CHAPTER 6

CONCLUSIONS

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CHAPTER 6: Conclusions

N-substituted pyrrole monomers with liquid crystal and dendritic side groups have been synthesised. Monomers 1-7 were characterised using IR, MS & ^{1}H NMR, and the spectroscopic data confirmed the structure, purity and accurate mass of each monomer.

The following four main types of monomers were synthesised and polymerised, and their structures and physical properties were measured:-

1. Polypyrroles with terminally- and laterally-attached mesogenic side groups (monomers/polymers 1 & 2)
2. Polypyrroles with first and second generation dendritic side groups, terminated by alkyl chains (monomer/polymer 3)
3. Polypyrroles functionalised by first and second generation dendritic moities with hydrophilically-terminated alkyl chains (monomer/polymer 5)
4. Polypyrrole hybrid material: second generation dendrimer with terminal liquid crystal groups (monomer/polymer7)

Although it was aimed to synthesise 12 N-substituted polypyrroles, 9 were successfully synthesised, characterised and subjected to physical measurements. The final 9 polymers synthesised in this project are outlined in Table 6.1.

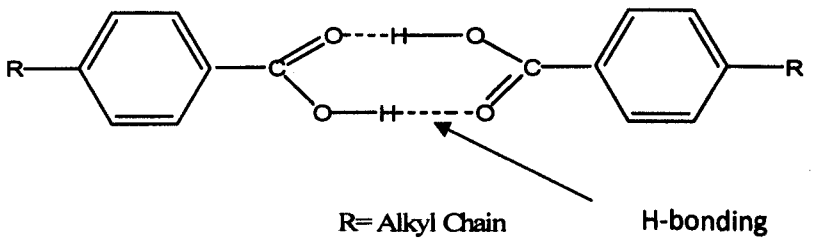
Chemical and electrochemical methods were employed for polymerisation. It can be concluded that monomers (1) and (3) were successfully polymerised via electrochemical methods, as the cyclic voltammograms showed characteristic redox properties of N-substituted polypyrroles. Polymer (1) was found to have a doping potential of 480mV, de-doping potential of 50mV and an oxidation potential of 1500mV with respect to SCE. Polymer (3) was found to have a doping potential of 100mV, de-doping potential of 500mV and an oxidation potential of 1500mV. Although the voltammograms indicated that polymerisation was

occurring and there was observable growth of a thin polymer film on ITO glass, the product yield was too low, so this method of polymerisation was abandoned.

Chemical polymerisation was attempted for monomers 1-7 and proved to be viable for the following: (1), (2), (3), (5), & (7). Monomers (4) and (6) appeared to undergo polymerisation as the appearance and mass of the product was similar to the other polymers; however, due to very poor solubility in most organic solvents, they could not be characterised further. IR and ^{1}H NMR were used to characterise the novel polymers, and upon interpretation of the spectroscopic data, it was concluded that absorption bands and chemical shifts of the main functional groups were present. Polymers (1), (2), (5) & (7) were subjected to hydrolysis to yield the corresponding polymers with terminal carboxylic acid groups. The conversion from ester to acid yielded very interesting results and significantly improved the overall polymer properties.

6.1 Physical Measurement

Conductivity measurements using simple 2-probe and van der Pauw 4-probe methods were carried out on all of the polymers. The values obtained indicated that the conductivity increased by two orders of magnitude upon mild doping with iodine. Polymers (1), (5) and (7), when hydrolysed to acids, exhibited conductivities of 2.2×10^{-4}, 3.17×10^{-6} and 7.84×10^{-5} Sm^{-1} respectively. These values fall into the range of semi-conductors, and it was found that laterally-attached liquid crystal polymers had the highest conductivity values, followed by terminally-attached liquid crystal polymers. The significant improvement in conductivity upon hydrolysis was believed to arise from intermolecular hydrogen bonding between adjacent carboxylic acid groups, giving rise to a pseudo-ring structure. The effect of the pseudo-ring can either improve or preserve the overall planarity and conjugation of the polymer backbone. This may therefore increase the conductivity of the polymer material, as was observed in the cases of polymers (1), (5) and (7).



The films of polymers (1), (1a) and (3) were analysed using UV-visible spectrophotometry. The energy gaps were calculated using the Planck equation and the values obtained were 3.9, 1.8 and 2.9eV respectively. These values indicate that polymer (1a) had the smallest band gap followed by (1) and (3). This was in accordance with the results of the conductivity measurements which indicated that polymer (1a) was a semi-conductor, and polymers (1) and (3) were insulators. When the band-gap values were compared to the literature values for neutral polypyrrole (3.2eV) [Kaiser, MacDiarmid] it was suggested that polymers (1a) and (3) may have had a greater extent of conjugation. N-substitution of polypyrrole with electron donating species such as the hexyl spacer group (in the case of polymer (3)), has been shown to lower the ionisation potential for p-type doping.[Kaiser, MacDiarmid]. The increased electron density along the conjugated system allows for easier removal of the electrons during oxidation, which may also contribute slightly to the smaller Eg for polymer (3) than the parent monomer. However the reduced band-gap value for polymer (1a) is also likely to have been due to hydrogen bonding between adjacent carboxylic acid groups increasing the planarity of the polymer backbone, which in turn improved the effectiveness of π-bond conjugation.

Differential scanning calorimetry was used to determine the thermal behaviour of monomers (1) and (2) and their corresponding carboxylic acid polymers (1a) and (2a). The DSC thermograms indicated that no phase transitions were observed for the monomers, but 2-3 phase transitions were observed for the polymers. The size of the peaks on the thermograms indicated that the phase transition energies were very small, consistent with liquid crystal transitions. The temperature regions where the phase transitions, melting and

decomposition of the polymers were likely to occur were also provided by the thermograms. To further investigate the findings provided by the DSC, hot-stage microscopy was used. The images showed that polymer (1a) began to soften at 70°C, showed a nematic phase texture from 120-130 °C, a clearing point at 250°C and decomposition at 310°C. Polymer (2a) had very similar findings, as expected since they were structurally related. At 75-100°C softening occurred, from 110-175°C a textured nematic phase was observed, at 195°C there was a clearing point and finally decomposition at 240°C. All the results of the hot-stage microscopy were consistent with the findings of the DSC, and it can be concluded polymers (1a) and (2a) displayed nematic liquid crystallinity at the temperatures quoted.

Scanning electron microscopy was used to determine the morphology of the dendritic liquid crystal conducting polymers. The images indicated that generally the N-substituted polypyrroles with dendritic side groups were found to have more porous morphologies, while N-substituted polypyrroles with potentially mesogenic side groups appeared to have more continuous and smoother morphologies. However, polymer (7a) was found to have the most porous morphology and it also had an unexpectedly high conductivity value. Polymer (7a) was the only polypyrrole hybrid material synthesized in this project, and it appeared that combining all three polymeric units (dendrimers, LC and CP) into one polymer system improved the planarity of the polymer backbone and encouraged the formation of a porous structure which would facilitate p-type doping of the polymer by iodine vapour.

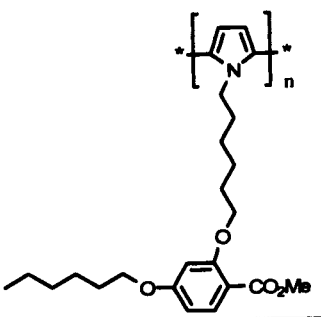
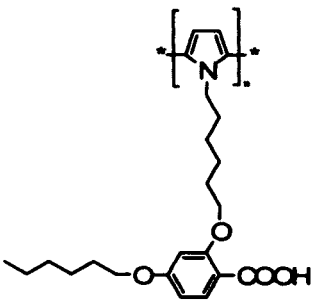
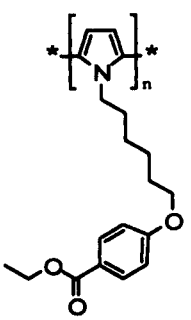
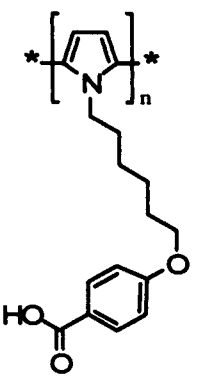
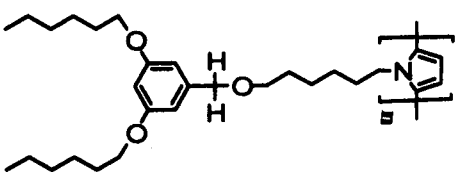
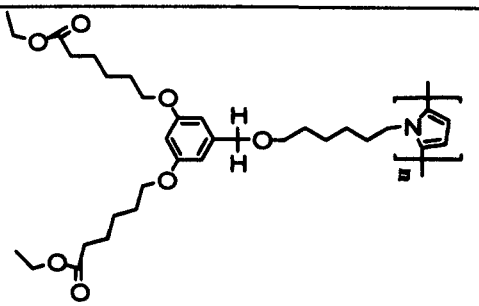
To summarise, the polymers synthesised in this project comprised 3 types:

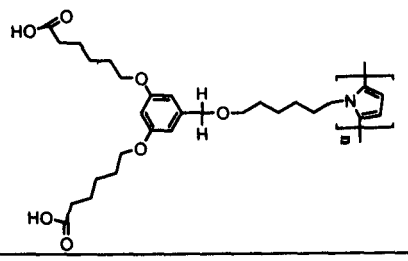
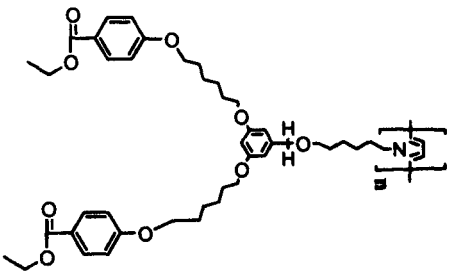
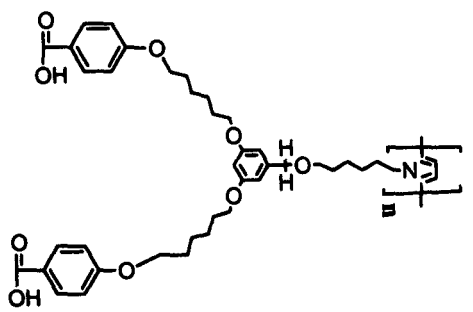
1. Conducting polymers
2. Liquid Crystal polymers
3. Dendritic Polymers

As each polymer sub-unit possessed its own unique structural features and properties, it was anticipated that the novel materials, (which brought all three classifications of polymers into one system) might exhibit some characteristics of each sub-unit. This prediction was proven to be accurate as the polymers showed characteristics of conducting polymers,

liquid crystals and dendritic polymers. In addition the generation of the liquid crystal phase; probably via the formation of a pseudo-ring system, appeared to improve the planarity and conjugation in the polypyrrole backbone. This was reflected in the relatively high conductivity values and small band-gap transitions found in the carboxylic acid analogues of the ester polymers.

Table 6.1

The nine N-Substituted polypyrroles synthesised within this project	
(1) 	(1a) 
(2) 	(2a) 
(3) 	

(5a) 	(7) 
(7a) 	

CHAPTER 7

FUTURE WORK

CHAPTER 7: Future Work

There are many areas in which the research outlined in this thesis can be expanded upon. After completing the practical work, and compiling all the findings into one document, it becomes apparent to many researchers that there may have been a number of adaptations to the synthetic strategy, methods of characterisation and physical measurements of the novel polymer materials. However it is generally understood that it is not necessary to conduct every possible characterisation and physical measurement, in order to ascertain the general behaviour and polymer properties of the novel compounds. In addition time, costs and availability to different instrumentation can be limiting factors, as well as the properties of polymer itself, (i.e. solubility) may dictate the amount of information that can be acquired from each novel material.

For this particular project there are small scale measurements which could have been conducted, such as temperature-dependent conductivity,. Secondly there are various synthetic strategies that can be explored, in order to generate novel polymer compounds with unique properties and behaviours.

Temperature-dependent conductivity would provide useful information about the conductive ability of each polymer material at various temperatures. As some of the compounds are liquid crystalline at different temperatures, they tend to undergo structural changes with temperature variation. These structural changes could either improve or hinder the conjugation of the polymer backbone, thus affecting the polymers ability to conduct electricity as the electrons are free to flow.

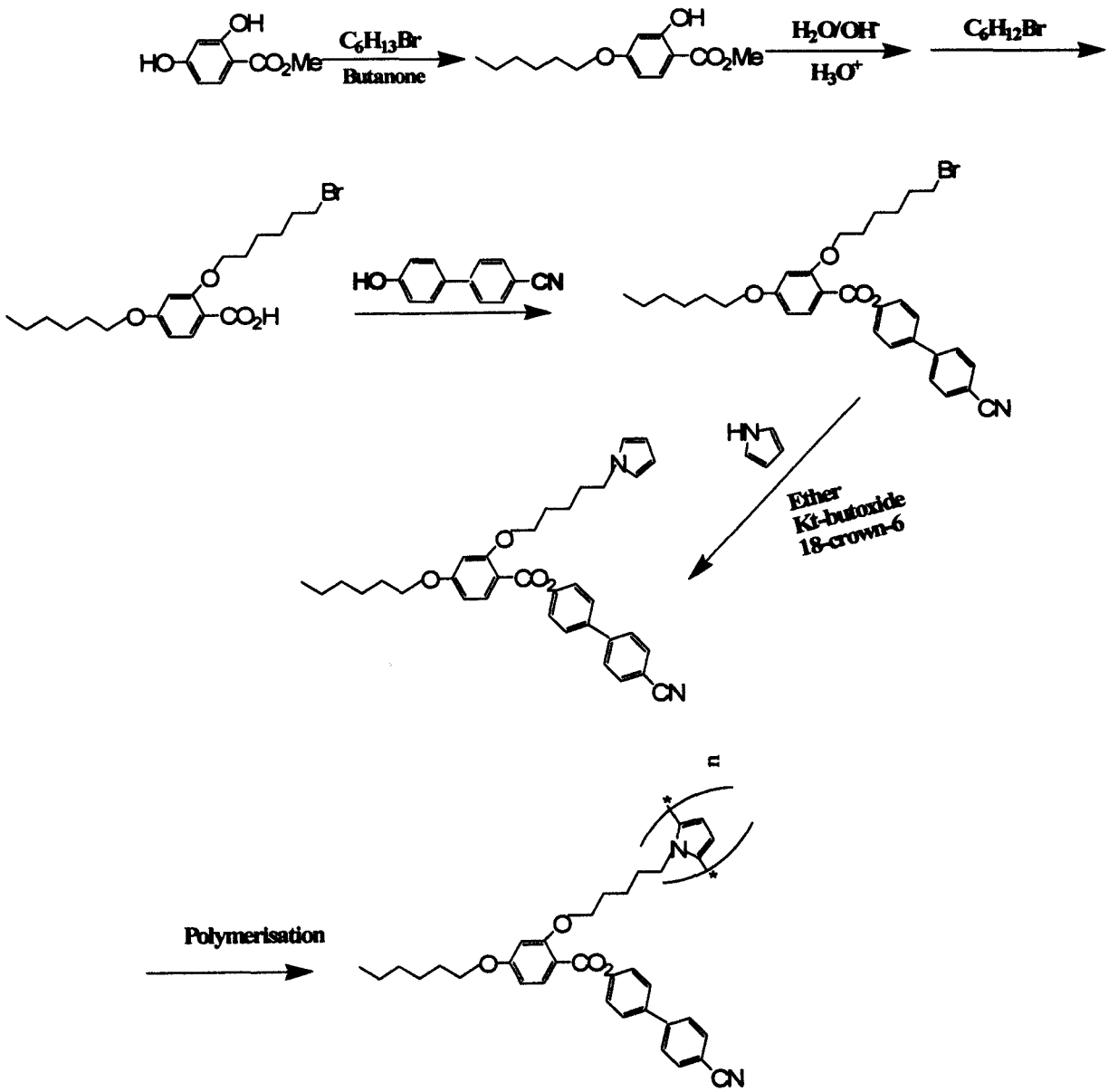
7. 1 Adaptation of Liquid Crystal Side Groups

Different liquid crystal side groups can be attached to the spacer groups, in order to investigate what liquid crystal phases may emerge. Within this project, we hydrolysed esters to carboxylic acids to generate the liquid crystal mesogens as they underwent inter-molecular hydrogen bonding with adjacent alkoxybenzoic acids, thus forming pesudo-ring systems which resulted in dimerisation and generated the liquid crystallinity. Liquid crystallinity can also arise from having molecules such as bi-phenyls which provide a certain amount of rigidity to the overall polymer system and provides the anisotropic molecular structure [Priestley]. The ring systems can be either linked directly or via a central linking group, which allows elongation of the molecule and therefore possible mesophase formation.

