while heating on DSC. This is peculiar to polymers and nanocomposites. From XRD data, it is apparent that the composites did not exhibit columnar structures but a smectic layering. The composite **6.9/6.12** shows a plasmonic response at 540 nm. The data for plasmonic behaviour of other composites will be investigated further. These materials are the first of their kinds, this is gold nanoparticles functionalised as macroinitiators resulting after polymerization in AuNP side chain liquid crystal polymer (AuNP-SCLCP) composites.

Experimental procedures

1. Disulfanediylbis(ethane-2,1-diyl) bis(2-bromo-2-methylpropanoate) (6.3)^{3, 22}





2-bromoisobutyryl bromide (**6.2**) (6.60 ml, 5.34×10^{-2} mol) was added dropwise to a stirred solution of 2, 2'-dithioldiethanol (**6.1**) (3.40 g, 2.21 x 10^{-2} mol) and pyridine (4.30 ml, 5.32 x 10^{-2} mol) in dry chloroform (60 ml) at 0 °C (ice bath) under nitrogen atmosphere.

The solution mixture was stirred at 0 °C for 1 h and then at room temperature for 24 h. Solvent was removed *in vacuo* and the oily mixture dissolved in ether (50 ml), washed with saturated NH₄Cl solution, dried over Na₂SO₄, filtered and the ether removed. Purification by column chromatography (ethyl acetate: hexane, 1:4 or DCM) gave a colourless oil, 9.97 g (100 %). L1

Elemental analysis: Analytical calculated values for C₁₂H₂₀Br₂O₄S₂ (MW = 452.22): C, 31.87; H, 4.46; Br, 35.34; O, 14.15; S, 14.18 %. Found: C, 31.66; H, 4.24 %.

¹**H NMR (400 MHz, CDCl₃):** $\delta = 1.93$ (s, 12H, CH₃), 2.99 (t, 4H, SCH₂), 4.45 (t, 4H, OCH₂).

¹³C NMR (100 MHz, CDCl₃): $\delta = 171, 63.4, 55.4, 36.6, 30.6$.

2. Methacryloyl chloride²³

Pending the arrival of the commercial methacryloyl chloride, it was prepared as follows. Methacrylic acid (21.5 g, 0.25 mol) and benzoyl chloride (105.4 g, 0.75 mol) and hydroquinone (0.5 g). The mixture was distilled at a fairly rate at first with the fraction boiling at 110-130 °C collected, which was the re-distilled. The fraction boiling at 95-97 °C was collected, yield above 65 %.

3. Polymerization of compound 6.6 using compound 6.3 as the initiator $(6.7)^3$



Scheme 6.8

Two different methods used for the synthesis of compound **6.7**.

Method i

Compound **6.3** (50 mg, $1.11 \ge 10^{-4}$ mol), Cu(I)Br (16 mg, $1.11 \ge 10^{-4}$ mol) and compound **6.6** (1.58 g, $1.13 \ge 10^{-2}$ mol) were dissolved in 5.5 ml of dry toluene. The solution was degassed three times by evacuation with nitrogen. Finally, 2, 2'-bipyridine (35 mg, 2.22 $\ge 10^{-4}$ mol) was added and the mixture degassed twice.

The mixture was then place in pre-heated oil bath at 90 °C for 4h. The reaction was quenched by removing it from the oil bath and the polymer dissolved in chloroform (20 ml) and washed with distilled water (10 ml). The water containing the catalyst was

discarded while the chloroform evaporated. This process was repeated for at least five times so as to ensure the complete removal of the Cu catalyst.

The polymer was re-dissolved in THF and divided into two portions; one precipitated in cold hexane and the other in cold methanol.

Samples were analysed by GPC, ¹H NMR and ¹³C NMR.

Method ii (Bulk polymerization)

2, 2'-bipyridine (42 mg, 0.266 mmol) was added to Cu(I)Br (38.2 mg, 0.266 mmol) in a flask. The mixture was degassed by nitrogen purging for 5 min. Compound **6.6** (3.73 g, 26.6 mmol) was added to the mixture and then degassed for 10 min by nitrogen purging. Finally, the initiator, compound **6.3** (0.23 g, 0.532 mmol) was added and the flask placed in an oil bath pre heated to 90 °C. The reaction was allowed for 4 h. The polymer was dissolved in THF and filtered through alumina (0.063-0.200 nm or 70-230 mesh ASTM) to remove the catalyst. A sample was taken for GPC while the rest was concentrated to with minimum amount of solvent and precipitated in cold methanol. It was kept in fridge overnight. The methanol was decanted and the polymer dried *in vacuo*. Samples were analysed by GPC, ¹H NMR and ¹³C NMR.

¹**H NMR (400 MHz, CDCl₃):** δ = 1.35 (s, 12 H, CH₃), 2.09 (s, 6 H, CH₃), 2.37 (q, 4 H, CHCH₂), 3.04 (t, 4 H, SCH₂), 4.15 (t, 4 H, CH₂OCO), 4.38 (t, 4 H, SCH₂CH₂), 5.09 (m, 4 H, CH₂CH), 5.08 (m, 2 H, CH₂CH).

Note: The signals at $\delta = 5.66$ and 6.01 are from monomer CH=CH2 which precipitated along with the polymer.

4. Polymer 6.17 from disiloxane-containing mesogen (5.5) and polymer (6.7)





Pt catalyst (10 μ l) was added to compound **6.7** (0.075 g, 0.0588 mol) (n=29, M_n=8490 from GPC) in dry toluene (8 ml) and activated by air (oxygen). Compound **5.5** (0.2 g, 1.71 mmol) in dry toluene (2 ml) was added and the mixture stirred for 24 h at 30 °C.

The polymer was precipitated in cold methanol and kept in the fridge overnight after which then methanol was decanted and the polymer dried in vacuo.

Yield was 0.16 g.

From 1H NMR integration, about 50 % of the double bonds in polymer **17** were left unreacted which also implies that the yield is about 50 %.

¹H NMR (400 MHz, CDCl₃): δ = 0.14 (s, 12 H, SiCH₃), 0.54 (q, 4 H, SiCH₂), 0.88 (t, 6 H, CH₃), 1.30 (m, 28 H, CH₂), 1.43 (m, 4 H, CH₂), 1.56 (s, 6 H, CH₃), 1.82 (m, 8 H, CH₂), 2.17 (s, 3 H, C(Br)CH₃), 2.39 (t, 2 H, SCH₂), 4.04 (m, 10 H, OCH₂), 6.50 (d, 1 H, CH_{arom}), 6.95 (d, 1 H, CH_{arom}), 7.16 (d, 1 H, CH_{arom}), 7.23 (d, 2 H, CH_{arom}), 7.48 (d, 2 H, CH_{arom}), 7.54 (d, 2 H, CH_{arom}), 8.03 (d, 1 H, CH_{arom}).





Scheme 6.10

Nitrogen purged distilled water was added dropwise to a mixture of compound **6.8** (0.116 g, 0.05 mmol, M_n =2215 form GPC) and tris(2-carboxyethyl)phosphine (TCEP) (0.028 g, 0.01 mmol) until all the TCEP completely dissolved. This was followed by the addition of THF until clear solution is obtained. The clear solution was stirred at room temperature for 24 h. Chloroform (20 ml) was added followed by distilled water (10 ml) and the organic layer separated, dried over MgSO₄, filtered and the solvents removed *in vacuo*.

The cleaved polymer, compound **24** was re-dissolved in minimum amount of THF, precipitated in cold methanol and kept in a fridge overnight. Methanol was removed and samples were taken for GPC and NMR analysis.

Note: The above procedure was repeated with the cleavage reaction running for 5 days. The same results were obtained. ¹H NMR (400 MHz, CDCl₃): δ = 0.14 (s, 12 H, SiC*H*₃), 0.54 (q, 4 H, SiC*H*₂), 0.88 (t, 6 H, C*H*₃), 1.30 (m, 28 H, C*H*₂), 1.43 (m, 4 H, C*H*₂), 1.56 (s, 6 H, C*H*₃), 1.82 (m, 8 H, C*H*₂), 2.17 (s, 3 H, C(Br)C*H*₃), 2.39 (t, 2 H, SC*H*₂), 4.04 (m, 10 H, OC*H*₂), 6.50 (d, 1 H, C*H*_{arom}), 6.95 (d, 1 H, C*H*_{arom}), 7.16 (d, 1 H, C*H*_{arom}), 7.23 (d, 2 H, C*H*_{arom}), 7.48 (d, 2 H, C*H*_{arom}), 7.54 (d, 2 H, C*H*_{arom}), 8.03 (d, 1 H, C*H*_{arom}).

