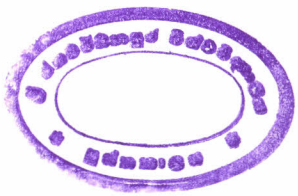
Synthesis of Liquid crystal polymers

By

Hiranya Daniel

This thesis was submitted in partial fulfillment of the requirement for the Masters Degree of Science in Polymer Science and Technology of the Faculty of Applied Science, University of Sri Jayawardanapura, Sri Lanka.

December 2001



ABSTRACT

Synthesis of chiral liquid crystals

Low molecular mass liquid crystals are important components of liquid crystal displays and mostly showing in all sorts of instrumentation including portable computers and televisions.

It has been observed that low molecular mass liquid crystals display chiral nematic phases over a broad temperature. The aim of this project was to study the synthetic approaches outlined below would produce the desired low molecular mass monomers and enable us to proceed in the synthesis of liquid crystal polymers.

Reaction scheme (1)

Boronic ester was synthesized (fig 1) in an inert atmosphere.
White crystalline product was obtained as the product.
^{1}H NMR ($CDCl_3$) and mass spectrum was obtained for the product.
δ 8.1(d,2ArH,a), 6.9(d,2ArH,b), 1.625(m,2H,d), 1.9(m,2H,e), 4.1(q,1H,f),
3.9(m,2H,g), 1.15(s,3H,h), 1.125(s,3H,I), 0.79(m,1H,j), 1.39(d,3H,k), 1.3(d,3H,l).
Resolution of isoprppyl peaks were not clear in the spectrum.
According to the mass spectrum most probable peak observed was 355.2.
Compound was melted at 126^{0}c.

Reaction scheme (2)

The byphenyl ether (fig 2) synthesized was a white crystalline solid and was analysed By ^{1}H NMR spectrometer in DMSO.
δ 7.59(D,2ArH,a), 7.0(d,2ArH,b), 4.05(t,2H,c), 1.9(m,2H,d), 1.8(m,2H,e),
3.47(m,1H,f), 5.5(t,1H,g).
According to the mass spectrum a strong peak of 390.3 could be observed.
The sample melted at 240^{0}c.

Reaction scheme (3)

The product obtained in the scheme was a white solid (fig 3) and ^{1}H NMR ($CDCl_3$) was recorded.
δ 6.8(d,2ArH,a), 7.35(d,2ArH,b), 3.35(t,2H,c), 3.6(m,1H,I)
According to the mass spectrum a strong peak of 371.3 was recorded.
The sample melted at 119.9^{0}c

Reaction scheme (4)

The product synthesized (fig 4) was a white crystalline solid and 1H NMR (CDCl3) was recorded.
δ 7.45(d,2ArH,a), 7.35(d,2ArH,b), 7.4(d,2ArH,c), 6.85(d,2ArH,d), 3.95(t,2H,e), 1.85(q,2H,f), 2.2(q,2H,g), 3.625(m, 1H,h), and 3.35(t,1H,I).

Reaction scheme (5)

Three crystalline products were synthesized .
An ether was synthesized (fig 5) using 4 bromo (1,1/ biphenyl)4-ol which was a white solid.
^{1}H NMR ($CDCl_3$) was recorded.
δ 7.45 (d,2ArH,a), 7.35(d,2ArH,b), 7.3(d,2ArH,c), 6.8(d,2ArH,d), 3.9(t,2H,e), 1.4(m,2H,f), 1.75(m,2H,g), 1.55(m,2H,h), 3.2(m,2H,I), 3.4(q,2H,j), 3.65(m,1H,k), 3.45(t,2H,I)
According to the mass spectrum strong peak of 393.4 was recorded and the sample melted at 121.3^{0}c.

The ether synthesized by using 4 bromo phenol (fig 6) was yellowish oil.
^{1}H NMR ($CDCl_3$) recorded at δ 7.225(d,2ArH,a), 6.65(d,2ArH,b), 3.475(t,2H,c), 1.65(m,2H,d), 1.35(m,2H,e), 3.6(m,2H,h), 3.6(q,1H,I), and 3.375(m,2H,j).

The white crystalline dimmer (fig 7) synthesized by using 4,4/ dihydroxi biphenyl was a heavy solid.
^{1}H NMR ($CDCl_3$) was recorded at δ 7.325(d,2ArH,a), 6.8(d,2ArH,b), 3.45(t,2H,c), 1.7(m,2H,d), 3.58(m,1H,I), 3.35(t,2H,j).
Strong peak of 471.5 was recorded in the mass spectrum and the compound melted at 141.2^{0}c.

CONTENTS

	page no
1. Introduction	7
1.1. Historical perspective	7
1.2. Orientational and positional order of liquid crystals	8
1.3.Types of liquid crystals	10
1.3.1. Phase structure of calamatic liquid crystals	12
1.3.2 Phase structure of discotic liquid crystals	14
1.4.Structure and property relationship	15
1.4.1. Calamatic liquid crystals	15
1.4.2 Discotic liquid crystals	16
1.5 Chiral liquid crystals	17
1.5.1. The chiral nematic phase	17
1.5.2 Ciral smectic phases	19
1.6 Liquid crystalline polymers	19
1.6.1 Liquid crystalline main chain polymers	19
1.6.2 Liquid crystalline side chain polymers	20
1.6.3 Phase behavior relative to the molecular structure.	21
1.7 Properties of liquid crystalline polymers and applications	22
1.8 Main applications	23
1.9 Synthesis of liquid crystalline polymers	25
1.10 Identifying liquid crystalline phases phases	29
1.10.1 Visual appearance and texture	30
1.11 Optical polarizing microscopy	31
1.12 Differential scanning calorimetry	33
2. Experimental	35
2.1. Synthetic reaction scheme (1)	35
2.2 Synthetic reaction scheme (2)	39
2.3 Synthetic reaction scheme (3)	42
2.4 Synthetic reaction scheme (4)	45
2.5 Synthetic reaction scheme (5)	48
3. Results and discussion	55
3.1. Reaction scheme (1)	55
3.2 Reaction scheme (2)	58
3.3 Reaction scheme (3)	59
3.4 Reaction scheme (4)	60
3.5 Reaction scheme (5)	60
4. Conclusion	62
5. General references	63
6. Appendix	64