One example of a proposed synthetic route for the synthesis of another N-substituted pyrrole-based polymer is outlined below in scheme (Y), figure 7.1.

Figure 7.1 Proposed reaction scheme for the synthesis of 1-(N-pyrrole)-6-[(4-cyano-biphenyl-4'-yl)-4-n-hexyloxy-2-oxybenzoate]hexane and its subsequent polymerisation.

SCHEME (Y)



7.2 Variation in Chain Length of Spacer Group

Another area of future work will involve varying the number of carbon atoms of the spacer group between C-2 and the pyrrole ring. This may have a positive or negative effect on the overall conductivity and liquid crystallinity of the polymer and further investigations may involve looking at the polymer's electronic and thermal properties in relation to these changes in the length of the spacer group.

CHAPTER 8

EXPERIMENTAL

CHAPTER 8: Experimental

8.1 Introduction

The first part of the experimental section will outline the method employed to synthesise all seven N-substituted pyrrole monomers with either the liquid crystal or dendritic side groups.

The second section will outline the methods used to polymerise the five monomers, which were sufficiently soluble to characterise.

The final part of the experimental section will then outline the hydrolysis of the ester groups to carboxylic acids and the physical measurements carried out to determine the polymer properties.

The order in which the experimental section appears is indicative of the order in which the synthesis was approached. It was decided that the monomers should be synthesised first, then polymerised before hydrolysing the ester groups to carboxylic acids as this would prevent interaction occurring between the carboxylic acid group and the polymer backbone if hydrolysis were to occur before polymerisation. In addition, if un-polymerised pyrrole were exposed to harsh acidic conditions it could cause the monomer to undergo spontaneous polymerisation and cross linking. Therefore it was decided that the best approach would be to polymerise the monomers before hydrolysing the ester groups, as the regio-regular alignment of the polypyrrole backbone would improve its stability and enable the polymer to be exposed to acidic conditions during hydrolysis without decomposing or initiating unwanted cross linking of the polypyrrole chains.

Physical measurements (electrical conductivity, scanning electron microscopy, hot-stage optical microscopy, solubility testing and differential scanning calorimetry) were carried out

on the polymers synthesised, in order to determine the general natures and to indicate any possible applications of the novel polypyrrole materials.

However, one of the main obstacles in investigating more of the novel polymer properties was poor solubility. Although the polymers exhibited some degree of solubility, physical measurements such as molecular weight determination were unable to be carried out as the polymers did not dissolve sufficiently.

8.2 Methods and Materials

Chemicals and solvents

All chemicals used during the course of this research were purchased from Sigma Aldrich, and were used as supplied, unless stated otherwise. All solvents used during reaction, work-ups and purification procedures were commercially available.

Chromatography - Thin Layer Chromatography (TLC)

The purity and progress of the reactions were examined using silica gel 60 F24 on plastic sheets (fluorescent plates) purchased from Merk. The thin-layer chromatography (TLC)plates were then visualised using ultraviolet irradiation silica gel of pore diameter 60Å with a fluorescent indicator. The TLC plate was then visualized by UV light and on some occasions, aqueous solution of potassium permanganate was also used.

Gas Chromatography (GC/MS)

GC-MS was used to determine the purity and molecular weight of the products. GC-MS was recorded using an Agilent Technologies 5973 Network Mass Selective Detector and Enhanced Chemstation, MSD Chemstation D.02.00.275: © Agilent Technologies 1989-2005 Spectroscopy Techniques

Direct Insertion Mass Spectrometry (DI/MS)

DI-MS was used for compounds with molecular masses greater than 400.

Infra-red IR

Infra–red spectra were recorded using a Perkin–Elmer (1600 series. PARAGON 1000)

^{1}H NMR

Proton nuclear magnetic resonance spectra were measured using JEOL Eclipse $^+$ 400. Chemical shifts are reported in δ (PPM).

Ultraviolet-Visible (UV-Vis)

Compounds were analysed using CARY 10 Scan UV-Visible spectrophotometer and a Cary Win UV Scan Application, 2002 Version: 3.00 (182) software.

Elemental Analysis

Elemental analyses were performed by Medac Ltd. Results within ± 0.4% of the expected values were accepted as representation of a pure sample. The purity of the monomer was also indicated by GCMS. Some of the liquid compounds were purified by small scale distillation using Kugelrohr apparatus.

Physico – chemical Measurements

Transition Temperatures – Differential Scanning Calorimetry (DSC)

The liquid crystal transition temperatures were studied and measured using Differential Scanning Calorimetry (DSC) and Hot-stage Polarising Microscopy. DSC equipment was a Mettler DSC 20 and DSC 25 with thermal-analysis processor, Mettler TC 10A based on a TA 3000 system with Graphware TA 72 software. A nitrogen atmosphere was used in the furnace and an empty aluminium pan was used as a reference.

Hot-stage Microscopy

After the transition temperatures had been determined using DSC, the liquid crystal mesophases were observed using a Linkam HFS 91 Hot-stage, Nikon Polarising Microscope fitted with a Linkam TMS-600 heating stage. The optical textures were observed and stored on a computer connected directly to the microscope. Heating was controlled using TMS 91 display and keyboard, a VTO 232-video text overlay and CS 196 cooling system.

Cyclic Voltammetry (CV)

CV was used to study the redox properties of the polymers and the instrument used was a BAS 100B Electrochemical Analyzer using BASv 100W software, Version 2.31: © 1992-2002 Bioanalytical systems, Inc.

Electrical conductivity

Electrical conductivity is measure of a material's ability to conduct an electric current. The electrical conductivity measurements of solid samples, were made using a Keithley 617 Programmable Electrometer and Keithley 224 Programmable Current Source. These measurements were computer controlled using substrates with two probe & four probe contacts.

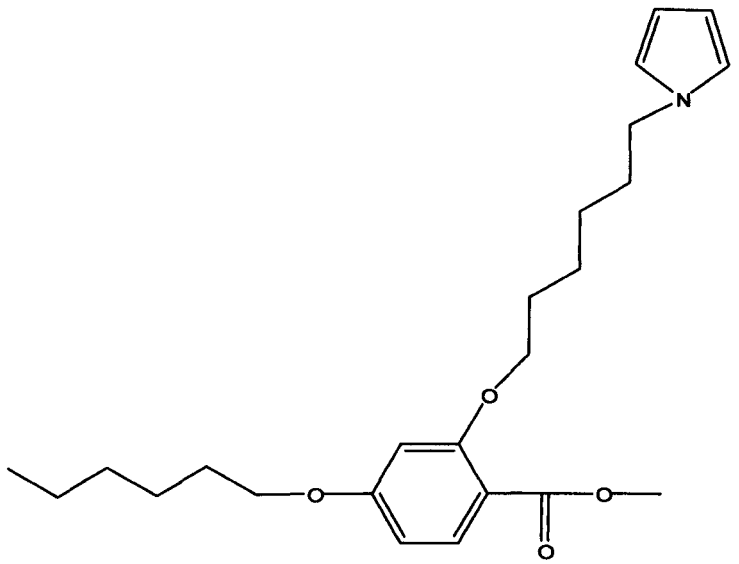
The electrical conductivity was calculated using the following equation:

$$Conductivity = \frac{Thickness}{Resistance\ x\ Area\ of\ pellet}$$

Scanning Electron Microscopy (SEM)

Zeiss EVO 50 SEM was used in conjunction with INCA system to allow the qualitative and quantitative x-ray analysis by two techniques known as Energy Dispersive Spectrometry (EDS) and Wavelength Dispersive Spectrometry (WDS). 20 kV, 1.5nA-probe size.

8.3 Synthesis of Methyl 2-(6-(1H-pyrrol-1-yl)hexyloxy)-4-(hexyloxy)benzoate-Monomer (I)

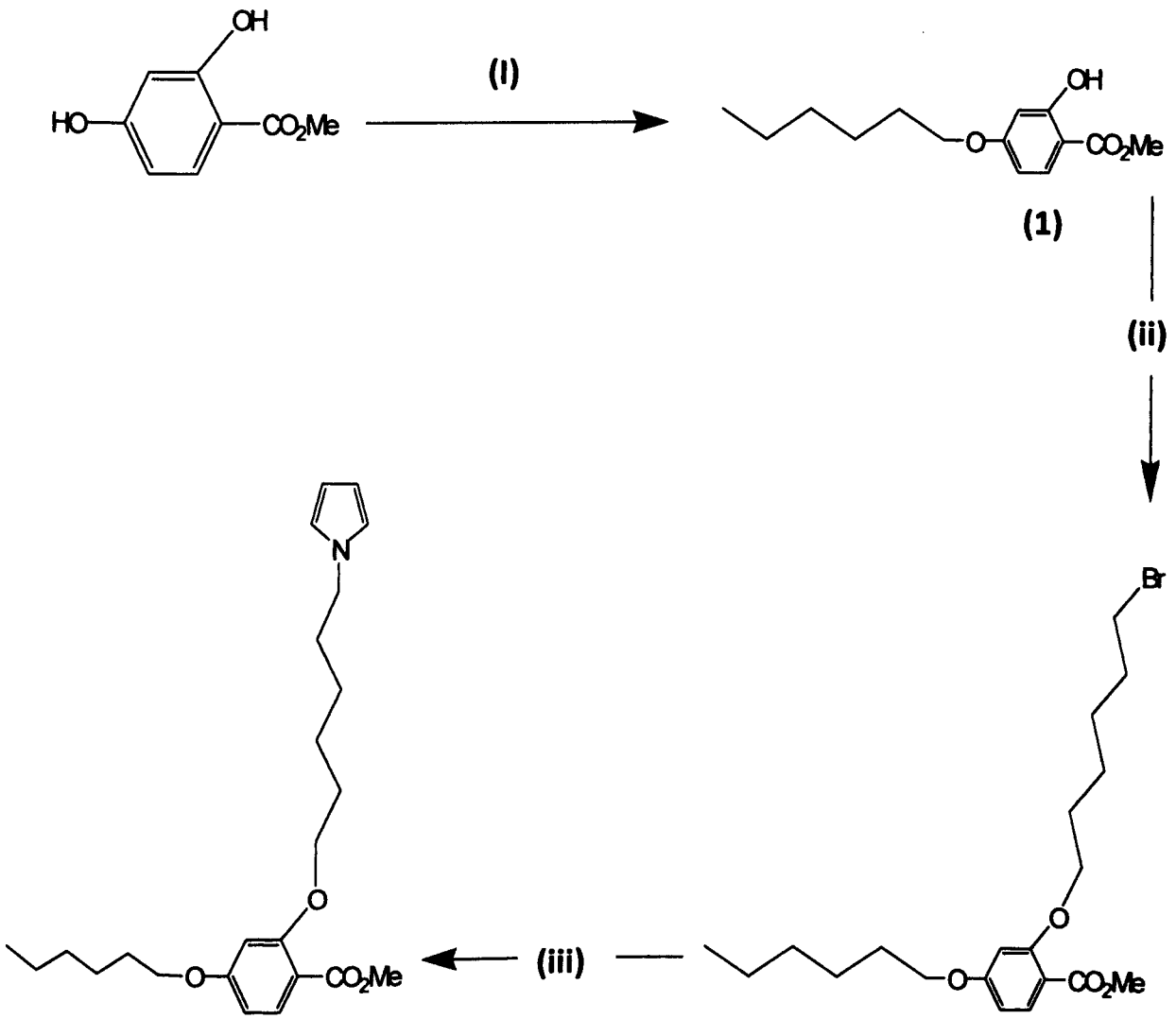


Monomer (I)

***RMM = 401**

***Laterally attached Liquid Crystalline Monomer**

8.4 Reaction Scheme 1 - Synthetic Route for the preparation of Methyl 2-(6-(1H-pyrrol-1-yl) hexyloxy)-4-(hexyloxy)benzoate – Monomer (I)



Monomer (1)

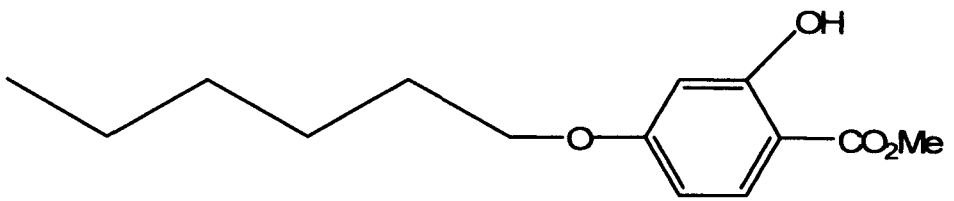
REAGENTS USED

(I) = 1-Bromohexane, anhydrous potassium carbonate, 2-butanone.

(ii) = 1,6-Dibromohexane, anhydrous potassium carbonate, 2-butanone.

(iii) = Anhydrous potassium *tert* butoxide, 18-crown-6, pyrrole, diethyl ether.

8.5 Synthesis of Methyl-2-hydroxy-4-n hexoxybenzoate – Compound (1)



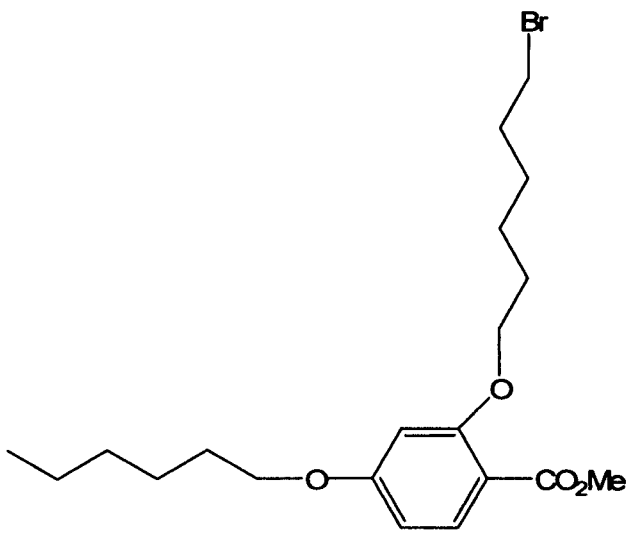
(1)

Preparation:

Methyl 2,4-dihydroxybenzoate (5.0g, 0.03mol), anhydrous potassium carbonate (23.3g, 0.17mol), 1-bromohexane (5.94g, 0.036mol) and dry butanone (60ml) were all placed in a round bottomed flask (250ml) and heated under reflux with the protection of a calcium guard tube for 24 hours. The reaction mixture was monitored by TLC, in which the eluting solvent was a mixture of petroleum ether 60-80°C/ethyl acetate on a ratio of 2:1. The potassium carbonate was filtered off and the solvent was removed in vacuo. The remaining product was a dark yellow oil, which after re-crystallisation from methanol twice, gave very fine white crystals. Overall yield 5.5g, 79%, m.p = 56.9-59.4°C

MS m/z 252 (M^+); **^{1}H NMR δ(CDCl$_3$)** 11.0 (1H, s, OH), 7.7 (1H, d, Ar-H), 7.2 (1H, s, Ar-H), 6.4 (1H, d, ArH), 3.98 (2H, t, O-CH_2), 3.90 (3H, s, O-CH_3), 1.8 (5H, m, CH_2-alkyl), 1.5-1.2 (2H, m, CH_2-akyl-), 0.9 (3H, t, CH_3); **^{13}C NMR 100 MHz** 170.5(C=O), 165.3, 163.8, 131.2, 108.0, 105.2, 101.1(C-ar), 68.3(C-O), 52.0(CH_2-O), 31.6, 29.0, 25.7, 22.6(CH_2), 14.1(CH_3). **IR (thin film)** 3682(Broad OH stretch), 2937(CH_3-CH_2 alkyl chain sp^2), 1721(C=O of ester), 1605(aromatic C=C) **cm^{-1}.**

8.6 Synthesis of 1-bromo-6-(methyl 4-n-hexyloxy-2-oxybenzoate)hexane- Compound (2)



(2)

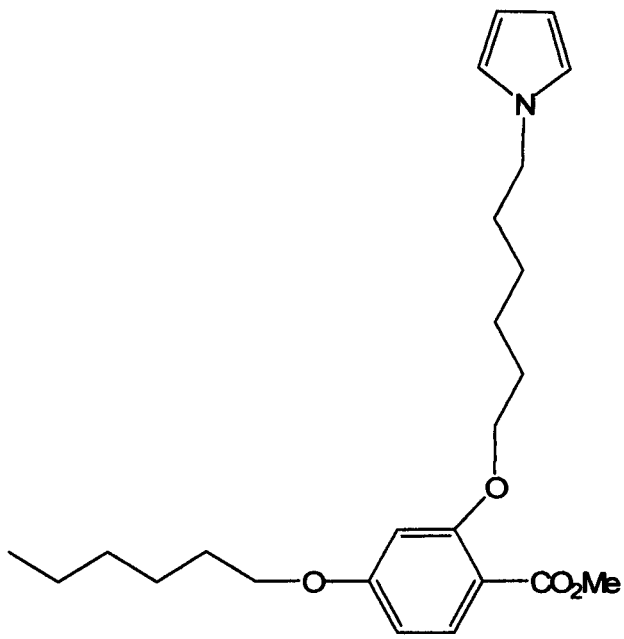
Preparation:

Methyl 2-hydroxy-4-n-hexoxybenzoate (Compound (1)) (1.35g, 0.005mol) was stirred and heated under reflux with anhydrous potassium carbonate (3.5g, 0.025mol), 1,6-dibromohexane (6.1g, 0.025mol excess) in dry butanone (30ml) with the protection of a calcium guard tube for 24 hours. Intermediate TLCs were taken to follow the progress of the reaction and the eluting solvent system was a mixture of petroleum sprit (60-40^{0}C)/ ethyl acetate in a ratio of 3:1 on a silica gel plate. After the reaction had gone to completion the mixture was poured into a beaker of water (50ml), extracted with ethyl acetate (50ml) washed with 5% sodium hydroxide solution (50ml) and water (50ml). Finally the organic layer was dried over magnesium sulphate and the solvent removed in *vacuo* to yield a pale yellow oil as the final product. The crude product was purified by high vacuum distillation (Kugelrohr 87°C/0.1mmHg)

Yield = 1.63g, 74%. Melting point range = 37-40.1°C.