6. Coupling of compound 24 with gold nanoparticles (6.9)



Scheme 6.11

Compound **24** (52 mg) was added to gold nanoparticles (AuNPs (3 nm), 13 mg) dissolved in dry DCM (10 ml) and the mixture stirred at room temperature for 5 days. The solvent was reduced to 1 ml under pressure at temperature below 30 °C and ethanol (12 ml) added with brief sonication. This was then centrifuged at 5000 rpm for 10 min with supernatant solution removed. Ethanol was added, briefly sonicated and centrifuged again. This process was repeated twice to leave a black compound which was dried *in vacuo*. 7. Cleavage of disulfanediylbis(ethane-2,1-diyl) bis(2-bromo-2-methylpropanoate) (6.3)
to give 2-mercaptoethyl 2-bromo-2-methylpropanoate (6.10)



Scheme 6.12

Nitrogen purged distilled water was added dropwise to a mixture of compound **6.3** (0.5181 g, 1.11 mmol) and tris(2-carboxyethyl)phosphine (TCEP) (0.3184 g, 2.0 mmol) until all the TCEP completely dissolved. This was followed by the addition of THF until clear solution is obtained. The clear solution was stirred at room temperature for 7 h. Chloroform (50 ml) was added followed by distilled water (20 ml) and the organic layer separated. The aqueous layer was extracted with chloroform (2 x 20 ml), the combined organic layer was dried over MgSO₄, filtered and the solvents removed *in vacuo* to obtain a golden yellow oily compound with thiol-characteristic smell.

Yield was 0.48 g (95%).

Rf (Ether) =0.63

¹**H NMR (400 MHz, CDCl₃):** δ = 1.59 (s, 1 H, SH), 2.08 (s, 6 H, CH₃), 2.80 (t, 2 H, SCH₂), 4.2 (t, 2 H, OCH₂).

¹³C NMR (100 MHz, CDCl₃): $\delta = 121, 68, 55, 30, 22$.

8. Coupling of 2-mercaptoethyl 2-bromo-2-methylpropanoate (6.10) with gold nanoparticles (6.11)



Scheme 6.13

Compound **6.10** (93.2 mg) in 1 ml DCM was added to gold nanoparticles (AuNPs (2 nm), 23.3 mg) dissolved in dry DCM (10 ml) and the mixture stirred at room temperature for 5 days.

The solvent was reduced to 1 ml under pressure at temperature below 30 °C and ethanol (12 ml) added with brief sonication. This was then centrifuged at 5000 rpm for 10 min with supernatant solution removed. Ethanol was added, briefly sonicated and centrifuged again. This process was repeated twice to leave a black compound which was dried *in vacuo*. The same procedure was used for AuNPs (3 nm) (20.4 mg) and compound **6.10** (82.3 mg). Both compounds were characterised by ¹H NMR.

9. Direct synthesis of 6.11 from 6.3 (One pot cleavage and capping)



Scheme 6.14

The method used for the synthesis of AuNP-capped with dodecane thiol was modified to synthesise **6.11** directly from **6.10**.

To a solution of Gold(III)chloride (0.2065 g in 0.5 ml H₂O), was added THF (5 ml) and AM-13 (0.060 g, 13.3 mmol) and sonicated for 5 min. Solution of NaBH₄ (0.1101 g in 0.6 ml H₂O) was added while sonication continued for 10 min. The black solution of **6.11** was poured in cold ethanol (80 ml) and centrifuged (5000 rpm, 5 min) to remove free compound **6.3**. The black residue was re-dispersed in ethanol and centrifuged again (four times) to ensure complete removal of unreacted/free compound **6.3** and compound **6.10**. The residue was dried in vacuo and sample taken for analysis.

10. Polymerization of compound 5.6 using compound 6.11 as the initiator (6.12)



Compound **6.11** (2 nm) (5.8 mg), compound **5.6** (0.3046 g, 0.033 x 10^{-2} mol), CuBr (1.05 mg, 0.73 x 10^{-5} mol) were dissolved in dry toluene and degassed by purging with nitrogen gas for 30 min. Bipyridine (8.8 mg, 0.56 x 10^{-4} mol) was dissolved in 2 ml of dry toluene, added to the mixture and degassed for additional 10 min. It was then placed in oil bath pre heated to 90 °C and stirred for 24 h. The reaction was quenched; chloroform (30 ml) was added followed by distilled water (20 ml) and the organic layer was separated. This process was repeated twice to ensure the removal of the entire catalyst from the polymer.

The solvent was removed in vacuo and the polymer precipitated in cold methanol. This was then kept in fridge overnight. The methanol was removed to leave a black residue. Samples were analysed by GPC and NMR.

The above procedure was repeated for compound **6.11** of 3 nm (5.5 mg) and compound **5.6** (0.3878 g, 0.042×10^{-2} mmol), with the same amount of catalyst, Bpy and solvent. Similar results were obtained.

11. Synthesis of composite 6.15 from compound 5.9 and 6.11



Scheme 6.16

Compound **6.11** (48.6 mg), **5.9** (88.6 mg, 0.12 mmol), CuBr (4.8 mg, 3.33×10^{-5} mol) were dissolved in dry toluene (2 ml) and degassed by purging with nitrogen gas for 30 min. Bipyridine (7.5 mg, 4.76 $\times 10^{-5}$ mol) was dissolved in 2 ml of dry toluene, added to the mixture and degassed for additional 10 min. It was stirred at 30 °C for 24 h. The reaction was quenched; chloroform (30 ml) was added followed by distilled water (20 ml) and the organic layer was separated. This process was repeated four times to ensure the removal of the entire catalyst from the polymer, solvent reduced and centrifuged.

The residue was dissolved in minimum THF and precipitated in cold methanol. The methanol was decanted and the residue re-dissolved in THF and centrifuged to remove free polymer. The residue was dried *in vacuo*.

Samples were analysed by GPC and NMR.

12. Polymerization of 5.12 using 6.10 (6.16)



Scheme 6.17

Compound **6.10** (25 mg, 1.11 x 10^{-4} mol), Cu(I)Br (16 mg, 1.11 x 10^{-4} mol) and compound **5.12** (1.80 g, 1.13 x 10^{-2} mol) were dissolved in 5 ml of methanol. The solution was degassed three times by evacuation with nitrogen. Finally, 2, 2'-bipyridine (35 mg, 2.22 x 10^{-4} mol) was added and immediately the mixture turned brown. The mixture degassed twice by nitrogen purging and then place in pre-heated oil bath at 50 °C for 24 h. As the polymerization proceeded the colour of the mixture gradually turned green. The reaction was quenched by removing it from the oil bath and the catalyst was removed by filtering through neutral alumina column using methanol as the eluent. The solvent was reduced to very minimum amount and the polymer precipitated in cold diethyl ether. Ether was removed and the polymer re-dissolved in minimum amount of methanol and precipitated in cold diethyl ether. The process was repeated three times to obtain off-pink to white polymer with Mn GPC = 8460 g/ mol, Mw GPC = 12736 g/mol, Mw/Mn = 1.50, n~54.

¹**H NMR (400 MHz, CDCl₂):** d = 0.9 (m, 3n H, CH₃), 1.0 (s, 1H, HS), 1.1 (s, 3n H, CCH₃), 1.65 (s, 2n H, CH₂C), 1.66 (s, 2n H, CH₂), 1.68 (m, 2n H, CH₂), 1.92 (m, 2n H, CH₂), 2.10 (s, 3n H, CH₂CBr), 2.40 (m, 2 H, CH₂SH), 2.80 (m, 2 H, CH₂OCO), 3.44 (t, 2n H, CH₂OCO), 3.46 (m, 2n H, CH₂OH), 4.00 (s, n H, OH)



13. Gold nanoparticle-6.16 composite (6.17)

Scheme 6.18

Polymer **6.16** (151.5 mg, 0.018 mmol, Mn _{GPC} = 8640 g/mol) was dissolved in THF (6 ml). To this was added **AuNP** (3 nm, 64.5 mg) and the mixture stirred for 5 days. After 24 h of reaction, a portion was taken, centrifuged with supernatant removed. THF was added to the precipitate and centrifugation repeated. These processes were repeated twice and black residue dried in vacuo. There was no evidence of attachment of the polymer to the NPs from ¹H NMR.