MS m/z 414 & 416(M^+); **^{1}H NMR δ($CDCl_3$)** 7.6 (1H, d, ArH), 7.0 (1H, s, ArH), 6.6 (1H, d, ArH), 4.3 (4H, t, $ArOCH_2C$), 3.7 (3H, s, OCH_3), 3.4 (2H, t, CH_2 Br), 2.0 (6H, m, CH_2CO), 1.7 (8H, m, CCH_2C), 1.5 (2H, m, CH_3CH_2C), 0.9 (3H, t, CH_3C) **^{13}C NMR 100 MHz** 171.4(C=O), 164.3, 162.3, 134.1, 108.0, 106.2, 102.1(C-ar), 67.2(C-O) 52.0, 51.7(CH_2-0) 30.15, 31.1, 31.6, 29.0, 25.7(CH_2), 33.7 (CH_2-Br), 14.1(CH_3). **IR (thin film)** 2937 (CH_3-CH_2 alkyl chain sp^2), 1721 (carbonyl C=O of ester), 1605 (aromatic C-C) **cm^{-1}**

8.7 Synthesis of Methyl 2-(6-(1H-pyrrol-1-yl)hexyloxy)-4-(hexyloxy)benzoate - Monomer (I)



Monomer (I)

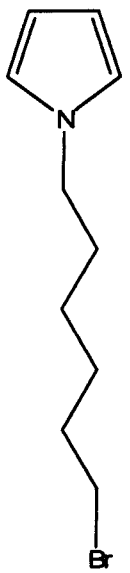
Preparation:

To a continuously stirred mixture of 18-crown-6 (0.38g, 0.004mol) in dry ether (80ml), potassium *tert*-butoxide (1.62g, 0.0145mol) and pyrrole (0.97g, 0.0145mol) were added, and the mixture was left to stir for 15 mins. Compound (2) (1.2g, 0.0029mol) was dissolved in dry ether(15ml) and was added to the reaction mixture. The flask was fitted with a $CaCl_2$ guard tube and left to stir for two days. The reaction was quenched by the addition of water (120ml) and the organic layer extracted with dichloromethane (2x40ml). The combined organic layers were washed with saturated NaCl solution (40ml), water (40ml) and dried over magnesium sulfate. The solvent was removed on the rotary evaporator to yield a pale yellow oil, which was purified by column chromatography using petroleum sprit and ethyl acetate ratio of 2:1. Yield = (0.23g, 45%)

MS m/z 401(M^+); **H^1 NMR δ($CDCl_3$)** 8.6 (1H, d, Ar-H), 7.0 (1H, s, Ar-H), 6.4 (1H, d, Ar-H), 6.2 (2H, d,d Ar-H of py), 5.7 (2H, d, Ar-H of py), 4.1 (2H, t, CH_2-N), 3.9 (2H, t, Ar-O-$\underline{CH_2}$-C), 3.7 (2H, t, C-$\underline{CH_2}$), 3.5 (2H, t, Ar-O-CH_2-C), 3.3 (3H, s, O-CH_3), 1.9 (7H, m, CH_2-alkyl), 1.8 (2H, m, C-CH_2-C-O), 1.5 (6H, m, C-CH_2-C), 1.2 (2H, Q, CH_3-CH_2). **IR (thin film)** 3200 (=CH stretch), 1739 (C=O ester), 1662,1630 (1 substituted pyrrole C=C & C=N vibrations), 1498 (pyrrole ring vibration), 1400 (pyrrole ring vibration) 1281 (N-C oarmatic ring stretch), 1129 (C- esters) **cm^{-1}**

Elemental analysis, Calculated: C (71.79), H (8.79. **Found:** C (71.77), H (8.67).

8.8 Synthesis of Spacer Group (3) which can be incorporated into all Synthetic Routes.



(3)

The above spacer group (compound 3) was synthesised using the method outlined below. Intermediate dendritic and liquid crystal compounds, were then attached to the spacer group via nucleophilic substitution, (S_N2) at either terminal or lateral positions. Compound (3) provided an alternative method for the synthesis of all 7 of the N-substituted pyrrole monomer. Figure 8.1 is a representation of how the spacer group can be incorporated into each synthetic route.

The attachment of Compound (3) to dendritic and liquid crystal intermediates to yield the final N-substituted pyrrole monomers.

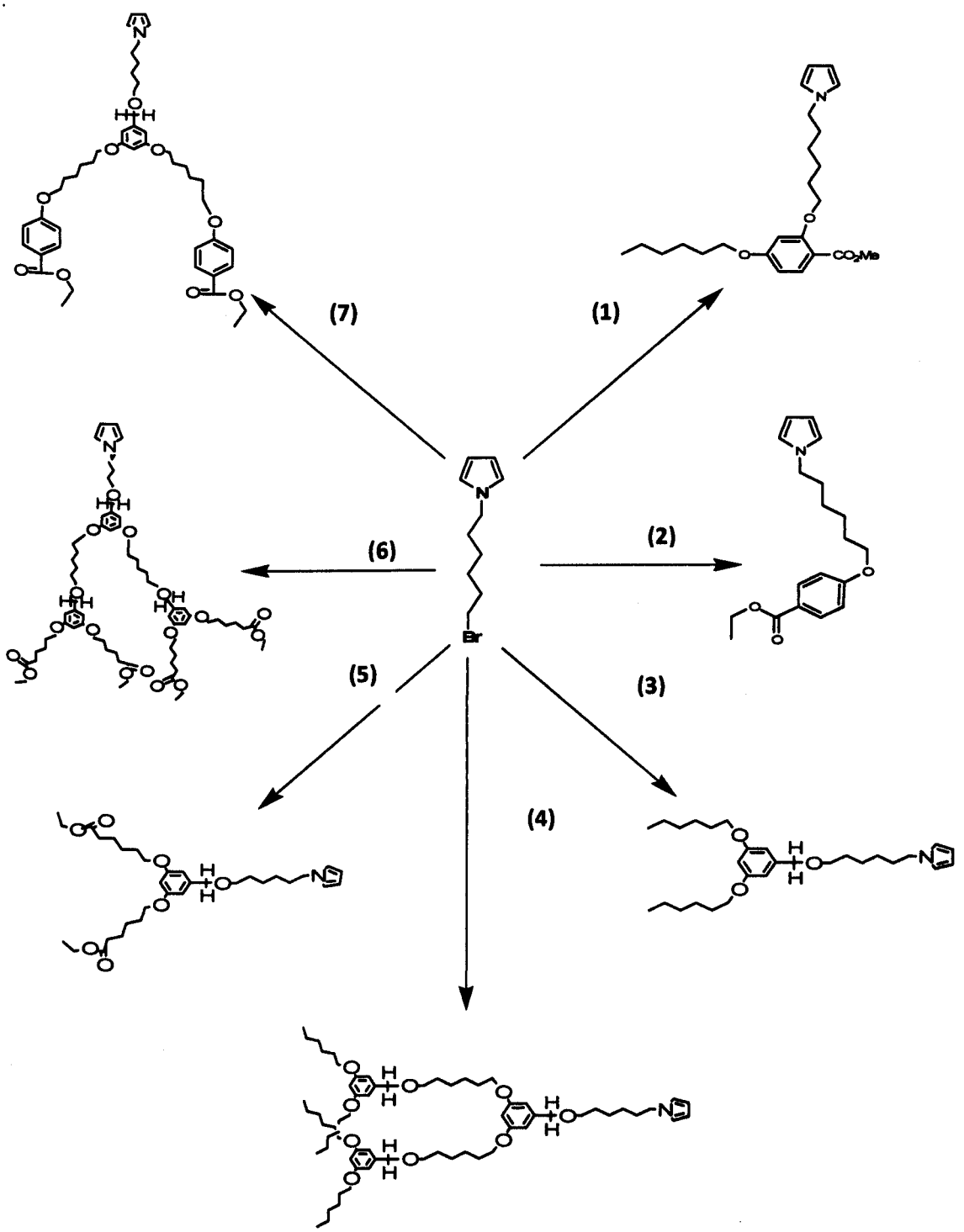


Figure 8.1 A schematic overview, of the attachment of Compound (3) (hexyl spacer group) into each synthetic route to yield the final N-substituted pyrrole monomer.

REAGENTS USED

(1) = Compound (1), anhy K_2C0_3, 2-butanone.

(2) = Ethyl 4-hydroxybenzoate, anhy K_2C0_3, 2-butanone

(3) = Compound (5), 18-crown-6, potassium *tert*-butoxide, DEE.

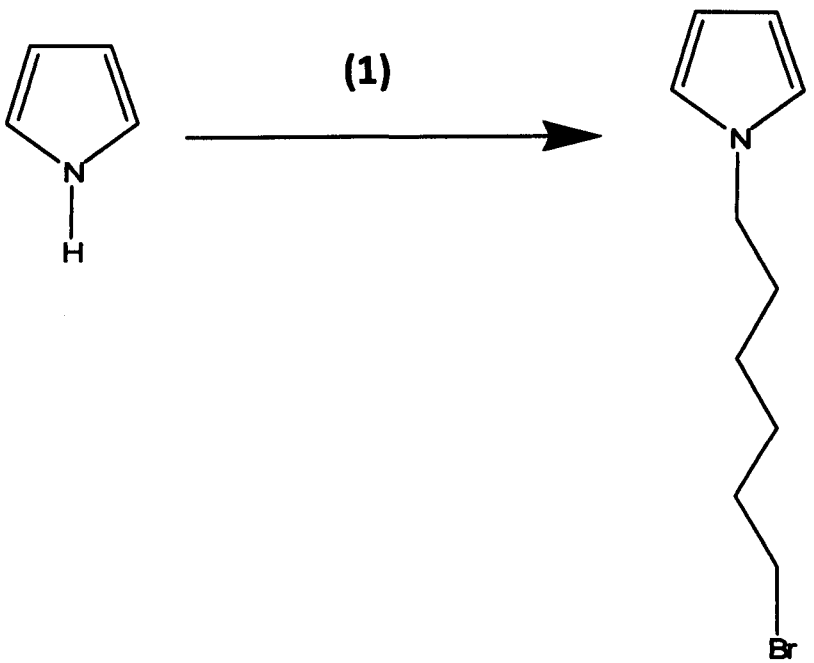
(4) = Compound (7) 18-crown-6, potassium *tert*-butoxide, DEE

(5) = Compound (9) 18-crown-6, potasisum *tert*-butoxide, DEE.

(6) = Compound (11), 18-crown-6, potassium *tert*-butoxide, DEE

(7) = Compound (12) 18-crown-6, potassium *tert*-butoxide, DEE

8.9 Synthesis of 1-(6-bromohexyl)-1H-pyrrole – Spacer Group (3)



(3)

(1) = 18-crown-6, potassium *tert*-butoxide, 1,6-dibromohexane, diethyl ether.

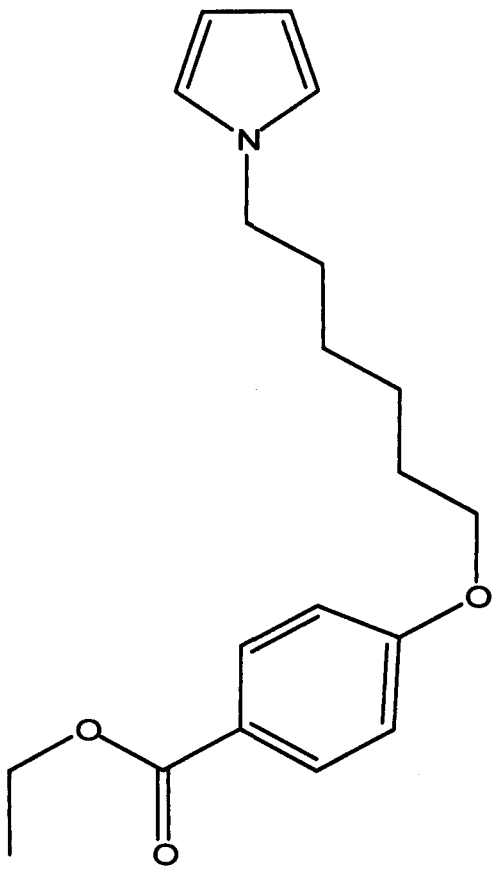
Preparation:

A mixture of 18-crown-6 (0.38g, 0.0014mol) in ether (80ml) was stirred at room temperature and potassium *tert*-butoxide (1.62, 0.0145mol) was added. After 10 minutes pyrrole (0.97g, 0.0145 mol) was added in one portion, a calcium guard tube was fitted and stirring continued for a further 15 minutes. Next, 1,6-dibromohexane was added dropwise carefully over 10 minutes and the reaction mixture was left to stir for 12 hours. The reaction was followed by TLC and upon completion, water (120ml) was added to the reaction mixture and extracted with dichloromethane (2x50ml). The combined organic layers were washed with

saturated NaCl solution (100ml) and dried with $MgSO_4$ for approximately 45 minutes. The solvent was removed under reduced pressure to give a slightly viscous, colourless liquid. From TLC and GC/MS it became apparent that there was a large excess of 1,6-dibromohexane still present, so high vacuum distillation (Kugelrohr 87°C/0.1mmHg) was used to purify the product. The final product was characterised by ^{1}H NMR, ^{13}C NMR, GC/MS and IR. **Yield** = 2.81g, 84%.

MS m/z 229 & 231(M^+); **^{1}HNMR δ($CDCl_3$)** 7.0 (2H, d, C-H of py), 6.5 (2H, d, C-H of py), 3.86 (2H, t, N-$\underline{CH_2}$), 3.30 (2H, t, CH_2-Br), 1.77(4H, m, N-CH_2-$\underline{CH_2}$-CH_2-), 1.4-1.25 (4H, m,CH_2-alkyl), **IR(thin film)** 3100-3000(C-H stretch aromatic), 3000-2850(C-C stretch of alkyl chain), 1600-1400(C=C aromatic, multiple bands), 1281(C-N pyrrole), 600-500(C-Br) cm^{-1}.