The rest of the mixture was stirred for 5 days, the solvent was removed *in vacuo* and the residue re-dispersed in methanol (2 ml). This was centrifuged (5000 rpm, 7 min), the supernatant was removed and the process repeated twice to ensure complete removal of unreacted/free **6.16**. The black residue **6.17** was dried in vacuo. From ¹H NMR, the polymer has completely attached to the gold nanoparticles.

14. Functionalization of 6.17 by compound 5.13 (6.18)



Scheme 6.19

(i) Method 1

To **6.17** (9.3 mg) in DMF (2 ml) was added imidazole (1 mg, 0.01 mmol) and **5.13** (0.1 g, 0.13 mmol) and the reaction mixture stirred for 24 h. The mixture was centrifuged (5000 rpm, 5 min), the supernatant removed and the black residue re-dispersed in THF or toluene. The process was repeated three times and the black residue dried in vacuo.

From ¹H NMR, there was no signals due to mesogenic silane (compound **5.13**).

The above procedure was repeated using dry THF instead of DMF but similar result was obtained.

When the above procedure was repeated for a longer time 3 days using DMF, there was little evidence of attachment though not prominent. Base on this, the reaction was repeated with **6.17** (58 mg) in DMF (5 ml), added imidazole (580 mg, 5.8 mmol) and **5.13** (0.4335 g, 0.56 mmol) and the reaction mixture stirred for 3 days.

Although, there was no strong signals due to the mesogenic silane in ¹H NMR spectra, from the UV-vis spectra there is a red shift which is evidence of change in the environment of AuNPs.

Composite **6.17** (52.9 mg) was dispersed in THF (5 ml), triethyl amine (1.75 ml, 1.27 g, 12.6 mmol) was added to the mixture and stirred vigorously. To this was added compound **5.13** (2.5 g, 3.3 mmol) and the stirring continued for 24 h. The solvent and excess triethyl amine was removed *in vacuo* and the composite re-dispersed in toluene to remove unreacted compound **5.13**. The process was repeated twice and the composite dried *in vacuo*.

To confirm the reaction between silane and the hydroxyl group, two methods were investigated on the monomer **5.12**.

(a) Monomer **5.12** (1.0 g, 6.3 mmol), imidazole (1.08 g, 15.75 mmol) and chlorotrimethylsilane (0.82 g, 1.2 molar equiv of **5.12**) were stirred in DMF (3 ml) for 24 h. The reaction was monitored by TLC which confirmed the presence of product and starting material.

(b) To monomer **5.12** (1.0 g, 6.3 mmol), triethyl amine (1.27 g, 1.75 ml, 2 molar equiv of **5.12**) in THF (5 ml) was added chlorotrimethylsilane (0.82 g, 1.2 molar equiv of **5.12**) and stirred for 24 h. The reaction was monitored by TLC which confirmed the complete conversion of starting materials to the product.

Polymer 50 ($Mn_{GPC} = 5397 \text{ g/ mol}$).

15. Functionalization of compound 6.17 by compound 4.11 (composite 6.18)





To a mixture of composite **6.17** (6.1 mg), compound **4.11** (101.5 mg, 0.12 mmol) in chloroform (2 ml) was added 1 M NaOH (40 μ l) and ethanol (0.5 ml). The mixture was stirred at room temperature for 24 h. The mixture was centrifuge (5000 rpm, 7 min) and the supernatant removed, while the residue was re-dispersed in toluene with repeated centrifugation (x 2). The residue was dried *in vacuo* and analysed.

There was no signal due ethoxysilane mesogen in the ¹H NMR.

16. Composite 6.20 (Polymerization of 5.14 using 6.11 as initiator)



Scheme 6.21

New macroinitiator **6.11** was synthesised by dispersing AuNP (0.13 g) in solution of **6.10** (0.75g) in DCM (5 ml) and the mixture stirred at rt for 3 days. The DCM was removed at low temperature and the residue re-dispersed in ethanol and purified by centrifugation (5000 rpm, 5 min, x 4). The macroinitiator **6.11** was the dried in vacuo and used in the polymerization of **5.14**.

Bipyridine (35 mg, 0.22 mmol) in dry toluene (0.5 ml) was added to the mixture of **6.11** (53.3 mg), **5.14** (0.28 g, 0.32 mmol) and Cu(I)Br (16 mg, 0.11 mmol)in dry toluene (5 ml). The mixture was purged with nitrogen for 30 min and placed in pre-heated oil (35 $^{\circ}$ C) with stirring for 30 h.

Solvent was removed in vacuo at low temperature (using high vacuum capacity pump with liquid nitrogen). The composite was dispersed in ethanol and centrifuged (5000 rpm, 5 min, x 5). The supernatant containing the catalyst was gently removed until a clear solution was obtained. The residue was dried in vacuo and analysed. The supernatant was kept safe and
it was noticed that the free polymer precipitated from the solvent. This was used to determine the degree of polymerization and average molecular mass of the polymer. Elemental analysis: C 39.27%, H 6.22%, S 4.18%.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.0$ (s, 6 H, SiCH₃), 0.37 (t, 2 H, SiCH₂), 0.81 (t, 8 H, CH₂), 1.23 (m, 27 H, CH₂), 1.39 (m, 6 H, CH₂), 1.73 (m, 7 H, CH₂), 1.96 (s, 3 H, CH₃), 3.61 (t, 2 H, SiOCH₂), 3.90 (m, 6 H, CH₂OCH₂), 4.01 (t, 2 H, CH₂CO), 6.42 (m, 2H, CH arom), 6.89 (m, 2 H, CH arom), 7.15 (m, 2 H, CH arom), 7.46 (m, 4 H, CH arom), 8.08 (d, 1 H, CH arom).

17. 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-((methylsulfonyl)oxy)pentyl)oxy)-4-





Scheme 6.22

Mesylation of compound **5.8** was carried out in DCM under nitrogen gas. To a cold (0 °C) solution of compound **5.8** (0.51g, 0.76 mmol) in dry DCM (5 ml) was added triethyl amine (0.25 ml, 1.8 mmol) followed by methylsulfonyl chloride (0.07 ml, 0.90 mmol) dropwise. The solution was stirred for 1h at rt and saturated NH₄Cl solution (1.2 ml) was added. Organic layer was washed with saturated NaCl solution (1.2 ml x 2). The aqueous layers were pooled, back-extracted with DCM (10 ml) and the combined organic layers dried over Page | 263

MgSO4 (leave to stand for at least 15 min) the solvent was removed and the product stored at ca. 4 °C.

 $R_{\rm f}$ (DCM) = 0.78

Elemental analysis: Analytical calculated values for C₄₄H₆₄O₈S (MW = 753.05): C, 70.18; H, 8.57; O, 17.00; S, 4.26 %. Found: C, 70.00; H, 8.53; S, 4.40 %.

¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 6 H, CH₂CH₃), 1.28 (m, 22 H, CH₂CH₂), 1.5 (m, 8 H, CH₂CH₂), 1.60 (m, 4 H, OCH₂CH₂), 1.90 (m, 2 H, OCH₂CH₂), 3.0 (s, 3 H, OSOCH₃),
4.00 (t, 8 H, OCH₂), 6.52 (m, 2 H, CH arom), 6.96 (m, 2 H, CH arom), 7.23 (m, 2 H, CH arom), 7.54 (m, 4 H, CH arom), 8.05 (d, 1 H, CH arom).

¹³C NMR (100 MHz, CDCl₃): δ = 14, 23, 26, 28, 29, 30, 32, 40, 47, 69, 70, 101, 105, 106, 115, 122, 129, 132, 133, 137, 149, 158, 161, 165, 170.

18. 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-azidopentyl)oxy)-4-(octyloxy)benzoate,





To a solution of **6.21** (0.55 g, 0.7 mmol) in DMF (5 ml) under nitrogen was added NaN₃ (0.8 g, 2 x mol of Ms) and TEA (0.04 ml, 10% mol of Ms) and the reaction stirred at 68 °C for 24 h. It was cooled to rt and water (5 ml) was slowly added while stirring vigorously. The precipitate was filtered and washed with 1:1 DMF/water (10 ml), 3:7 DMF/water (10 ml) and finally water (10 ml). The resulted yellow crystal was dried.

 $R_{\rm f}$ (DCM) = 0.76

(6.22)

Elemental analysis: Analytical calculated values for $C_{43}H_{61}N_3O_5$ (MW = 699.98): C, 73.78; H, 8.78; N, 6.00; O, 11.43 %. Found: C, 73.47; H, 8.05; N, 5.92 %.

¹H NMR (400 MHz, CDCl₃): δ = 0.9 (t, 6 H, CH₂CH₃), 1.26 (m, 26 H, CH₂CH₂), 1.43 (m, 4 H, CH₂CH₂), 1.50 (m, 2 H, CH₂CH₂), 1.70 (m, 4 H, CH₂CH₂), 1.79 (m, 2 H, OCH₂CH₂), 4.00 (t, 6 H, OCH₂), 6.52 (m, 2 H, CH arom), 6.96 (m, 2 H, CH arom), 7.23 (m, 2 H, CH arom), 7.54 (m, 4 H, CH arom), 8.05 (d, 1 H, CH arom).

¹³C NMR (100 MHz, CDCl₃): δ = 14, 23, 26, 28, 29, 30, 32, 47, 69, 70, 101, 105, 106, 115, 122, 129, 132, 133, 137, 149, 158, 161, 165, 170.

19. But-3-yn-1-yl methacrylate (6.23)





To a solution of **6.23** (10 g, 0.14 mol), triethyl amine (36 ml, 0.26 mol) in DCM (1000 ml) at 0 $^{\circ}$ C under nitrogen was added methacryloyl chloride (25 ml, 0.26 mol) dropwise and the reaction stirred at rt for 16 h.

This was partitioned between diethyl ether (400 ml) and 10% HCl (400 ml). The aqueous layer was extracted with ether and the combined organic layers dried over MgSO4. The solvent was removed and the crude product purified by column chromatography (DCM) to yield golden colour oil (18.67 g, 94 %).

 $R_{\rm f}$ (DCM) = 0.58

Elemental analysis: Analytical calculated values for C₈H₁₀O₂ (MW = 138.17): C, 69.55; H, 7.30; O, 23.16 %. Found: C, 69.52; H, 7.22 %.

¹H NMR (400 MHz, CDCl₃): δ = 1.5 (s, 1 H, CCH), 2.0 (s, 3 H, CH₃), 2.5 (t, 2 H, CCH₂),
4.3 (t, 2 H, OCH₂), 5.1 (s, 1 H, CH₂), 6.3 (s, 1 H, CH₂).

¹³C NMR (100 MHz, CDCl₃): $\delta = 18, 19, 63, 70, 80, 127, 136, 167.$

20. 4'-(undecyloxy)-[1,1'-biphenyl]-4-yl 2-((5-(4-(2-(methacryloyloxy)ethyl)-1H-1,2,3-





Scheme 6.25

Compound **6.4** (0.48 g, 3.5 mmol), **6.22** (2.24 g, 3.2 mmol) and Cu(I)I (67 mg, 0.35 mmol) were dissolved in DMF/THF mixture (1:1, 4 ml) under nitrogen. TEA (35 mg, 0.35 mmol) was added and the mixture stirred at 35 °C for 24 h. Brine (2 ml) was added and extracted with ethyl acetate (5 ml x 4). The organic layer was dried over Na₂SO₄, filtered and concentrated in vacuo to afford a yellow product.

 $R_{\rm f}$ (Ether) = 0.71

Elemental analysis: Analytical calculated values for $C_{51}H_{71}N_3O_7$ (MW = 838.14): C, 73.09; H, 8.54; N, 5.01; O, 13.36 %. Found: C, 72.23; H, 8.66; N, 4.98 %.

¹H NMR (400 MHz, CDCl₃): δ = 0.9 (t, 6 H, CH₂CH₃), 1.26 (m, 26 H, CH₂CH₂), 1.43 (m, 4 H, CH₂CH₂), 1.50 (m, 2 H, CH₂CH₂), 1.70 (m, 4 H, CH₂CH₂), 1.79 (m, 2 H, OCH₂CH₂),
4.00 (t, 6 H, OCH₂), 6.52 (m, 2 H, CH arom), 6.96 (m, 2 H, CH arom), 7.23 (m, 2 H, CH arom), 7.54 (m, 4 H, CH arom), 8.05 (d, 1 H, CH arom).

¹³C NMR (100 MHz, CDCl₃): δ = 14, 23, 26, 28, 29, 30, 32, 47, 69, 70, 101, 105, 106, 115, 122, 129, 132, 133, 137, 149, 158, 161, 165, 170.

21. Synthesis of composite 6.26

Scheme 6.26

Compound **6.25** (2.5 g) was dissolved in dry toluene (2 ml) and macroinitiator **6.11** (63 mg) was added to the solution. Cu(I)Br (16 mg, 1.1×10^{-4} mol), was added to the mixture and purged with nitrogen for 20 min followed by the addition of bipyridine (35 mg, 2.22 x 10^{-4} mol) and further purged for 10 min. The mixture was placed in pre-heated oil (35 °C) and stirred for 30 h. The solvent was removed (using high efficiency pump at low temperature) and the composite dispersed in ethanol and centrifuged (5000 rpm, 5 min) the supernatant was removed and the residue re-dispersed in ethanol and the process repeated four times (until the supernatant was colourless). It was observed that the first supernatant was green in colour which indicates the removal of the catalyst from the system and this

also contained the free polymer which was used for the determination of Mn and polymer dispersity index.

Elemental analysis: C 26.43%, H 3.36%, N 1.40%, S 3.26%.

¹H NMR (400 MHz, CDCl₃): δ = 0.9 (t, 6 H, CH₂CH₃), 1.26 (m, 26 H, CH₂CH₂), 1.43 (m, 4 H, CH₂CH₂), 1.50 (m, 2 H, CH₂CH₂), 1.70 (m, 4 H, CH₂CH₂), 1.79 (m, 2 H, OCH₂CH₂), 4.00 (t, 6 H, OCH₂), 6.52 (m, 2 H, CH _{arom}), 6.96 (m, 2 H, CH _{arom}), 7.23 (m, 2 H, CH _{arom}), 7.54 (m, 4 H, CH _{arom}), 8.05 (d, 1 H, CH _{arom}).

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CHAPTER SEVEN

COMPOSITES OF GOLD NANORODS AND SIDE-CHAIN LIQUID

CRYSTALLINE POLYMERS



Introduction

7.1

Nanorods are synthesised from metals and semiconductors with aspect ratio (ratio of length to width) between 3 and 5. AuNRs are of great interest due to their strong optical absorption in the visible and near infrared region. AuNRs are excellent candidates of sensing, photonic, optical and other applications due to their ability to have different absorbance bands with different local materials of different refractive indexes. Gold nanorods (AuNRs) have many potential sensing applications due to their tunable localized surface plasmon resonance (LSPR) frequency that changes with aspect ratio¹. Also, the aspect ratio of AuNRs can be tuned by varying the synthetic conditions, which will, in turn, control the length and/or width of the NRs. AuNRs characterized with near IR absorption are capable

of being excited by laser to generate heat which is useful in photothermal therapeutic applications.

Based on the above benefits, researches on AuNRs, in science and technology, are indispensably necessary. Polymeric materials are of good properties that can found application in mechanics, biology, optics, photonics, electrical/electronic and display (Fig. $7.1)^{2,3}$. This is based on the nanostructures and composites materials formed by them and inorganic nanomaterials⁴.