8.10 Synthesis of Ethyl 4-(6-(1H-pyrrol-1-yl) hexyloxy)benzoate - Monomer (2)

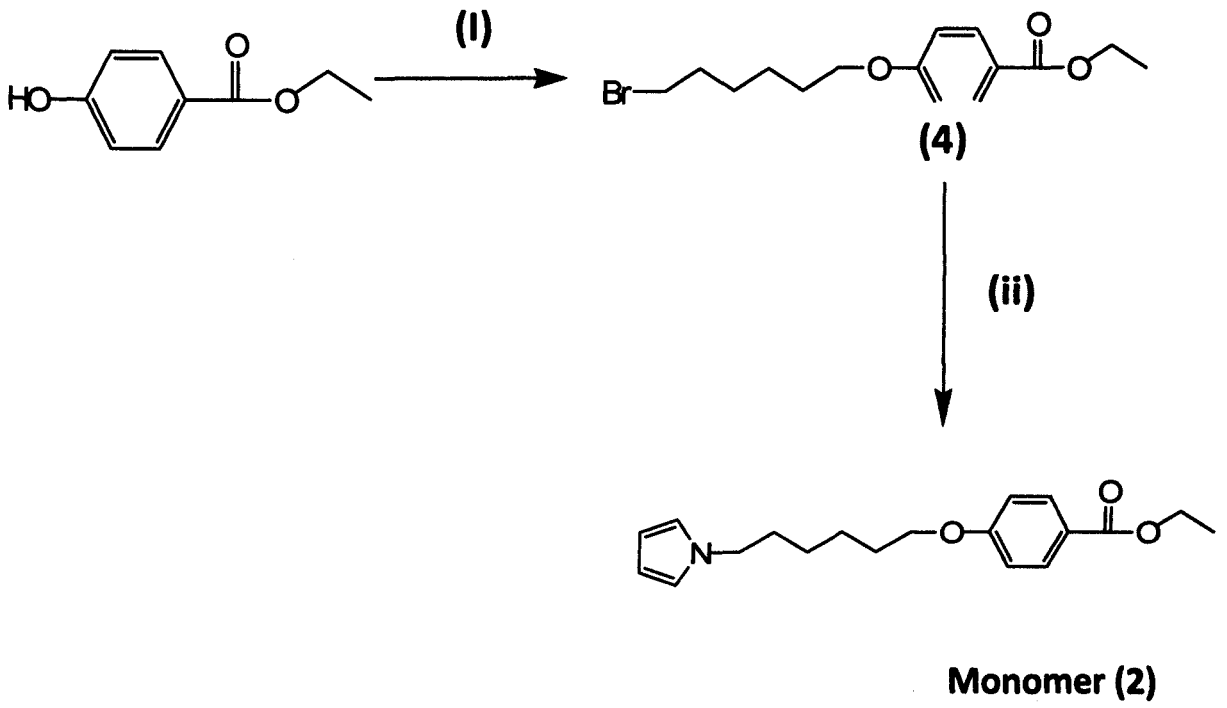


Monomer (2)

***RMM = 315**

***Terminally attached Liquid Crystal Precursor**

8.11 Reaction Scheme 3 - Synthetic Route for the preparation of Ethyl 4-(6-(1H-pyrrol-1-yl)hexyloxy)benzoate - Monomer (2)



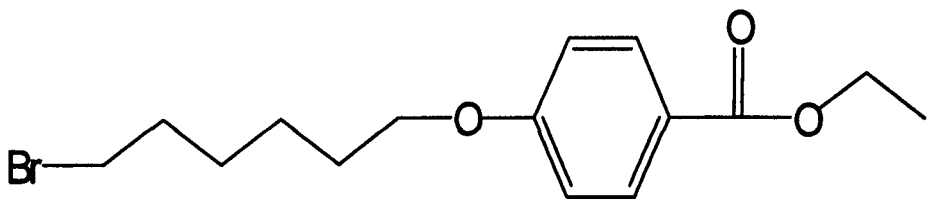
Monomer (2)

REAGENTS USED

(I) = 1,6-dibromohexane, K_2CO_3, dry butanone

(Ii) =18-crown-6, diethyl ether, potassium *tert*-butoxide, pyrrole.

8.12 The Synthesis of Ethyl 4-(6-bromohexyloxy)benzoate- Compound (4)

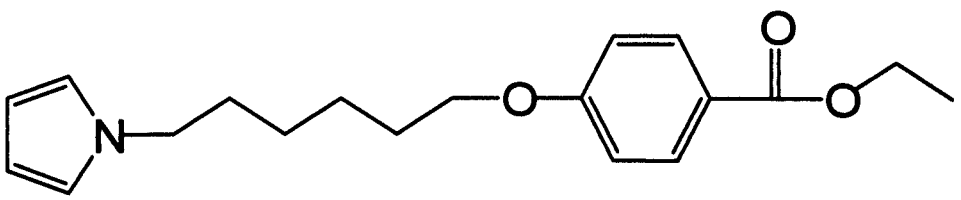


(4)

In a single neck conical flask anhydrous potassium carbonate (12.42g, 0.09mol), was stirred with dried 2-butanone (30ml) for 10 minutes, before ethyl 4-hydroxybenzoate (5g, 0.030mol) was added. Then 1,6-dibromohexane (14.58g,0.06mol) was added dropwise over 15 minutes. The reaction was refluxed for 48 hours and TLC was used to follow the progress. Once the reaction had gone to completion, the mixture was poured into water (50ml) and the crude product was obtained by extraction using DCM (3 x 50ml). The combined organic layers were dried over anhydrous magnesium sulfate for 20 minutes, and then filtered under vacuum. The solvent was removed by reduced pressure to yield a white solid with an oily residue. The crude product was then purified by re-crystallisation using IMS and then by high vacuum distillation (Kugelrohr 87°C/0.1mmHg) to remove the excess 1,6-dibromohexane. Characterisation was then carried out. **Yield = 5.4g, 55%**

MS m/z 328.07 & 330.41 (M^+); **H^1 NMR δ($CDCl_3$)** 7.8 (2H,dd, C-H aromatic), 7.0 (2H,dd,C-H aromatic), 4.3 (2H,quartet, CH_3-$\underline{CH_2}$-O), 4.0 (2H,t,O-CH_2), 3.3 (2H,t,-$\underline{CH_2}$-Br-), 1.7-1.4 (8H, m, -CH_2-alkyl), 1.3 (3H,t,CH_3); **^{13}C NMR 100 MHz** 165.7 (O-C=O), 161.1 (C-O), 131.0, 130.3 (C-H benzene), 127.1 (C-C=O), 117.1 116.1(C-H benzene), 67.4 (O-C), 59.7 (O-C-C), 33.2 (C-Br), 32.2, 30.0, 28.9,26.2 (CH_2), 14.4(C-CH_3); **IR(thin film)** 2940-2870 (CH_2-CH_3 alkyl chain), 1730 (C=O of ester), 1606(C=C aromatic), 1374 1322 (C-O aryl ether), 1274-1195 (C-O), 1163 (O-C=C), 836 (C-H bend) cm^{-1}.

8.13 The Synthesis of Ethyl 4-(6-(1H-pyrrol-1-yl)hexyloxy)benzoate–Monomer (2)



Monomer (2)

Preparation:

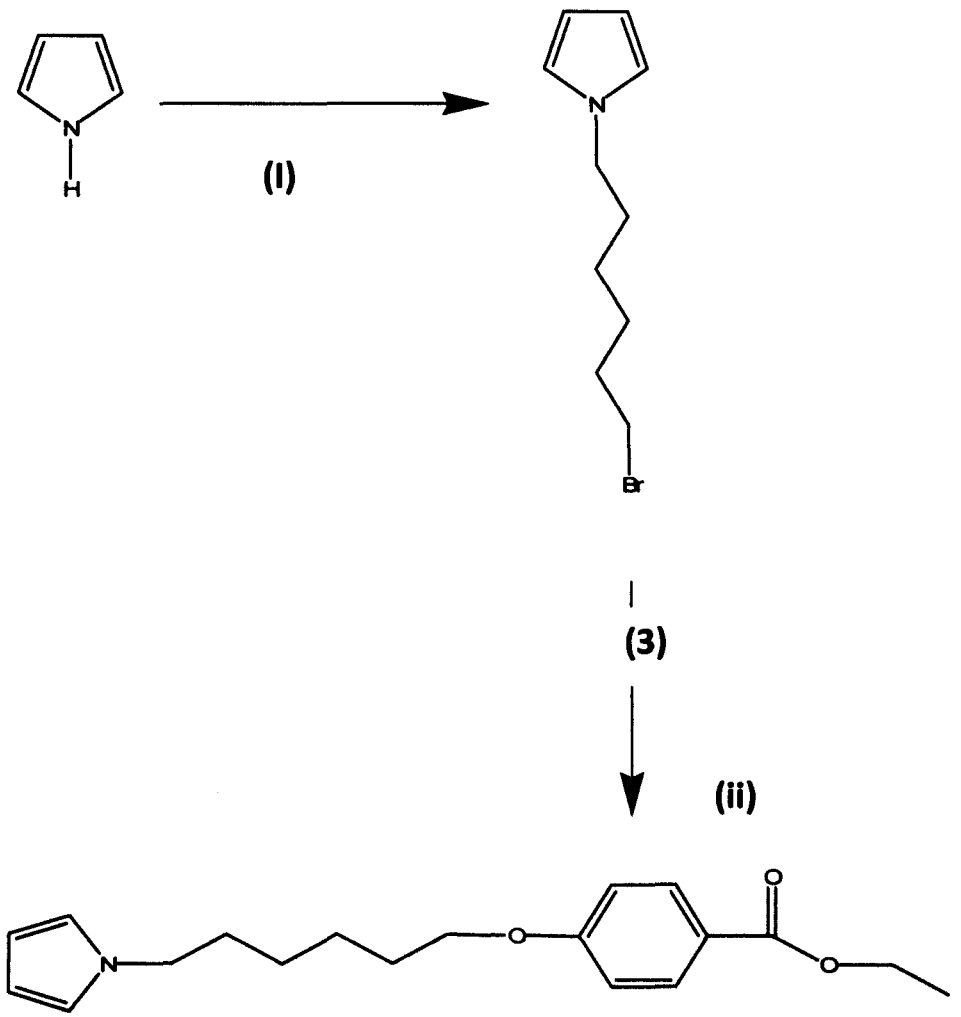
To a single-neck conical flask (100ml) anhydrous potassium *tert*-butoxide (3.41g, 0.030mol) was stirred at room temperature with dried diethyl ether (30ml) for 10 minutes before 18-crown-6 (0.80g,0.0030mol) was added. The mixture was left to stir for a further 10 minutes before pyrrole (2.04g, 0.0304mol) was added in one portion. Compound (4) (2.0g, 0.0060mol) was added to the reaction mixture and a calcium chloride guard tube was fitted and left to stir for 48 hours. The reaction was followed by TLC, and upon completion water (50ml) was added to the reaction mixture. The crude product was obtained by extraction using DCM (3x50ml), and the combined organic layers were washed with saturated NaCl (50ml) solution and water (50ml). The organic layer was dried over anhydrous magnesium sulphate for 20 minutes. The solvent was removed under reduced pressure to yield a dark brown oil. The crude product was purified by column chromatography petroleum ether (60-80^{o}C) and ethyl acetate 2:1 ratio, and characterisation was carried out. Yield = 1.2g, 63%

MS m/z 315.18 (M^+); **H^1 NMR δ($CDCl_3$)** 8.0 (2H, d, Ar-H), 7.0 (2H, d, Ar-H), 6.2 (2H, d,d,C-H of pyrrole), 5.7 (2H, d,d, Ar-H py), 4.2 (4H, q, CH_2-CH_3 overlapping O-CH_2), 3.7 (2H,t,-N-CH_2), 1.9-1.5 (4H, m, -CH_2-alkyl), 1.5 (4H,m, CH_2-alkyl), 1.2 (3H,t, -CH_2-CH_3)

^{13}C NMR 100 MHz 122.5 (2xC-C pyrrole), 108.4 (2xC-C pyrrole), 56.1 (C-N), 33.4 (C-Br), 32.2, 30.0, 28.9,26.2 (CH_2) : **IR(thin film)** 2990-2760 (CH_2-CH_3 stretch alkyl chain), 1732 (C-O of ester), 1600 (C-C aromatic), 1499 (N-H bending), 800-724 (meta substituted benzene ring) cm^{-1}.

Elemental analysis, Calculated: C (72.35), H (7.99). **Found:** C (72.51), H (7.62).

8.14 Alternative Synthetic Route for the preparation of Ethyl 4-(6-(1H-pyrrol-1-yl)hexyloxy) benzoate - Monomer (2)



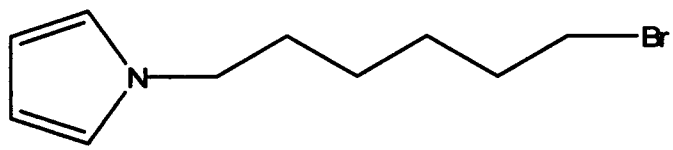
Monomer (2)

REAGENTS USED

(i)= 1,6-dibromohexane, K_2CO_3, dry butanone

(ii) = Ethyl 4-hydroxybenzoate, anhydrous potassium carbonate, 2-butanone

8.15 The Synthesis of 1-(6-bromohexyl)-1H-pyrrole – Compound (3)



(3)

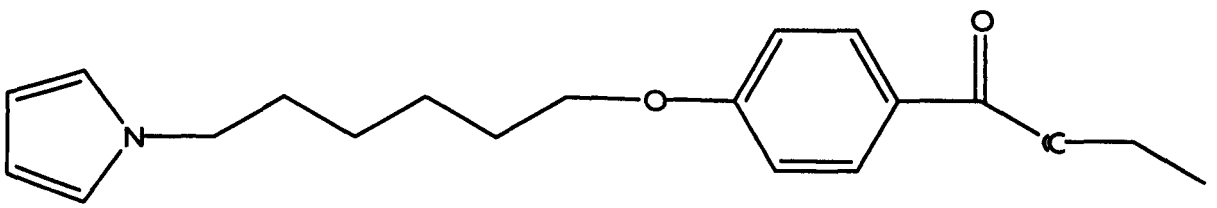
Preparation:

Anhydrous potassium *tert*-butoxide (17.56g, 0.157mol) was stirred in dried diethyl ether (40ml) for 10 minutes befor adding 18-crown-6 (2.36g, 0.009mol). Freshly distilled pyrrole (3.00g, 0.04470mol) was added in one portion and the mixture continued to stir for a further 10 minutes. The mixture was slowly added to 1,6-dibromohexane (27.16g, 0.1117mol) dropwise over 15 minutes. The mixture was fitted with a condenser and calcium guard tube and refluxed for 32 hours. The progress of the reaction was followed by TLC and upon completion, the reaction was quenched by the addition of water (50ml). The crude product was extracted with DCM (3x50ml) and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield a yellow oil and the excess of 1,6-dibromohexane was removed by high vacuum distillation (Kugelrohr 87^{O}C/0.1mmHg). Yield = 7.2g, 70%

Yield = 2.81g, 84%. **MS m/z** 229 & 231(M^{+}); **^{1}HNMR δ($CDCl_3$)** 7.0 (2H, d, C-H of py), 6.5 (2H, d, C-H of py), 3.86 (2H, t, N-$\underline{CH_2}$), 3.30 (2H, t, CH_2-Br-), 1.77 (4H, m, N-CH_2-$\underline{CH_2}$-CH_2-), 1.4-1.25 (4H, m, CH_2-alkyl), **IR(thin film)** 3100-3000(C-H stretch aromatic), 3000-2850(C-C

stretch of alkyl chain), 1600 (C=C aromatic, multiple bands), 1281(C-N pyrrole), 579 532 (C-Br) cm^{-1}.

8.16 The Synthesis of Ethyl 4-(6-(1H-pyrrol-1-yl)hexyloxy)benzoate – Monomer (2)



Monomer (2)

Preparation:

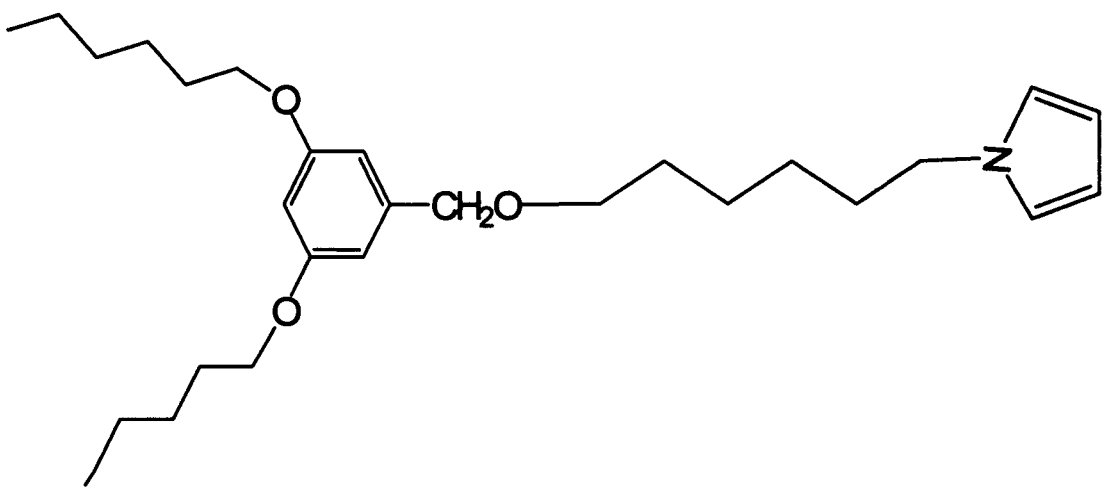
In a round bottom flask (150 cm^3), anhydrous potassium carbonate (0.9g, 0.006mol) was stirred in dry butanone (100ml) for 15 minutes before ethyl 4-hydroxybenzoate (0.2g, 0.0014mol) was added. Compound (3) (0.5g, 0.002mol) was added to the reaction mixture, a reflux condenser fitted with a calcium guard tube was attached, and the reaction proceeded for 24 hours. The progress of the reaction was followed by TLC, and upon completion, the reaction was quenched with water and extracted with dichloromethane (3x50ml). The combined organic layers were washed with saturated sodium chloride solution (3x50ml) and dried with magnesium sulfate. The crude product was filtered by Buchner filtration and the solvent was removed under reduced pressure. The product was purified by column chromatography using DCM as the eluent to give a final product as yellow oil. (0.27g, 45%)

MS m/z 315.18 (M^+); **H^1 NMR δ($CDCl_3$)** 8.0 (2H, d, Ar-H), 7.0 (2H, d, Ar-H), 6.2 (2H,C-H of py), 5.7 (2H, d,d, Ar-H py), 4.2 (4H, q, CH_2-CH_3 overlapping O-CH_2), 3.7 (2H,t,-N-CH_2), 1.9-1.5 (4H, Multiplet, -CH_2-alkyl), 1.5 (4H,m, CH_2-alkyl), 1.29 (3H,t, -CH_2-CH_3) **^{13}C NMR 100 MHz** 122.5 (2xC-C pyrrole), 108.4 (2xC-C pyrrole), 56.1 (C-N), 33.4 (C-Br), 32.2, 30.0, 28.9,26.2

(CH_2) : **IR(thin film)** 2906-2770 (CH_2-CH_3 stretch alkyl chain), 1709 (C-O of ester), 1600(C=C aromatic), 1549 (N-H bending) 1216 (O-C=O)cm^{-1}.