Figure 7.1: Applications of polymeric materials

7.1 Gold nanorod synthesis and ligand exchange

Using either one step⁵ or seed-mediated synthetic methods^{6,7}, AuNRs of different aspect ratios can be easily synthesised. Modification of the AuNRs' surfaces posed researchers a lot of challenges as their surfaces are fragile and thereby aggregating quite easily. Even changing of surrounding medium (e.g solvent) may lead to irreversible aggregation of AuNRs. Other noticeable factors are temperature, vigorous stirring, etc. Since AuNRs were Page | 273 synthesised in water by using water-soluble ligand (CTAB), it is necessary to modify the surface so as to make the AuNRs soluble in organic solvents for easy processability and applications. Several methods were exploited in order to exchange the CTAB ligands with thiol ones (Fig. 7.2). These involved 1-dodecanethiol, compound **6.10**, 11-mercapto-1-undecanol and its ester moiety, in different solvents such as THF, DMF, chloroform, acetone, hexane and toluene.



Figure 7.2: Thiol ligand exchange of CTAB on AuNRs

Many of which led to the irreversible aggregation of the AuNRs as evidenced from the broadening of the absorption peaks on UV-vis spectra.

The first successful exchange was achieved by adding excess 1-dodecanethiol (DDT) to concentrated CTAB-capped AuNRs and extracted into the DDT layer by acetone until the aqueous layer became clear indicating no NRs presence again. The organic layer was separated and toluene added followed by methanol to removed excess DDT. After removal of methanol layer, toluene was gently removed with high vacuum pump at low temperature (≤ 50 °C).

Fig. 7.3 shows the picture of AuNRs (a) CTAB-capped (as prepared) in water floating on chloroform layer and (b) after CTAB on AuNRs are exchanged with DDT, DDT-capped AuNRs now soluble in chloroform and not in water.



Figure 7.3: (a) CTAB-capped AuNRs on chloroform (b) after exchanged with DDT in chloroform under water.

Another procedure that gave positive result was the one in which acetone and toluene were added alternatingly and the organic layer removed while the aqueous layer continuously extracted into toluene by acetone. Although, in this method, the AuNRs were successfully transferred to the organic layer, it required extremely large amount of solvents.

7.2 Synthesis of composite 73

The DDT-modified AuNRs were subject to ligand exchange by thiol **6.10** to have macroinitiator used for the ATRP of mesogenic methyl methacrylate silane monomer, **5.14**.





The SEM images of the composite **7.2** confirmed the presence of NRs in the polymer. (Fig. 7.4).



Figure 7.4: SEM images of 7.2: (a) Back Scattered detector image (b) Secondary electron imaging.

The glittering spots represent AuNRs (a) while the SEI image shows the topology of the composite which is that of polymeric composite.

The EDS of the corresponding scanned area shown in fig. 7.5 and it confirms the presence of Au, C, Br, Si and N.



Figure 7.5: EDS of **7.2**.

Figure 7.6 shows the TEM of the composite **7.2**.



Figure 7.6: TEM images of composite 73

The shape of the NRs remains intact even after the polymerization. The size distributions of the AuNRs are shown in table 7.1 with average length of 26.38 nm, average width of 7.46 nm and average aspect ratio of 3.66 (table 7.2). These values and their relationships are depicted in fig. 7.7.

Entry	1	2	3	4	5	6	7	8	9	10
L (nm)	23.69	22.71	27.20	25.20	24.70	22.04	30.36	30.30	28.39	29.25
B (nm)	5.56	6.41	8.37	8.11	6.95	9.76	7.93	9.36	6.88	5.30
A/R (L/B)	4.3	3.5	3.2	3.1	3.6	2.3	3.8	3.2	4.1	5.5

Entry	11	12	13	14	15	16	17	18	19	20
L (nm)	31.10	22.94	28.41	23.15	26.60	29.99	30.98	26.84	29.85	22.57
B (nm)	8.49	7.26	8.11	8.37	5.73	9.07	7.52	8.14	6.41	7.93
A/R (L/B)	3.7	3.2	3.5	2.8	4.6	3.3	4.1	3.3	4.7	2.8

Table 7.1: Size distribution of **7.2**.



Figure 7.7: Chart showing the lengths, widths and A/R of 7.2.

	Min	Max	Ave
L (nm)	22.04	30.36	26.38
B (nm)	5.30	9.76	7.46
A/R (L/B)	2.3	5.5	3.66

Table 7.2: Average dimension and A/R of 7.2.

Elemental composition	%
С	10.66
Н	1.07
S	0.42
N	2.45

The elemental composition (C, H, S, N) of composite 7.2 is given in table 7.3.

Table 7.3: Elemental composition 7.2.

The plasmonic properties of the composite shows that the longitudinal surface plasmon resonance blue shifted (form 790 to 765 nm) and while transverse surface plasmon resonance red shifted (from 540 to 575 nm) (fig. 7.8)



Figure 7.8: UV-vis of **7.2**.

The changes in the plasmonic band is due to the change in the surface properties of the AuNRs and this is in turn caused by the surface modification by the polymer chains. The thermal behaviour of composite **7.2** as observed on POM is shown in fig. 7.9.



Figure 7.9: POM textures of composite 7.2 (x 400).

There was no observable phase transition on POM and the texture obtained is peculiar to composite of this nature due to high content of Au.

Fig. 7. 10 shows the heating and cooling curves for the composite **7.2**. Transition was observed at 56 $^{\circ}$ C with transitional enthalpy of 0.29 J/g.



Figure 7.10: DSC curves of **7.2**.

Thermogravimetry analysis of the composite was investigated by subjecting it to temperature up to 950 °C. TGA thermograph (fig. 7.11) reveal a single step mass loss of 37 % which commence at about 200 °C and ended at about 400 °C.



Figure 7.11: TGA thermogram of 7.2.

This mass loss is attributed to the polymer content of the composite which means the Au content is 63 % (the residue).

7.3 Total replacement of CTAB by 6.10 on AuNRs $(7.3)^8$

In order to completely substitute the CTAB on AuNRs by the initiator, **6.10**, CTAB capped AuNRs was concentrated to 1-2 ml (by centrifugation) and dispersed dropwise into solution of initiator, **6.10**, in DMF or THF with brief stirring before allowing to stand for 12 h and purified by centrifugation (7000 rpm, 7 min).

The macroinitiator obtained (7.3) was soluble in toluene and other organic solvents but no longer in water (fig. 7.12). This was a great success as polymerization using 7.3 as macroinitiator was possible and made easy in toluene.



Figure 7.12: CTAB capped AuNRs in water (left vial), **7.3** in toluene on water (right vial). The shape of the NRs were not affected by the polymerization processing as shown in the TEM image (fig. 7.13).



Figure 7.13: TEM images of **7.3**.

Also, the sizes of the NRs as well as the aspect ratio were not affected by the processing as there was no noticeable changes. Table 7.4 shows the size distributions of the NPs and the aspect ratios while table 7.5 shows their corresponding averages.

Entry	1	2	3	4	5	6	7	8	9	10
L (nm)	30.63	24.93	26.84	23.12	22.64	19.53	25.28	31.57	27.33	23.37
, , ,										
B (nm)	9.36	7.93	8.85	7.39	7.09	6.30	6.60	7.26	7.68	7.93
A/R (L/B)	3.3	3.1	3.1	3.1	3.2	3.1	3.8	4.3	3.6	2.9

Entry	11	12	13	14	15	16	17	18	19	20
L (nm)	20.02	19.10	27.70	23.74	26.62	28.62	21.66	22.99	28.55	21.29
B (nm)	5.06	6.41	6.85	10.59	7.87	8.14	7.78	7.09	5.98	8.37
A/R (L/B)	3.9	3.0	4.0	2.2	3.4	3.5	2.8	3.2	4.8	2.6

Table 7.4: Size distribution of **7.3**.



Figure 7.14: Chart showing the lengths, widths and A/R of 7.3.

	Min	Max	Ave
L (nm)	19.53	31.57	25.52
B (nm)	6.30	9.36	7.64
A/R (L/B)	2.9	4.3	3.35

Table 7.5: Average dimension and A/R of **7.3**.

The average length of the NRs is 25.52 nm, width 7.64 nm and the average aspect ratio is 3.6.

The elemental composition for **7.3** is shown in table 7.6.

Compositional	%
elements	
С	12.22
Н	1.35
S	4.04

Table 7.6: Elemental composition of **7.3**.

The absorption of **7.3** on UV-vis is shown in fig. 7.15 where the longitudinal surface plasmon resonance gave absorption at 725 nm while transverse surface plasmon resonance was at 525 nm.



Figure 7.15: UV-vis of **7.3**.

7.4 Polymerization at 60 °C (composite 7.4)

The initiator capped AuNRs, **A7.3**, was used as macroinitiator in the polymerization of monomer **5.14** at 60 °C for 24 h.



Scheme 7.2

The ¹H NMR spectrum of the composite **7.4** is as shown in fig 7.16.



Figure 7.16: ¹H NMR of **7.4**.

The NMR confirmed the success of the reaction as the methyl methacrylate signals in the monomer has disappeared in the composite.

The SEM images of the composite **7.4** is as shown if fig. 7.17 (a) and (b).



Figure 7.17:SEM images of **7.4**: (a) Back Scattered detector image (b) Secondary electron imaging. The presence of Au in the composite is seen in BSD image (a) as a glittering spots while SEI image (b) shows the topography of the composite and it confirmed presence of polymer in the composite.

The EDS of the corresponding area scanned is shown in fig 7.18. The element present in composite are Au, Si, Br, C and S.



Figure 7.18: EDS of **7.4**.

The TEM images of composite **7.4** is shown in fig. 7.19 while table 7.7 shows the size distribution of the NRs.



Figure 7.19: TEM images of composite 7.4.

There were little changes in the sizes of the NRs and this is depicted in the chart (fig. 7.20).

Entry	1	2	3	4	5	6	7	8	9	10
L (nm)	25.58	19.52	24.05	34.25	25.28	26.63	19.93	26.44	25.07	26.33
B (nm)	6.56	9.84	9.07	9.76	9.07	8.91	8.37	5.61	9.33	5.94
A/R (L/B)	3.9	1.9	2.7	3.5	2.8	3.0	2.4	4.7	2.7	4.4

Entry	11	12	13	14	15	16	17	18	19	20
L (nm)	20.54	22.45	22.96	22.35	28.18	24.76	18.89	22.88	26.44	24.43
B (nm)	8.11	8.60	8.11	8.46	12.52	9.46	9.88	8.37	7.69	6.49
A/R (L/B)	2.5	2.6	2.8	2.6	2.3	2.6	1.9	2.7	3.4	3.8

Table 7.7: Size distribution of **7.4**.



Figure 7.20: Chart showing the lengths, widths and A/R of 7.4.

The average dimensions and aspect ratio are summarised in table 7.8.

	Min	Max	Ave
L (nm)	19.52	34.25	25.31
B (nm)	5.61	9.84	8.25
A/R (L/B)	1.9	4.7	3.19

Table 7.8: Average dimension and A/R of 7.4.

From table 7.8, there is a decrease of 0.21 nm of the average length of the NRs when compared to that of **7.3** (25.52 nm to 25.31 nm), accounting for a 0.8 % decrement. Conversely, there is an increment of 0.61 nm (from 7.64 nm to 8.25 nm) in the average width of the composite **7.4** accounting for 8 % increment in width. The combined decrement in length and increment of width affected the average aspect ratio by given a decreased value of 3.19, accounting for 0.16 nm decrement (5 %).

Elemental	(%)
composition	
С	15.50
Н	1.35
N	4.71
S	4.04

The elemental composition of composite **7.4** is shown in table 7.9.

Table 7.9: Average dimension and A/R of **7.4**.

The plasmonic property of composite 7.4 is shown in fig. 7.21.



Figure 7.21: UV-vis of 7.4.

There was a broad absorbance between the wavelength of 640 nm and 945 nm. This is expected since from the TEM data it is apparent that there was a reduction in the length of the NRs and increase in their widths. With the broaden in its absorption, it means the NRs becomes 'fattened' and this is shown in TEM image of the composite. The factor responsible for the changes is the high temperature used for the polymerization. Another factor is the rate of stirring, as vigorous stirring can affect the size and shape of NRs.

The thermal behaviour of composite 7.4 as observed on POM is shown if fig. 7.22.



Figure 7.22: POM texture of **7.4**.

Composite **7.4** was subjected to combustion under nitrogen and the TGA thermograph is as shown in fig. 7.23.



Figure 7.23: TGA thermograph of **7.4**.

The TGA thermograph shows two steps of mass loss with the first almost linking to the second one. The first depth mass loss began at about 150 °C and ended at 450 °C while the second shallow mass loss was between 460 °C and 750 °C. The total mass loss was 50 % which accounted to the polymeric component of the composite. The Au content is also about 50 %.

7.5 Polymerization with a longer chain macroinitiator

Polymerizations using 11-mercaptododecyl 2-bromo-2-methylpropanoate capped AuNRs were investigated. Scheme 7.3 Shows the synthetic routes used to obtain the initiator.



Scheme 7.3

The 11-mercapto-1-undecanol (**7.6**) was synthesised from 11-bromo-1-undecanol (**7.5**) in 70 % yield⁹ was converted to disulfide diol (**7.7**)¹⁰. The terminal hydroxyl groups were esterified by 2-isobutyry bromide¹⁰ and eventually, the cleavage of the disulfide ester gave the targeted initiator (**7.9**)¹¹. Ligand exchange was carried out on CTAB capped AuNRs in THF using the synthesised initiator to obtain the targeted macroinitiator (**7.10**), which was used for the polymerization. **7.10** was soluble in organic solvent and not in water as demonstrated in fig. 7.24 in which it was dissolved in toluene (left) and floats on water (right).



Figure 7.24: 7.10 in tolune (left vial), 7.10 in toluene on water (right vial)

Also, the absorption of **7.10** in toluene and THF are shown in fig.7.25 and fig.7.26 respectively.



Figure 7.25: UV-vis of 7.10 in toluene.



Figure 7.26: UV-vis of 7.10 in THF.

The transverse surface plasmon resonance peak for the macroinitiator are the same in both solvents (525 nm) while the longitudinal surface plasmon resonance peak in toluene is 800 nm and 770 nm in THF.

7.6 Synthesis of composite 7.11

The mesogenic siloxane monomer was polymerized using **7.10** as the macroinitiator (scheme 7.4).



Scheme 7.4





Figure 7.27: ¹H NMR of **7.11**.

Figure 7.28 is the SEM images of **7.11**. (a) is the BSD image which confirmed the presence of AuNRs in the composite (glittering spots) while (b) is the topology of the composite and confirmed the that composite is polymeric.



Figure 7.28: SEM images of 7.11: (a) Back Scattered detector image (b) Secondary electron imaging.

The EDS of the corresponding area scanned is shown in fig. 7.29 and the presence of Au,



C, S, Si and Br were confirmed.

Figure 7.29: EDS of **7.11**.

The elemental composition of the composite is given in table 7.10.
Compositional	%
elements	
С	16.65
Н	3.28
Ν	4.19
S	2.26

Table 7.10: Elemental composition of **7.11**.

The plasmonic property of 7.11 as determined by UV-vis is as shown in fig. 7.30.



Figure 7.30: UV-vis of **7.11**.

The transverse surface plasmon resonance peak for the composite is at 525 nm (red shift of 5 nm when compared with that of macroinitiator) while the longitudinal surface plasmon resonance peak is at 765 nm (blue shift of 5 nm when compared with that of macroinitiator) in THF.

Below is the image of **7.11** when observed on POM (fig. 7.30).



Figure 7.31: POM image of composite 7.11.

No distinctive transition was observed and this is due to high Au content as confirmed by the elemental analysis.

The thermal behaviour of the composite as studied by DSC is shown fig. 7.32.



Figure 7.32: DSC curves of **7.11**.

On heating, **7.11** exhibits a broad absorption, although no prominent transition was observed, this type of behaviour is peculiar to materials of this kind.

The combustion of the composite gave a single step broad depth mass loss of 62 % between 200 °C and 450 °C. This mass loss is attributed to the polymeric content of the composite. The residue which is 38 % is Au content. TGA thermograph is given fig. 7.33.



Figure 7.33: TGA thermogram of 7.11.

7.6.1 Investigation of PMSE as a mixture (PMUE)

In order to study the behaviour of composite **7.11** as a mixture, **7.11** was synthesised (one at 40 $^{\circ}$ C (**7.12**) and the second at rt (**7.13**)) and precipitated in methanol to remove the Cu catalyst but without the removal of free polymers (centrifugation was not performed). The slurry of the composite was used for the study.

The SEM image is as shown in fig. 7.34.