Elemental analysis, Calculated: C (72.35), H (7.99). **Found:** C (72.51), H (7.62).

8.17 The Synthesis of 1-(6-(3,5 bis(hexyloxy) benzyloxy)hexyl)-1H-pyrrole-Monomer (3)

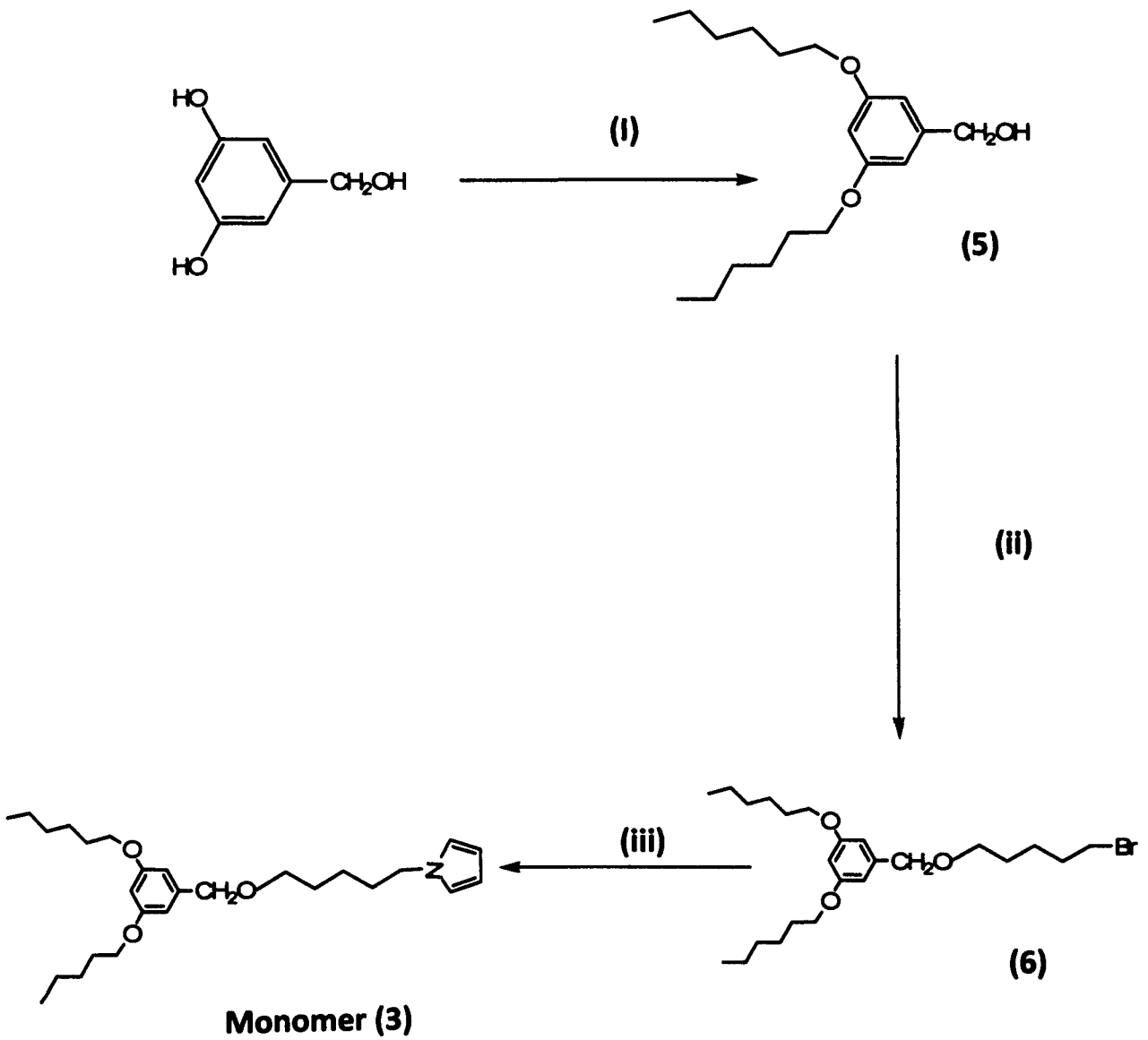


Monomer (3)

***RMM = 457**

***First generation Dendritic monomer**

8.18 Reaction Scheme 4- The preparation of 1-(6-(3,5 bis(hexyloxy)benzyloxy)hexyl)-1H-pyrrole - Monomer (3)



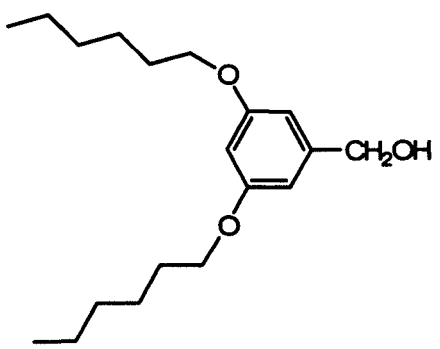
REAGENTS USED

(I) = Anhydrous potassium carbonate, 2-butanone, 1-bromohexane

(ii) = 1,6-dibromohexane, potassium *tert*-butoxide, 18-crown-6, DEE

(iii) = Pyrrole, potassium *tert*-butoxide, 18-crown-6, DEE

8.19 The Synthesis of 3,5-bis(hexyloxy)phenyl) methanol - Compound (5)



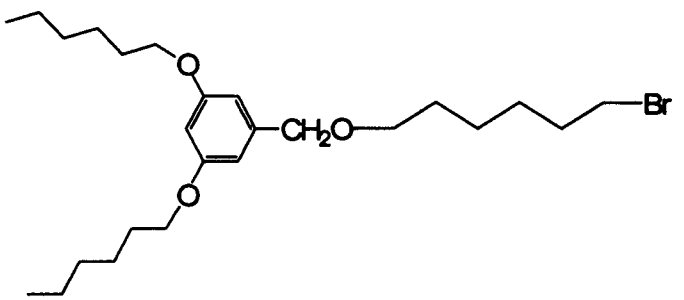
(5)

Preparation:

In a round bottom flask (150 ml), 3,5-dihydroxybenzyl alcohol (1g, 0.0071mol), anhydrous potassium carbonate(11.76g, 0.0147 mol), and 1-bromohexane(2.4g, 0.014mol) was added with butanone (75ml). A condenser equipped with a calcium chloride guard tube was attached and the reaction mixture was refluxed for 12 hours. Upon completion as indicated by TLC the reaction was quenched by pouring the mixture into distilled water (100ml). The product was then extracted using diethyl ether (3x50 ml) and the combined organic layers were dried over magnesium sulfate. The product was collected by filtering off the salt using Buchner filtration and the solvent was removed under reduced pressure. Characterisation tests indicated the absence of impurities; therefore no purification was required at this stage. The final product was a pale orange oil.

Yield= (1.37g, 65%). **MS m/s** 308(M^+); **IR (Thin film)** 3500(Broad OH stretch of CH_2-OH), 2890-2700 (CH_2-alkyl), 1579(C=C aromatic) 1253(strong OH bending), 832(meta substituted ring, 3 adjacent H's) ; **H^1 NMR δ($CDCl_3$)** 6.7 (1H, 2, Ar-H), 6.4 (2H, d, Ar-H), 5.5 (1H, s, CH_2OH), 4.8 (2H, d,, Ar-CH_2-O), 4.2 (4H, t, O-CH_2), 3.0-2.0 (16H,m, CH_2-alkyl), 1.29 (6H,t, -CH_2-CH_3).

8.20 The Synthesis of 1-((6-bromohexyloxy) methyl)-3,□-bis(hexyloxy)benzene- Compound (6)



(6)

Preparation:

To a solution of 18-crown-6 (0.8g, 0.003 mol) in dry ether (100ml), potassium *tert*-butoxide (3.34g, 0.03 mol) was added and the mixture was continuously stirred at room temperature while compound (5) (5.39g, 0.017□ mol) was added. A calcium chloride guard tube was fitted and the reaction mixture was left to stir for 15 minutes. Over a period of 10 minutes, 1,6-dibromohexane (30g 0.12 mol) was added dropwise to the flask, and the reaction was left to proceed for 24 hours. During this time TLC and GC/MS were carried out to trace the progress of the reaction and once satisfactory results were obtained the reaction was quenched with water (150 cm^3). The crude product was extracted with ether (3 x 50 cm^3), washed with saturated NaCl solution (3x50 cm^3), and the combined organic layers were dried with $MgSO_4$. Lastly the solvent was removed under reduced pressure and the first attempt to purify the product was by column chromatography using DCM as the eluting solvent. This was unsuccessful as the final yield of the product was reduced significantly, as some of it was trapped in the column. So high vacuum distillation (Kugelrohr 0.01mmHg/70^{0}C) was used to remove the excess 1,6-dibromohexane. Yield = 5.01g, 61%

MS m/z 470, 472 (M^+) ; **IR (thin film)** 2934(CH_2-CH_3 alkyl chain), 1604 (C-C aromatic), 837(3 adjacent H's in benzene ring, meta substitution) 685-775 (C-Br) **cm^{-1}** **^{1}H NMR δ($CDCl_3$)** 6.7

(1H, 2, Ar-H), 6.4 (2H, d, Ar-H), 4.8 (2H, s, Ar-CH_2-O), 4.2 (4H, t, O-CH_2), 3.5 (2H, t, O-CH2-), 3.2 (2H, t, CH_2-Br) 2.7-1.5 (24H,m, CH_2-alkyl), 1.29 (6H,t, -CH_2-CH_3).

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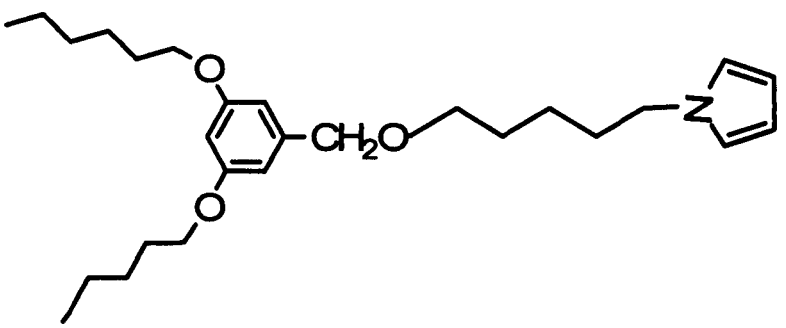
8.21 The Synthesis of 1-(6-(3,5-bis(hexyloxy) benzyloxy)hexyl)-1H-pyrrole-Monomer (3)



Monomer (3)

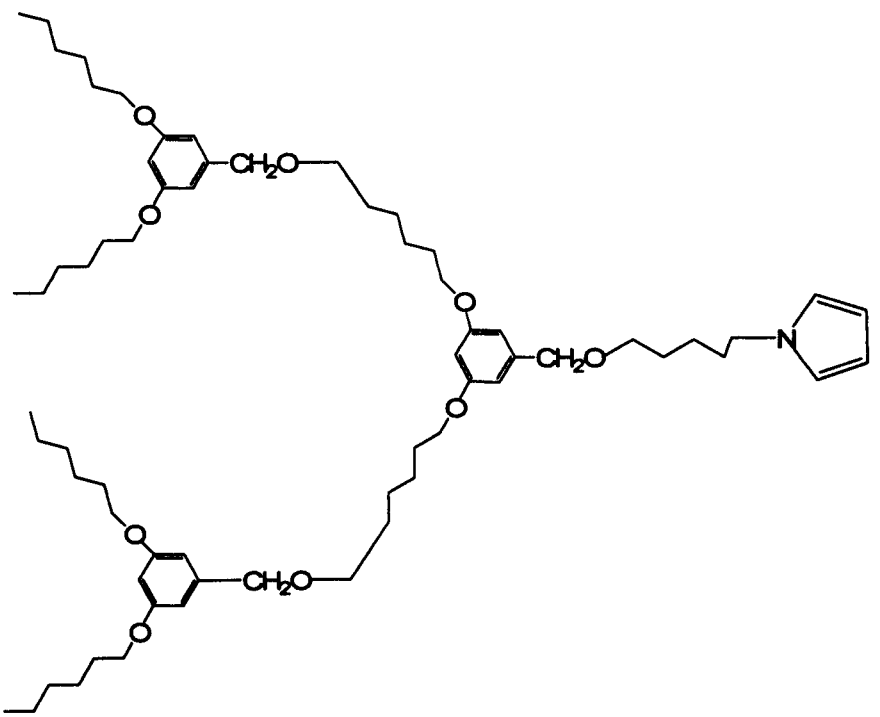
Preparation:

To a 150 cm^3 single neck conical flask, potassium *tert*-butoxide (3.36g, 0.03mol), 18-crown-6 (0.8g, 0.003mol), pyrrole (2.0g, 0.03mol) and diethyl ether (150ml) were stirred for 15 minutes before compound (6) (3g, 0.006mol) was added to the mixture. A calcium chloride guard tube was attached and the reaction proceeded for 36 hours. Upon completion, the reaction mixture was poured into distilled water and extracted with dichloromethane (3x50ml). The combined organic layers were washed several times with saturated sodium chloride solution and dried over magnesium sulfate. After removing the salt by Buchner filtration, the filtrate was collected and transferred to a pre-weighed round bottom flask. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2) in which the eluent was 2:1 solvent mixture of hexane : dichloromethane. The final product was a light brown oil. Yield = 0.92g, 34%

MS m/z 457(M^+) ; **^{1}H NMR** δ(**$CDCl_3$**) 7.0 (2H, d,d, Ar-H pyrrole), 6.5 (1H, t, Ar-H), 5.9 (2H, d, Ar-H), 5.4 (2H, d, Ar-H py), 4.7 (2H, s, Ar-CH_2-O), 3.8-3.3 (8H, t, O-CH_2 & N-CH_2-overlapping), 1.8-1.5 (12H, m,CH2-alkyl) 1.4-1.2 (12H, m, CH_2-alkyl), 0.9 (6H,t, -CH_2-CH_3) **IR (thin film)** 3200 (=CH stretch), 2974-2600 (C-C) 1596(C-C aromatic),1738 (C=O ester), 1662,1620 (1 substituted pyrrole C=C & C=N vibrations), 1508 (pyrrole ring vibration), 1400 (pyrrole ring vibration) 1271 (N-C aromatic ring stretch) **cm^{-1}.**

Elemental analysis, Calculated: C (71.79), H (8.79). **Found:** C (71.77), H (8.67). **cm^{-1}**