Figure 7.34: SEM images of 7.13: (a) Back Scattered detector image (b) Secondary electron imaging.

The EDS (fig. 7.35) showed the presence of Au, Br, C, Si, O, N in the composite.



Figure 7.32: EDS of **7.13**.

Elemental	7.12	7.13
composition	(%)	(%)
С	66.32	65.62
Н	9.03	9.26
S	19.72	18.96

The elemental composition of the nanosystems is as shown in table 7.11.

Table 7.11: Elemental composition.

High percentages of organic components is expected as the composite is a mixture.

The absorbance of the system was investigated in both toluene and THF and are show below. For **7.12**,



Figure 7.36: UV-Vis of 7.12 in toluene.



Figure 7.37: UV-Vis of 7.12 in toluene.

In toluene, the transverse surface plasmon resonance peak for the composite is at 600 nm (red shifted when compared with that of macroinitiator) while the longitudinal surface plasmon resonance peak is at 940 nm (red shifted when compared with that of macroinitiator). In THF the values are 575 nm and 840 nm respectively. The effect of high temperature is clearly seen on the plot.

For reaction at room temperature, **7.13**, the plasmonic properties are shown below.



Figure 7.38: UV-Vis of **7.13** in toluene.



Figure 7.39: UV-Vis of **7.13** in THF.

In toluene, the transverse surface plasmon resonance peak for the composite is at 535 nm (red shifted when compared with that of macroinitiator) while the longitudinal surface plasmon resonance peak is at 805 nm (red shifted when compared with that of macroinitiator). In THF the values are 525 nm and 790 nm respectively. Here, the nature of plots obtained reveals high temperature used in composite **7.12** affected the shapes of the NRs.

The POM images of composite **7.12** and **7.13** cooled with liquid Nitrogen are shown (fig. 7.40).



Figure 7.40: POM image of (a) **7.12** (b) **7.13.**

Both composites showed marble nematic textures.

The DSC heating and cooling curves of **7.12** and **7.13** are respectively shown below.



Figure 7.41: DSC curves of **7.12**.



Figure 7.42: DSC curves of 7.13.





Figure 7.43: TGA thermogram of 7.12.



Figure 7.44: TGA thermogram of 7.12.

For the mixture, different amount of mesogen **4.7** was added to **7.12** and **7.13** respectively to raise the isotropic temperature. Mixture **7.12** required 20 % of mesogen **4.7** while mixture **7.13** required 30 %. The image seen on POM and the DSC curves obtained are shown in fig. 7.45, 7.46 and 7.47 respectively.



Figure 7.45: POM image (x 400) of (a) - (b) 7.12 + 4.7 (20 %) (c) - (d) 7.13 + 4.7 (30 %)

Both showed nematic texture on POM.



Figure 7.46: DSC curves of **7.12**.



Figure 7.47: DSC curves of **7.13**.





Scheme 7.5

Composite **7.14** was synthesised using **7.10** as the macroinitiator for the polymerization of mesogenic methacrylate monomer **5.9**.

¹H NMR spectrum for the composite is as given in fig 7.48.



Figure 7.48: ¹H NMR of **7.14**.

The SEM images are shown in fig. 7.49. BSD image (a) confirmed the presence of gold although due to the nature texture of polymer formed, the colour appeared grey.



Figure 7.49: SEM images of 7.14: (a) Back Scattered detector image (b) Secondary electron imaging.

SEI (b) confirmed that the composite is polymeric.

Also, the EDS shown in fig. 7.50, confirmed the presence of Au, C, Br, O and S.



Figure 7.50: EDS of **7.14**.

The elemental composition of the composition is given in the table 7.12.

Compositional Element	(%)
С	2.45
Н	0.24
Ν	0.28
S	0.35

The plasmonic property of the composite as investigated on UV-vis is shown fig. 7.51.



Figure 7.51: UV-vis of **7.14**.

A broad absorption was observed for the composite.

The thermal behaviour observed on POM is shown in fig 7.52.



Figure 7.52: POM of composite 7.14 (a) at rt (b) - (c) at 50 °C

At room temperature, there was no birefringence observed on POM but when heated to 50 °C, birefringence was observed (glittering in fig. 7.52).

The DSC heating and cooling curves shown in fig. 7.53, shows the characteristic broad absorption peculiar to composites of this kind.



Figure 7.53: DSC curves of 7.14.

Finally, the TGA thermograph for the composite when subjected to temperature up to 950 °C is shown in fig.7.54.



Figure 7.54: TGA thermograph of 7.14.

The combustion of the composite starts immediately and gave a total mass loss of 37 % attributed to the polymer content of the system. The residue, which is Au accounted for 63 %.

7.8 Experimental procedures

7.8.1 Synthesis of 11-mercapto-1-undecanol (MUD)⁹





To a mixture of ethanol/water (1:1, 500 ml) was added 11-bromo-1-undecanol (**7.5**) (12.5 g, 50 mmol) and sodium thiosulfate (13.7 g, 55 mmol) and the solution reflux for 3 h. The solvents mixture was removed and the sodium 11-bromo-1-undecyl thiosulfate recrystallized from ethanol, filtered and dried. To this was added 6 M HCl (1000 ml) and refluxed for 6 h. The product was extracted with DCM, washed with 4 M NaCl (200 ml), dried over Na₂SO₄, filtered and the solvent removed to obtain a golden oily product which later crystallized to white powder (7.12g, 70 %)

 $R_{\rm f}$ (DCM) = 0.78

¹**H NMR (400 MHz, CDCl₃):** δ = 1.3 (m, 10 H, CH₂CH₂), 1.6 (m, 8 H, CH₂CH₂), 2.5 (t, 2 H, SCH₂), 3.6 (t, 2 H, CH₂OH), 5.3 (s, 1 H, OH).

¹³C NMR (100 MHz, CDCl₃): $\delta = 24, 25, 26, 28, 29, 30, 32, 34, 45, 62.$

7.8.2 Synthesis of 11,11'-disulfanediylbis(undecan-1-ol)¹⁰





To a stirred mixture of 11-mercapto-1-undecanol (**7.6**) (4.09 g, 20 mmol), 10% KHCO₃ (20 ml) and DCM (150 ml) was added bromine (1.6 g, 10 mmol) slowly. The organic layer was separated and the aqueous layer extracted with DCM (50 ml). The combined organic layer was dried over MgSO₄, filtered and the solvent removed to obtained the yellow oily product (6.92 g, 85 %).

 $R_{\rm f}$ (DCM) = 0.80

Elemental analysis: Analytical calculated values for C₂₂H₄₆O₂S₂ (MW = 406): C, 64.97; H, 11.40; S, 15.76. Found: C, 64.28; H, 11.27; S, 15.54 %.

¹H NMR (400 MHz, CDCl₃): δ = 1.36 (m, 20 H, CH₂CH₂), 1.70 (m, 16 H, CH₂CH₂), 2.70 (t, 4 H, SCH₂), 3.70 (t, 4 H, CH₂OH), 5.3 (s, 2 H, OH).

¹³C NMR (100 MHz, CDCl₃): $\delta = 26, 27, 28, 29, 30, 32, 33, 39, 45, 63$.

7.8.3 Synthesisofdisulfanediylbis(dodecane-11,1-diyl)bis(2-bromo-2-methylpropanoate)10





To a mixture of 11, 11'-disulfanediylbis (undecan-1-ol) (**7.7**) (2.8 g, 6.91 mmol), TEA (4.7 ml, 35 mmol) in DCM (180 ml) at 0 °C and under nitrogen, was added dropwise 2-bromo-2-methylpropanoyl bromide (2 ml, 16.5 mmol). The solution was stirred at the temperature for 1 h and then at 25 °C for additional 2 h. 2M Na₂CO₃ (50 ml) was added and the organic layer separated. Solvent was removed and the crude product purified by column chromatography (DCM) to obtain a yellow oily product (2.77g, 70 %).

 $R_{\rm f}$ (DCM) = 0.74

Elemental analysis: Analytical calculated values for $C_{32}H_{60}Br_2O_4S_2$ (MW = 730): C, 51.13; H, 8.71; S, 9.10. Found: C, 51.08; H, 8.62; S, 9.02 %.