8.22 Synthesis of 1-(6-(3,5-bis(6-(3,5-bis (hexyloxy)benzyloxy)hexyloxy)benzyloxy) hexyl)-1H-pyrrole- Monomer (4)

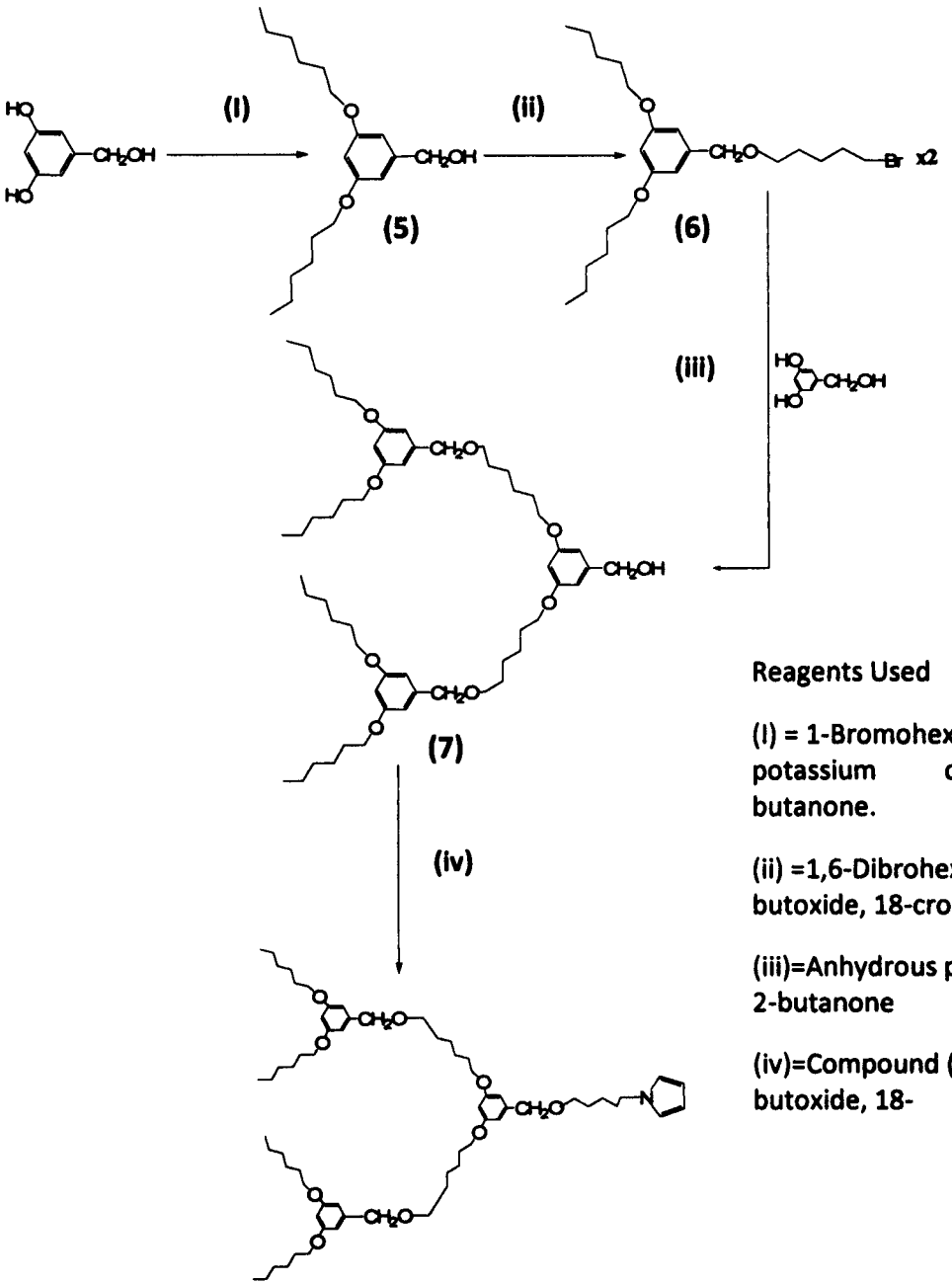


Monomer (4)

***RMM = 1069**

* 2nd Generation Dendritic Monomer

8.23 Reaction scheme for the preparation of – Monomer (4)



Monomer (4)

Reagents Used

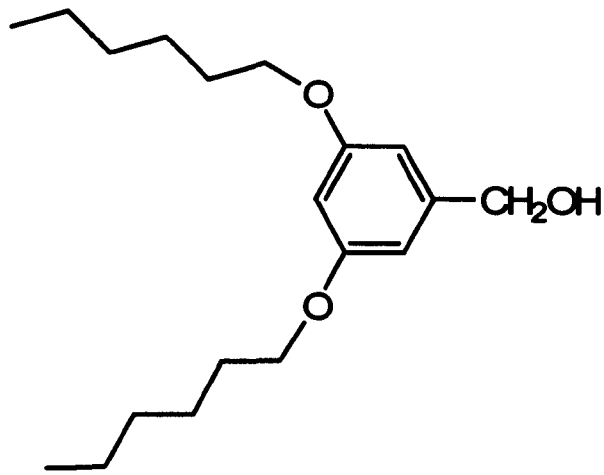
(I) = 1-Bromohexane, anhydrous potassium carbonate, 2-butanone.

(ii) =1,6-Dibrohexane, potassium *tert*-butoxide, 18-crown-6, ether.

(iii)=Anhydrous potassium carbonate, 2-butanone

(iv)=Compound (3), potassium *tert*-butoxide, 18- crown-6, DEE

8.24 The Synthesis of 3,5-bis(hexyloxy)phenyl) methanol - Compound (5)



(5)

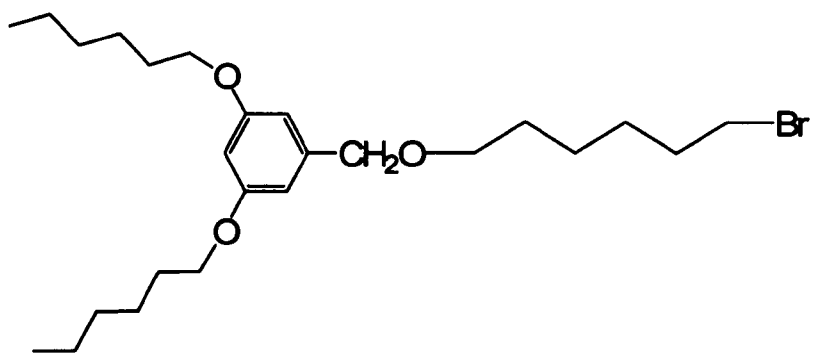
Preparation:

To a round bottom flask (150 ml), 3,5-dihydroxybenzyl alcohol (1g, 0.0071mol), anhydrous potassium carbonate(11.76g, 0.0147), 1-bromohexane(2.4g, 0.014mol) and butanone (75ml) were added. A condenser equipped with a calcium chloride guard tube was attached and the reaction mixture was refluxed for 12 hours. Upon completion as indicated by TLC (hexane: ethyl acetate 50:50) the reaction was quenched by pouring the mixture into distilled water. The product was then extracted using diethyl ether (3x50 ml) and the combined organic layers were dried over magnesium sulphate. The product was collected and the solvent was removed under reduced pressure. Characterisation tests indicated that there was not a significant amount of impurities therefore no purification was required at this stage. The final product was a pale orange oil. Yield= (1.37g, 65%).

MS m/s 308 (M^+); **H^1 NMR δ($CDCl_3$)** 6.7 (1H, 2, Ar-H), 6.4 (2H, d, Ar-H), 5.5 (1H, s, CH_2OH), 4.8 (2H, d,, Ar-CH_2-O), 4.2 (4H, t, α-CH_2), 3.0-2.0 (16H,m, CH_2-alkyl), 1.29 (6H,t, -CH_2-CH_3); **IR** (thin film) 3385(Broad OH stretch of CH_2-OH), 2870(alkyl chain CH_3-CH), 1599(aromatic C=C

bond) 1279(strong OH bending), 1160(C-O stretch of secondary alcohols), 832(meta substituted ring, 3 adjacent H's) cm^{-1}

8.25 The Synthesis of 1-((6 bromohexyloxy) methyl)-3,5-bis(hexyloxy)benzene- Compound (6)



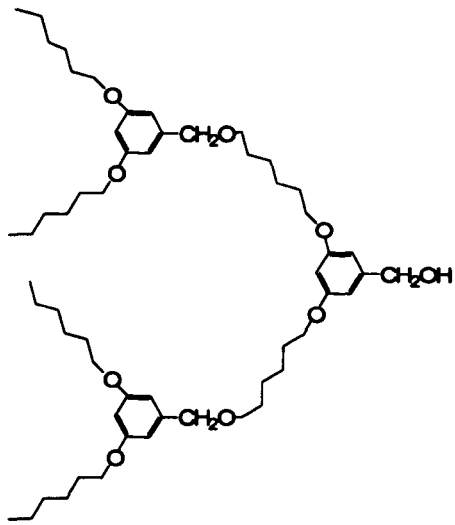
(6)

Preparation:

To a solution of 18-crown-6 (0.8g, 0.003 mol) in dry ether (100ml), potassium *tert*-butoxide (3.34g, 0.03 mol) was added and the mixture was continuously stirred at room temperature while compound (5) (5.39g, 0.0175 mol) was added. A calcium chloride guard tube was fitted and the reaction mixture was left to stir for 15 minutes. Over a period of 10 minutes, 1,6-dibromohexane (30g 0.12 mol) was added dropwise to the flask, and the reaction was left to proceed for 24 hours. During this time TLC & GCMS were carried out to trace the progress of the reaction and once satisfactory results were obtained the reaction was quenched with water (100 cm^3) and extracted with ether (3x 50 cm^3). The combined organic layers were washed with saturated NaCl solution (50 cm^3), and dried with $MgSO_4$. Lastly the solvent was removed under reduced pressure, and the first attempt to purify the product was by column chromatography using DCM as the eluting solvent. This was unsuccessful as the final yield of the product was reduced significantly, as some of it was trapped in the column. So high vacuum distillation (Kugelrohr 0.01mmHg/70^{0}C) was used to remove the excess of 1,6-dibromohexane. Yield = 5.01g, 61%

MS m/z 470, 472 (M^+) ; **H^1 NMR δ($CDCl_3$)** 6.7 (1H, 2, Ar-H), 6.4 (2H, d, Ar-H), 4.8 (2H, s, Ar-CH_2-O), 4.2 (4H, t, O-CH_2), 3.5 (2H, t, O-CH2-), 3.2 (2H, t, CH_2-Br) 2.7-1.5 (24H,m, CH_2-alkyl), 1.29 (6H,t, -CH_2-CH_3) **IR (thin films)** 2989-2765 (CH_2-CH_3 alkyl chain), 1596(C-C aromatic), 1218 (O-C=O), 837 (meta substitution), 712 (CH_2-Br) **cm^{-1}**

8.26 The Synthesis of - Compound (7)

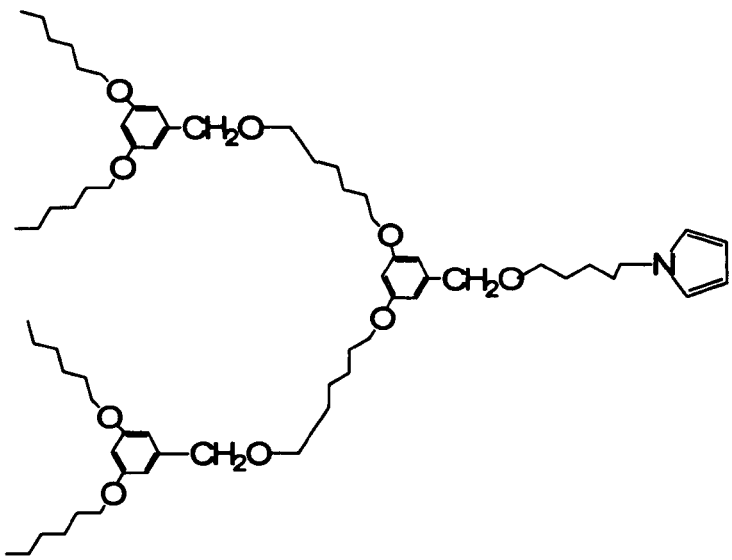


(7)

Preparation:

To a mixture of anhydrous potassium carbonate (2.6g, 0.018mol), 3,5-hydroxybenzyl alcohol (0.37g, 0.0025mol) dissolved in 2-butanone (100ml), compound (6) was added in one portion. A reflux condenser tube was fitted, and the reaction was left to proceed for 28 hrs. Upon completion, as determined by TLC, water (100ml) was added to the reaction mixture and the crude product was extracted using DCM (3x100ml). The combined organic layers were washed with saturated NaCl solution (3x100ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a cream coloured solid. The crude product was purified by column chromatography using a solvent mixture of chloroform and hexane (1:2 ratio). The solvent was removed under reduced pressure to give a white solid as the final product. Yield = 1.97g, 42% Yield= (1.37g, 65%). **MS m/s** 920.5 (M^+); **H^1 NMR** δ(**$CDCl_3$**) 6.7 (3H, 2, Ar-H), 6.4 (6H, d, Ar-H), 5.5 (1H, s, CH_2OH), 4.8 (10H, m, Ar-CH_2-O), 4.2 (12H, t, O-CH_2), 3.0-1.5 (48H,m, CH_2-alkyl), 1.29 (12H,t, -CH_2-CH_3). **IR (thin film)** 3375 (CH stretch of CH_2-OH), 2870(alkyl CH_3-CH), 1579(aromatic C-C bond) 1297(strong OH bending), 832(meta substituted ring) **cm^{-1}**

8.27 Preparation of 1-(6-(3,5-bis(6-(3,5 bis (hexyloxy)benzyloxy)hexyloxy)benzyloxy) hexyl)-1H-pyrrole- Monomer (4)



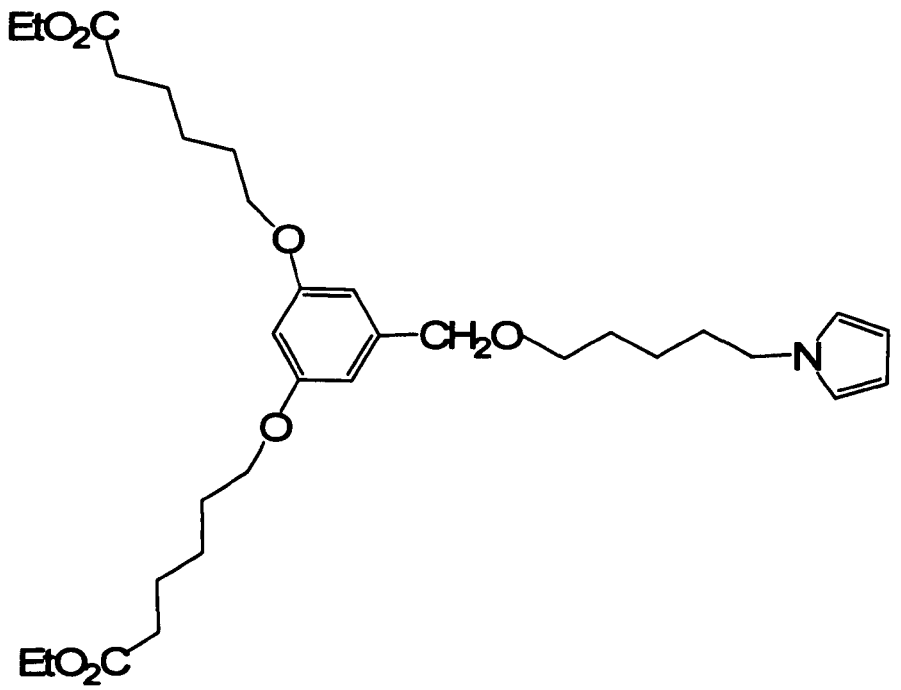
Preparation:

A mixture of 18-crown-6 (0.1g, 0.001mol), in ether (80ml), was stirred at room temperature and potassium *tert*-butoxide (0.17g, 0.0015mol) was added. The mixture was stirred while compound (7) (1g, 0.001mol) was added in one portion. A $CaCl_2$ guard tube was fitted and stirring continued for 15 mins. Compound (3) (0.3g, 0.0015mol) dissolved in ether (20ml) was added dropwise to the reaction mixture over a period of 10 min. The reaction was stirred for 24 hours. Water (120ml) was added to the reaction mixture and this was extracted with dichloromethane (2x40ml). The combined organic layers were washed with saturated NaCl solution (40ml) and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield a dark brown semi-solid. The crude product was purified by column chromatography using a mixture of chloroform:hexane, 1:3 ratio. Yield= 0.3g, 28%.

MS m/s 1069.2(M^+);; **H^1 NMR** δ(**$CDCl_3$)** 7.0 (2H, d,d, Ar-H pyrrole), 6.5 (3H, t, Ar-H), 5.9 (6H, d, Ar-H), 5.4 (2H, d, Ar-H py), 4.8 (10H, m, Ar-CH_2-O), 4.2 (12H, t, O-CH_2), 3.6 (2H, t, CH_2-N), 3.0 (2H, t, CH_2-O-CH_2), 2.5-1.2 (56H,m, CH_2-alkyl), 1.0 (12H,t, -CH_2-CH_3) **IR (thin film)** 2975(alkyl chain CH_3-CH), 1579(aromatic C=C bond) 1405 1399 (py ring vibration), 1223 (N-C aromatic ring stretch), 832(meta substituted) **cm^{-1}**

Elemental analysis, Calculated: C (71.79), H (8.79). **Found:** C (71.77), H (8.67).

8.28 Synthesis of Monomer (5)

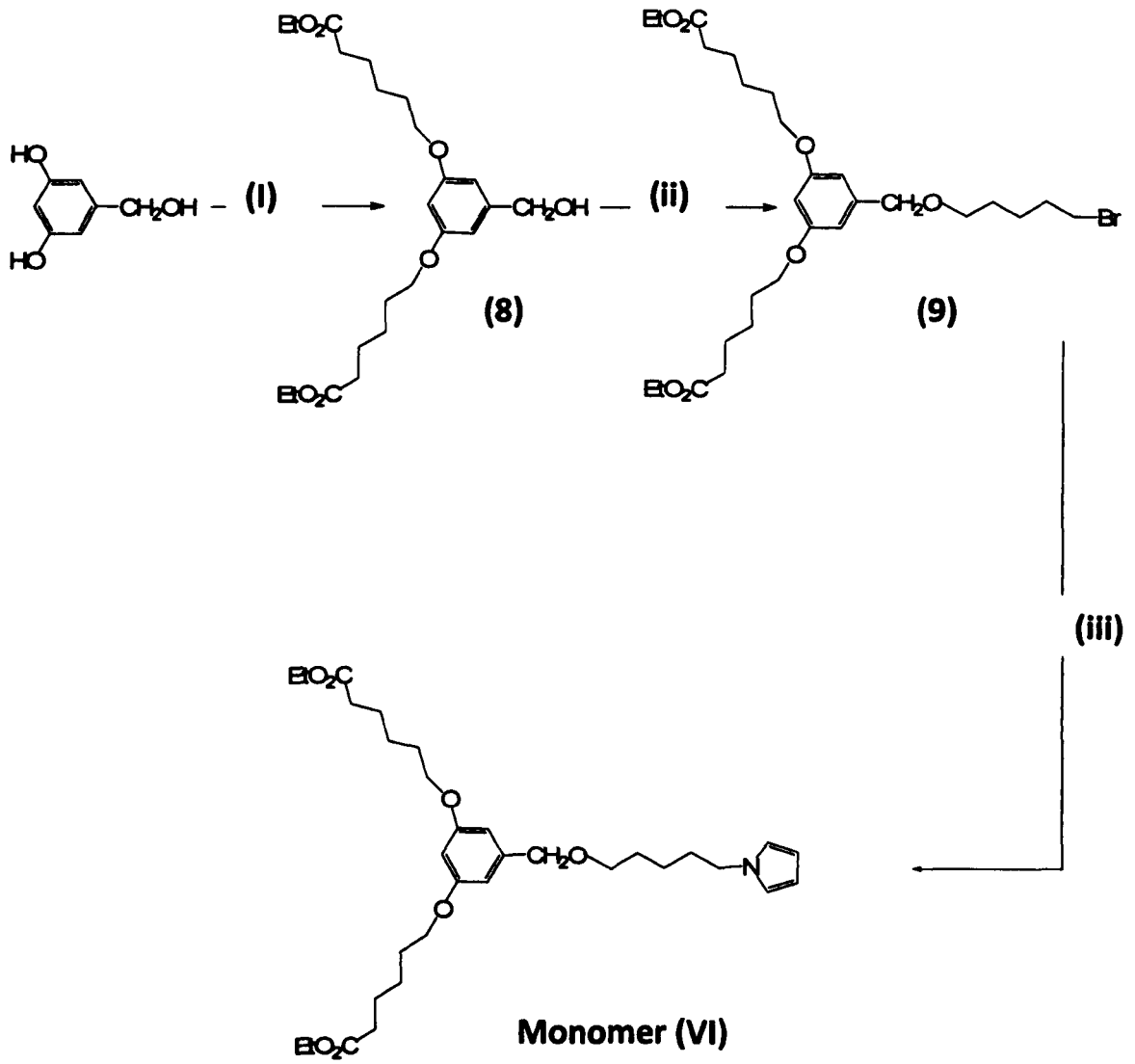


Monomer (5)

***RMM = 573**

***First generation Dendritic Precursor to hydrophilic terminal alkyl chain**

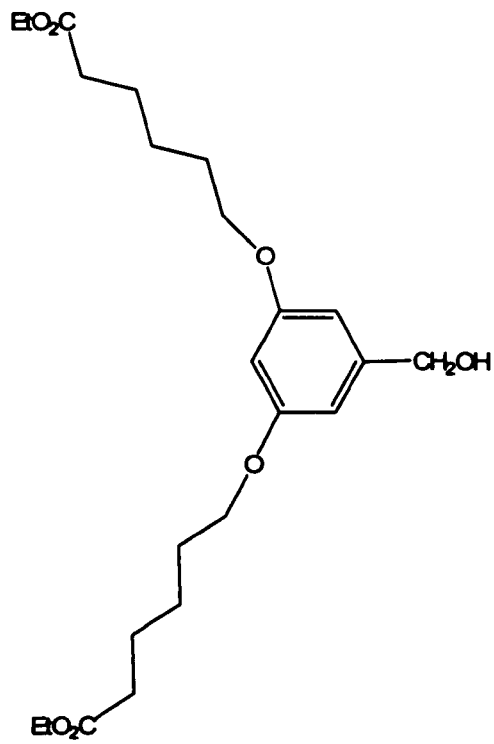
8.29 Synthetic Route for the Preparation of Monomer (5)



Reagents used in each step:

(I)= Anhydrous potassium carbonate, 2-butanone, ethyl 6-bromo-hexanoate.
(ii)= 1,6-Dibromohexane, 18-crown-6, potassium *tert*-butoxide, diethyl ether.
(iii)= Pyrrole, 18-crown-6, potassium *tert*-butoxide, diethyl ether.

8.30 The Synthesis of Diethyl 6,6-(5 (hydroxymethyl)-1,3- phenylene)bis (oxy)dihexanoate) Compound (8)



(8)

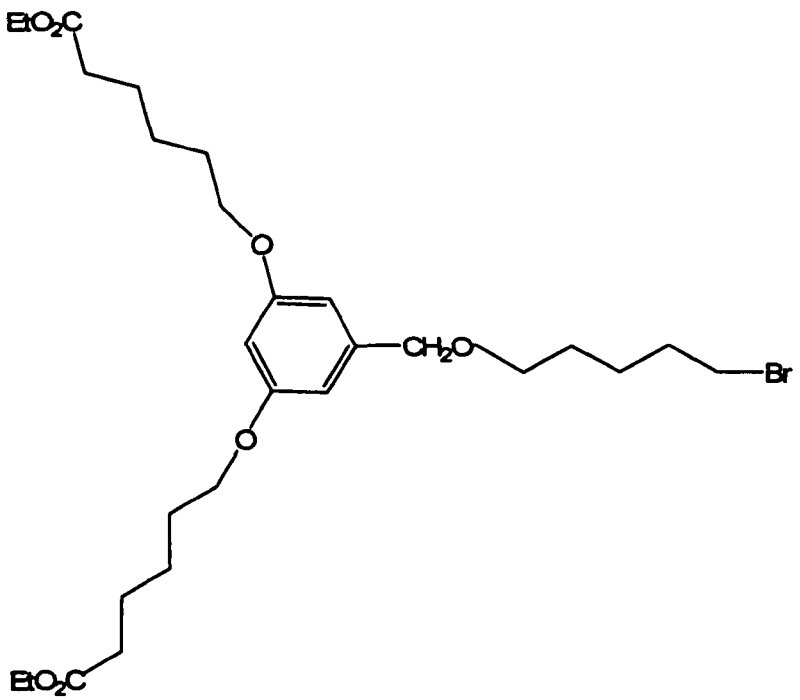
Preparation:

A reaction mixture of anhydrous potassium carbonate (15g, 0.110 mol) dissolved in dried diethyl ether (50ml) was stirred for 10 minutes before 3,5-dihydroxy benzyl alcohol (3g, 0.0214mol) and ethyl 6-bromohexanoate (9.55g, 0.043mol) were added. A reflux condenser was fitted and the reaction was left to proceed for 24 hours. Thin layer chromatography was used to follow the progress of the reaction. Upon completion, the reaction was quenched by the addition of water (50ml) and the crude product was obtained by extraction with dichloromethane (3x50ml). The organic layer was dried over anhydrous magnesium sulfate for 15-20 minutes and filtered under vacuum. The solvent was removed in *vacuo,* yielding a light brown oil. The crude product was

purified by high vacuum distillation to remove the excess of ethyl 6-bromohexanoate and characterisation tests were carried out to identify the final product. Yield= 7.4g, 81%

MS m/z 424 (M^+); **H^1 NMR** δ(**$CDCl_3$)** 6.49(1H, t, Ar-C-H), 6.35(2H, d, Ar-C-H), 5.30(1H, s, O-H), 4.61(2H, s, $\underline{CH_2}$-OH), 4.12(4H, Q, 2xCH_2), 3.93(4H, t, 2x-O-$\underline{CH_2}$ -CH_2), 2.32(4H, t, 2x-CH_2-$\underline{CH_2}$-C-O), 1.78(4H, m, 2x-CH_2-$\underline{CH_2}$-CH_2-), 1.6(4H, m, 2x-CH_2-$\underline{CH_2}$-CH_2), 1.49(4H, m, CH_2-$\underline{CH_2}$-CH_2), 1.25(6H, t, -CH_2-$\underline{CH_3}$) **^{13}C NMR 100 MHz** 173.8(2xC=O), 160.4(2x-O-C of ether), 143.3(C-C aromatic), 101.2(2xC-C aromatic), 100.5(C-C aromatic), 72.0(2xO-$\underline{CH_2}$-CH_2), 67.7(CH_2-OH), 60.3(2xCH_2-O of ester), 34.3, 28.9,26.2, 25.7, (8xCH_2), 14.3(2xCH_3), **IR(thin film),** 3500(broad O-H stretch), 2944-2770(CH_2-CH_3 stretch alkyl chain), 1706(C=O of ester), 1599(C-C aromatic), 1225 (O-C=O ester) **cm^1.**

8.31 The Synthesis of Diethyl6,6-5((6-bromohexyloxy) methyl)-1,3-phenylene) bis(oxy)dihexanoate - Compound (9)



(9)

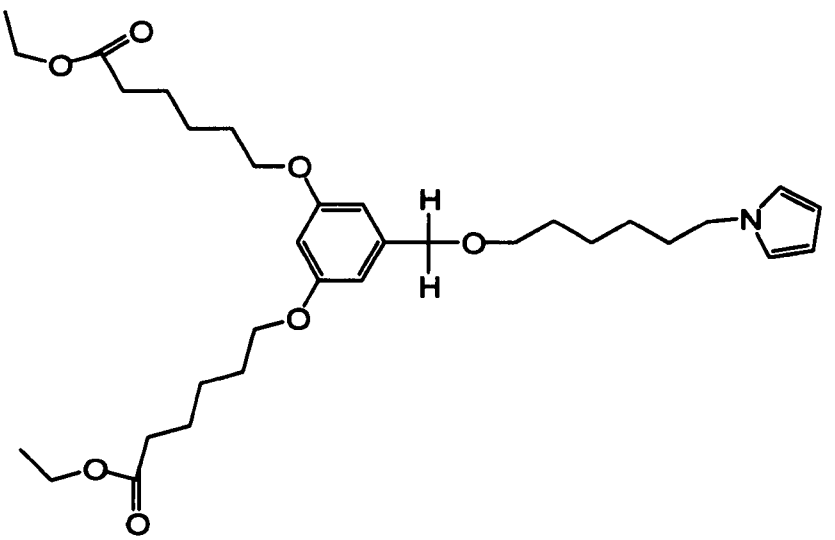
Preparation:

In a round bottom flask (100ml) , potassium *tert*-butoxide (0.9g, 0.0058mol) was stirred in dried diethyl ether for 5-10 minutes before 18-crown-6 (0.12g, 0.0004mol) was added. The mixture continued stirring for a further 10 minutes before compound (8) (1g, 0.0024 mol) was added. After 10-15 minutes 1,6-dibromohexane (1.0ml, 0.005 mol) was added dropwise over 15 minutes. Once all the reagents were added, a calcium chloride guard tube was fitted and the reaction mixture was left to reflux for 48 hours, and followed by TLC. Upon completion, the mixture was quenched by the addition of water (50ml) and the crude product was extracted using DCM (3x50ml). The combined organic layers were dried over

anhydrous magnesium sulfate and filtered under vacuum. The solvent was removed under reduced pressure. Initial attempts to purify the product were carried out using column chromatography, and although isolation of the product was successful, the yield was low. The second method of purification was high vacuum distillation. This was deemed to be a more useful method as the yield was substantial and the product was isolated from the impurity, 1,6-dibromohexane.

MS m/z 586.25 588.13 (M^+); **H^1 NMR δ($CDCl_3$)** 6.5 (1H, t, C-H-Ar), 6.2 (2H, d, C-H Ar), 4.6 (2H, S, Ar-$\underline{CH_2}$-O-), 4.20 (4H, quartet, O-$\underline{CH_2}$-CH_3), 3.99(4H, t, CH_2-alkyl), 3.71 (2H, t, -O-$\underline{CH_2}$ -CH_2), 3.42(2H, t, CH_2-$\underline{CH_2}$-Br), 2.05(4H,t,C=O-$\underline{CH_2}$- CH_2), 1.77(6H, quintet, -(CH_2-$\underline{CH_2}$-CH_2), 1.60(6H, q, CH_2-$\underline{CH_2}$-CH_2), 1.45(2H, m, -CH_2-alkyl), 1.29(7H,m, -CH_2-CH_2), 1.35(5H, m, 2xCH_3).**^{13}C NMR 100 MHz** 173.8(2xC=O), 160.4(2x-O-C of ether), 139.3(C-C aromatic), 102.2(2xC-C aromatic), 99.5(C-C aromatic), 75.2(Ar-$\underline{CH_2}$-O), 72.0(O-$\underline{CH_2}$-CH_2), 67.7(2x(C-$\underline{CH_2}$- CH_2), 60.3(2xCH_2-O of ester), 33.9, 33.4,32.2, 30.0,29.2, 28.9,26.2, 25.7,24.8 (CH_2), 14.3(2xCH_3), **IR(thin film)**2940-2870(CH_2-CH_3 stretch alkyl chain), 1742(C=O of ester), 1619(C-C aromatic) 1265-1184 (C-O esters) cm^{-1}.

8.32 The Synthesis of Diethyl6,6-(5((6-1*H*-pyrrol -1-yl)hexyloxy)methyl)-1,3 phenylene) bis(oxy)dihexanoate Monomer (5)



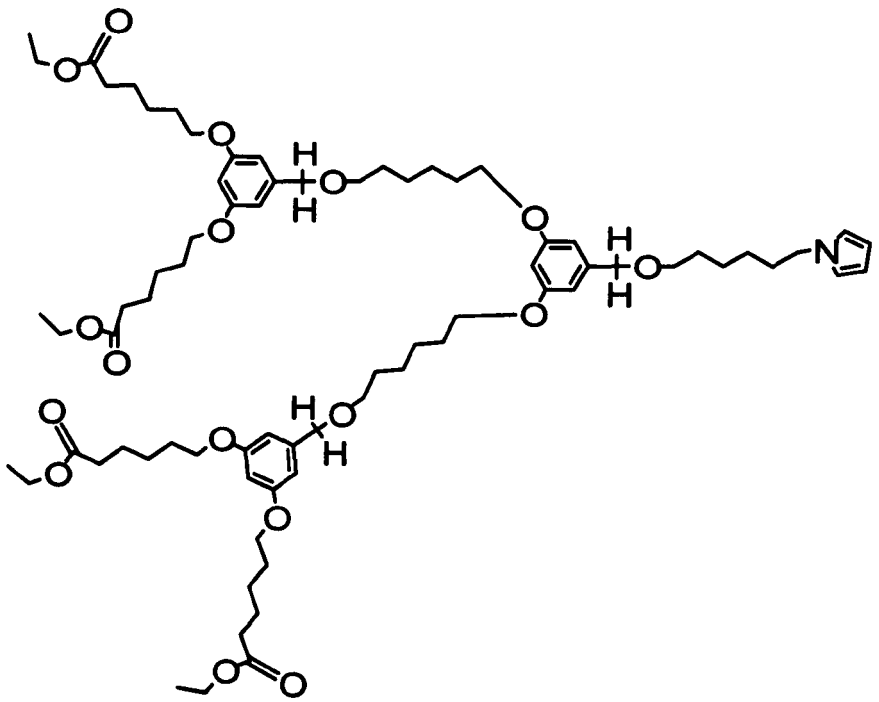
Preparation:

Potassium *tert*-butoxide (0.9g,0.006 mol)was stirred in dry diethyl ether for 5-10 minutes, when 18-crown-6(0.12g,0.0005 mol) was added. The mixture continued stirring for a further 10 minutes, then freshly distilled pyrrole was added (0.97g, 0.0145mol). After 15 minutes compound (9) (1.2g, 0.0029mol) was added and the flask was stoppered with a calcium guard tube and left stirring for two days. Upon completion, the mixture was poured into water (100ml) and extracted using DCM (3x50ml). The combined organic layers were washed with saturated NaCl solution (3x50ml) and the dried over anhydrous magnesium sulphate. Then $MgSO_4$ was filtered off under vacuum and the filtrate was transferred to a round bottom flask (200ml).The solvent was removed under reduced pressure to yield a dark brown viscous oil, which was purified by column chromatography.