¹H NMR (400 MHz, CDCl₃): $\delta = 1.3$ (m, 10 H, CH₂CH₂), 1.4 (m, 12 H, CH₂CH₂), 1.7 (m, 4 H, OCH₂CH₂), 1.9 (s, 12 H, CH₃), 2.7 (t, 4 H, SCH₂), 4.2 (t, 4 H, OCH₂). ¹³C NMR (100 MHz, CDCl₃): $\delta = 26, 28, 29, 30, 34, 39, 56, 65, 171.$





Scheme 7.9

A mixture of thioethanol (**7.8**) (2 ml, 28 mmol), TEA (0.1 ml, 0.72 mmol) and 11mercaptododecyl 2-bromo-2-methylpropanoate (0.32 g, 0.45 mmol) in chloroform (8 ml) were stirred for 12 h at 20 °C. Water (3 ml x 3) was added and the organic layer separated, dried over Na₂SO₄, and concentrated in vacuo.

 $R_{\rm f}$ (DCM) = 0.61

Elemental analysis: Analytical calculated values for C₁₆H₃₁BrO₂S (MW = 367): C, 52.31; H, 8.51; S, 8.73. Found: C, 51.83; H, 8.57; S, 8.59 %.

¹**H NMR (400 MHz, CDCl₃):** $\delta = 1.30$ (m, 10 H, CH₂CH₂), 1.60 (m, 6 H, CH₂CH₂), 1.9 (s, 6 H, CH₃), 2.7 (t, 2 H, SCH₂), 4.2 (t, 2 H, OCH₂).

¹³C NMR (100 MHz, CDCl₃): $\delta = 26, 28, 29, 30, 32, 39, 45, 56, 66, 171.$





2 batches of as-prepared AuNRs (diluted to 60 ml) was added dropwisely to a solution of thiol initiator (0.9 g,) in THF (350 ml) and stirred briefly. The solution was left undisturbed for 24 h and centrifuged (7100 rpm, 12 min). The supernatant was removed while the residue was re-dispersed in THF and the process repeated. The residue was re-dispersed in toluene and UV-Vis carried out.



Scheme 7.11

The macroinitiator synthesised above was divided into two portions (A and B, 1 ml each). To each was added Cu(I)Br (9 mg, 6.3×10^{-5} mol), compound **5.6** (3.5g, 3.76 mmol), and toluene (2 ml). The mixture was degassed by argon purging for 30 min followed by the addition of Me₆TREN (34 mg, 1.48 x 10⁻⁴ mol) and further purged for 10 min. The first portion was placed in pre-heated oil bath (40 °C) while the second portion was at room temperature. The two reactions were stirred for 24 h and precipitated in cold methanol. The composite was re-dissolved in toluene or THF and re-precipitated in methanol. Methanol was decanted and the composites (A and B) dried in vacuo.

The above procedure was repeated with less amount of monomer 20 (1.5 g, 1.61 mol) in toluene (2 ml), Cu(I)Br (9 mg, 6.3×10^{-5} mol), Me6TREN (40.8 mg, 1.77×10^{-4} mol) at 40 °C (C) and rt (D) respectively.

7.8.7 Synthesis of composite AuNR-PE7MC



Scheme 7.12

Polymerization was performed on the **7.10** using compound **5.9** as the monomer as follows.

To a degassed mixture of monomer **5.9** (5.5 g, 7.4 mmol) and Cu(I)Br (3.8 mg, 2.65 x 10^{-5} mol) in toluene (1 ml) was added Me₆TREN (7 mg, 3.05 x 10^{-5} mol). The mixture was further degassed for 20 min and gently stirred at room temperature for 30 h. The composite was precipitated in cold methanol and the methanol decanted to form a blackish precipitate. This was re-dissolved in minimum THF and centrifuged (5000 rpm, 5 min), the supernatant was removed and the process repeated (x4). The black residue was dried in vacuo and analysed.

7.8.8 Synthesis of Tris(2-dimethylaminoethyl)amine ligand, Me₆TREN



Scheme 7.13

Tris(2-aminoethyl)amine (TREN; 2 g, 13.6 mmol) was added to acetone (80 ml) and stirred to dissolve. Excess conc. HCl (3.2 ml) was added while stirring to form TREN.HCl salt. The pinkish-white salt was collected via filtration and dried in vacuo. Water (4 ml) was added to the salt, followed by excess 88 % weight formic acid solution (12.4 ml) and 37% wt formaldehyde solution (8.8 ml). After complete dissolution, the mixture was reflux for 12 h over oil bath (120 °C), allowed to cool to room temperature and the volatile components evaporated to give a dark orange solid (crude Me₆TREN.HCl salt). The salt was dissolved in 10% wt NaOH (in water) (32 ml), pH been 12 or above, and extracted with ether (3 x 40ml). The yellow-orange Me₆TREN solution was dried by stirring over KOH pellets for 12 h, and the ether removed to obtain an orange liquid, Me₆TREN, 2.03 g (64%).

¹**H NMR (400 MHz, CDCl₃):** $\delta = 2.10$ (s, 18 H, NCH₃), 2.30 (s, 6 H, NCH₂), 2.5 (s, 6 H, NCH₂).

¹³C NMR (100 MHz, CDCl₃): $\delta = 57.3, 53.1, 45.6.$

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General conclusion

Gold nanoparticles (AuNPs) of average sizes of 2.34 nm and 3.02 nm were successfully synthesized and fully characterized. It was observed that the sizes of the NPs decreased with increasing the concentration of capping agents and increased with an increase in the temperature of the reaction.

The CTAB capped gold nanorods with an aspect ratio of 3 were successfully synthesised and characterized. They have a surface plasmon band at 502 nm and 775 nm.

A nematic liquid crystalline mesogen (4.7) was synthesised. The conversion of a terminal alkene group into a thiol function was explored extensively and the yield of this reaction was improved significantly. Yields of more than 91% and of almost 100% are now achievable compared to 55 %, at the outset of the project., This is a significant improvement and achievement, especially as this is the last step in an eight step synthetic sequence.

The syntheses of the AuNP-liquid crystalline composites were investigated in which different ways of linking the NPs to the mesogen and their properties were determined.

Further, the synthesis of liquid crystalline polymeric nano composites, using both 'grafting from' and 'grafting to' methods were investigated further. 'Grafting from' was systematically performed by coating the surface of AuNPs with ATRP initiator and eventually polymerising a methacrylate mesogenic monomer. Also, the 'grafting to' method was explored carried out by polymerizing the mesogenic monomer by ATRP using a disulfide initiator to obtain polymer with disulfide bond which was subsequently cleaved and through ligand exchange bonded to the AuNPs. The attachments of the polymer to the NPs were confirmed by NMR. The NP sizes were not affected by the modification of their surface, as confirmed by TEM and XRD. Also, SEM images confirmed the presence of Au

in the polymers and showed that they are entangled in the polymers. The composites showed birefringence after sheared under OPM and gave a broad curve for **4.13** and **6.15** while heating on DSC. This is peculiar to polymers and nanocomposites. From XRD data it is apparent that the composites did not exhibit columnar structures but a smectic layering. The composite **6.9/6.12** showed a plasmonic response at 540 nm. These materials are the first of their class, this is gold nanoparticles functionalised as macroinitiators resulting after polymerisation in AuNP side chain liquid crystal polymer (AuNP-SCLCP) composites.

This work has demonstrated that the complete replacement of CTAB on AuNRs in just a step without affecting the NR sizes soluble in organic solvents is possible. This can served as a template for broad applications in the use of AuNRs most especially in nanotechnology where functionalizing AuNRs with organic moiety are really challenging.

The AuNR-SCLCP composites showed the characteristic red shifts in the longitudinal plasmon band when compared to the CTAB capped AuNRs. This is evidence that there were changes in the surfaces of the Au. SEM images confirmed the polymeric nature of the composites and their homogeneity. It also suggested the entanglement of the AuNRs by the polymers. TGA measurements indicated that, the organic components of these nanocomposites varied from 30 % to 60 %. This was judged to be responsible for the broad DSC curves though it was noted that these showed birefringence using optical polarizing microscopy.

Outlook

In the immediate future, it is planned to completely extend these synthetic methods to AuNPs with bigger sizes and of other geometrical shapes, and also, to other nanomaterials such as silver and quantum dot (eg CdSe) NPs.

Compounds identity