MS m/z 573.37 (M^+); **H^1 NMR δ($CDCl_3$)** 6.4 (2H, d,d, C-H of py), 6.2 (1H, t, C-H of py), 6.0 (2H, t, C-H aromatic), 5.7 (2H, d,d C-H of py), 4.9 (2H, t, Ar-$\underline{CH_2}$-O-), 4.1 (4H, q, O-$\underline{CH_2}$-CH_3), 3.8 (4H, m, Ar-O-CH_2), 3.7 (2H,t,-N-$\underline{CH_2}$-), 3.3 (2H, t, O-$\underline{CH_2}$), 2.5 (4H,t,C=O-$\underline{CH_2}$-), 1.8 (8H, m, -CH_2-alkyl), 1.5 (12H,m, CH_2-alkyl), 1.3 (6H, q, CH_2-CH_3). **^{13}C NMR 100 MHz** 173.8(2xC=O), 160.4(2x-O-C of ether), 139.3(C-C aromatic), 122.5(C-C pyrrole), 108.4(C-C pyrrole)102.2(2xC-C aromatic), 99.5(C-C aromatic), 75.2(Ar-$\underline{CH_2}$-O), 72.0(O-$\underline{CH_2}$-CH_2), 67.7(2xO-$\underline{CH_2}$- CH_2), 60.3(2xCH_2-O of ester), 56.1(C-N), 33.4,32.2, 30.0,29.2, 28.9,26.2, 25.7,24.8 (CH_2), 14.3(2xCH_3), **IR(thin film)**2939-2840(CH_2-CH_3 stretch alkyl chain), 1736(C=O of ester), 1599(C-C aromatic), 1576 (N-H bending), 1221 (O-C=O), 800-724(meta substituted benzene ring) **cm^{-1}.**

Elemental analysis Calculated C (69.08), H (8.96) **Found** C (68.09) H (8.79)

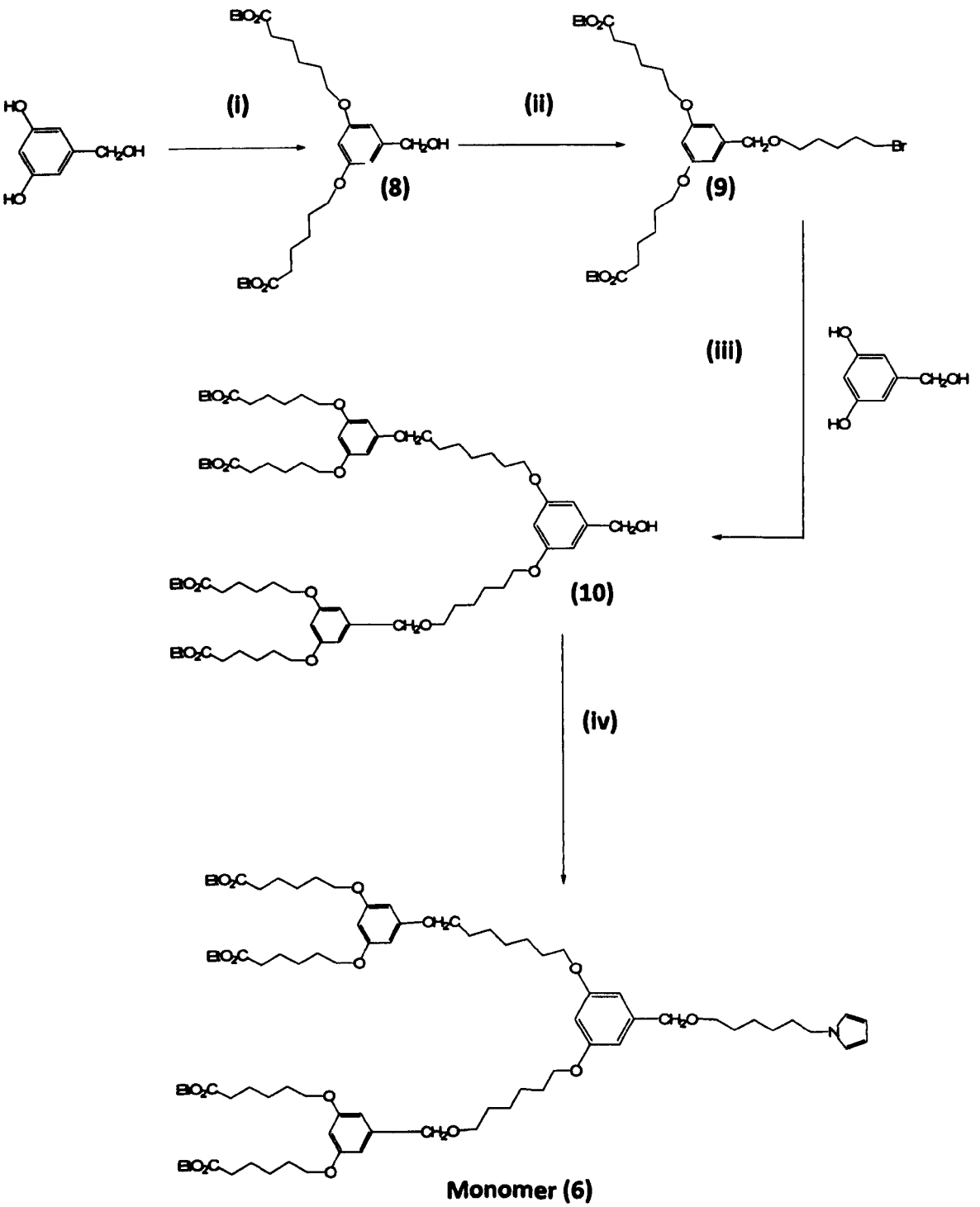
8.33 Synthesis of Monomer (6)



***RMM = 1301**

***Second generation dendritic precursor to hydrophilic terminal alkyl chain**

8.34 Preparation of Monomer (6)



REAGENTS:

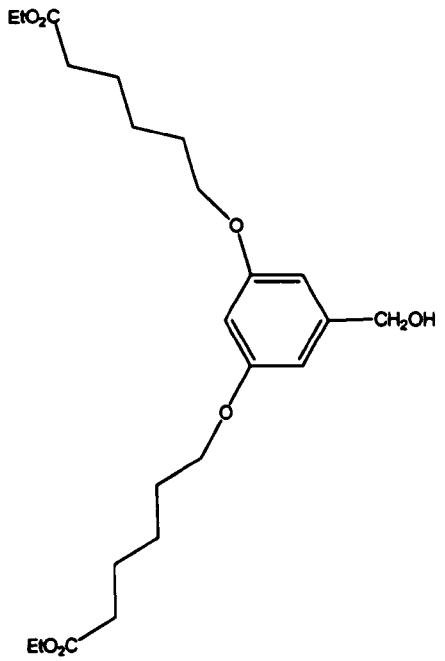
(i) = Ethyl 6-bromohexanoate, anhydrous potassium carbonate, 2-butanone

(ii) = 1,6-dibromohexane, 18-crown-6, potassium-*tert*-butoxide, DEE

(iii) = 2x compound (9), anhydrous potassium carbonate, 2-butanone.

(iv) =Compond (3), 18-crown-6, potassium *tert*-butoxide, DEE

8.35 Synthesis of Compound (8)



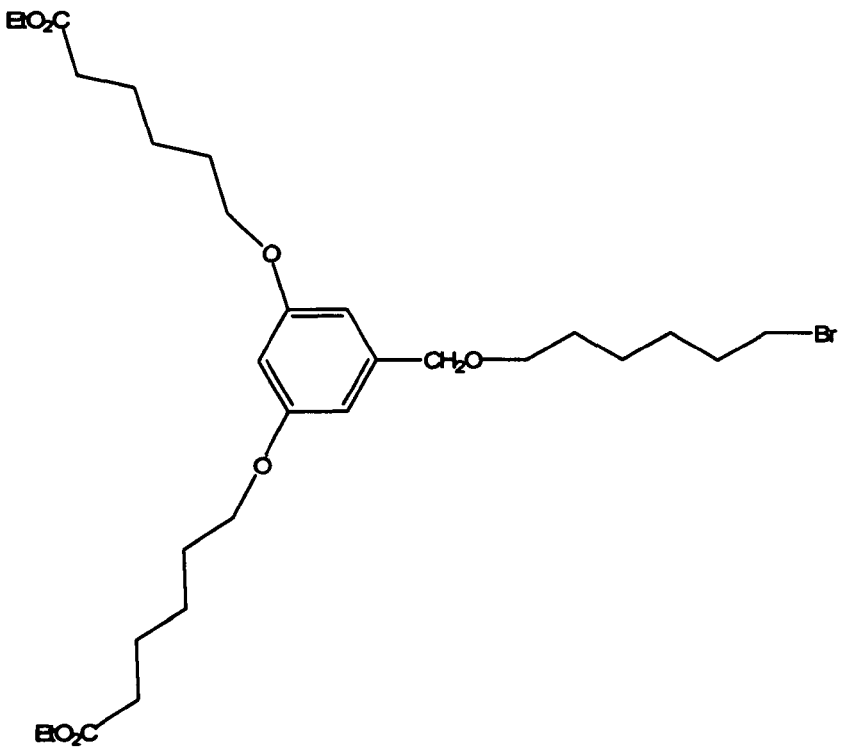
(8)

Preparation:

A mixture of anhydrous potassium carbonate (15g, 0.1075mol) dissolved in dried diethyl ether (50ml) was stirred for 10 minutes before 3,5-dihydroxy benzyl alcohol (3g, 0.0214mol) and ethyl 6-bromohexanoate (9.55g, 0.043mol) were added. A reflux condenser was fitted and the reaction was left to proceed for 32 hours, during which thin layer chromatography was used to follow the progress of the reaction. Upon completion, the reaction was quenched by the addition of water (50ml) and the crude product was obtained by extraction using dichloromethane (3x50ml). The organic layer was dried over anhydrous magnesium sulfate for 15-20 minutes and filtered under vacuum. The solvent was removed in *vacuo,* yielding a light brown oil. The crude product was purified by high vacuum distillation to remove the excess of ethyl 6-bromohexanoate, and characterisation tests were carried out to identify the final product. Yield= 67%

MS m/z 424 (M^+); **H^1 NMR** δ(**$CDCl_3$**) 6.49(1H, t, C-H), 6.35(2H, d, 2xC-H), 5.30(1H, s, O-H), 4.61(2H, S, $\underline{CH_2}$-OH), 4.12(4H, Q, 2xCH_2), 3.93(4H, t, 2x-O-$\underline{CH_2}$ -CH_2), 2.32(4H, t, 2x-CH_2-$\underline{CH_2}$-C-O), 1.78(4H, m, 2x-CH_2-$\underline{CH_2}$-CH_2-), 1.69(4H, m, 2x-CH_2-$\underline{CH_2}$-CH_2), 1.49(4H, m, (CH_2-$\underline{CH_2}$-CH_2), 1.25(6H, t, -CH_2-$\underline{CH_3}$) **^{13}C NMR 100 MHz** 173.8(2xC=O), 160.4(2x-O-C of ether), 143.3(C-C aromatic), 101.2(2xC-C aromatic), 100.5(C-C aromatic), 72.0(2xO-$\underline{CH_2}$-CH_2), 67.7(CH_2-OH), 60.3(2xCH_2-O of ester), 34.3, 28.9,26.2, 25.7, (8xCH_2), 14.3(2xCH_3), **IR(thin film]**, 3500(broad O-H stretch), 2940-2870(CH_2-CH_3 stretch alkyl chain), 1732(C=O of ester), 1599(C-C aromatic) 1175-1020 (C-O of ester)cm^1.

8.36 Synthesis of Compound (9)



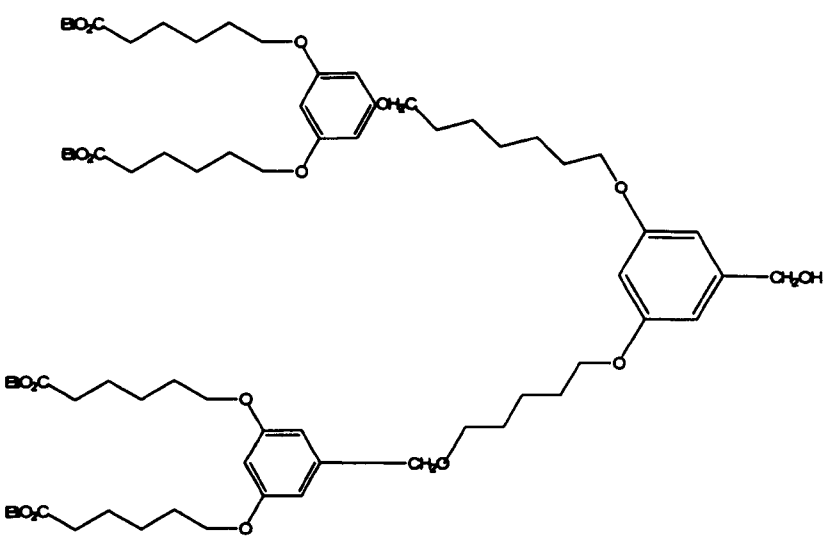
Preparation:

In a 100ml round bottom flask, potassium *tert*-butoxide (0.92g,0.006 mol)was stirred in dried diethyl ether(100ml) for 5-10 minutes before 18-crown-6 (0.12g,0.0005 mol) was added. The mixture continued stirring for a further 10 minutes before compound (8) (1g, 0.0023 mol) was added. After 10-15 minutes 1,6-dibromohexane(1.0ml,0.005 mol) was added dropwise over 15 minutes. A calcium guard tube was fitted and the reaction mixture was left to reflux for 48 hours, and followed by TLC. Upon completion, the mixture was quenched by the addition of water (50ml) and the crude product was extracted using DCM (3x50ml). The combined organic layers were dried over anhydrous magnesium sulfate and filtered under vacuum. The filtrate was transferred to a round bottom flask (250m) and the solvent was removed under reduced pressure. Initial attempts to purify the product were carried out using column chromatography, and although isolation of the product was successful, the yield was low. The second method of purification was high vacuum

distillation. This was deemed to be a more useful method as the yield was substantial and the product was isolated from the impurity of the excess 1,6-dibromohexane.

MS m/z 586.25 588.30 (M^+); **H^1 NMR δ($CDCl_3$)** 6.37(1H, t, C-H aromatic), 6.26(2H, d,d C-H aromatic), 4.41(2H, S, Ar-$\underline{CH_2}$-O-), 4.20(4H, quartet, O-$\underline{CH_2}$-CH_3), 3.99(4H, t, CH_2-CH_2), 3.85(2H, t, -O-$\underline{CH_2}$ -CH_2), 3.42(2H, t, CH_2-$\underline{CH_2}$-Br), 2.05(4H,t,C=O-$\underline{CH_2}$- CH_2), 1.77(6H, m, -CH_2-$\underline{CH_2}$-CH_2), 1.60(6H, quintet, CH_2-$\underline{CH_2}$-CH_2), 1.45(2H, m, -CH_2- $\underline{CH_2}$-CH_2-), 1.29(6H,m, -CH_2-CH_2), 1.35(6H, t, 2xCH_3).**^{13}C NMR 100 MHz** 173.8(2xC=O), 160.4(2x-O-C of ether), 139.3(C-C aromatic), 102.2(2xC-C aromatic), 99.5(C-C aromatic), 75.2(Ar-$\underline{CH_2}$-O), 72.6(O-$\underline{CH_2}$-CH_2), 67.7(2xO-$\underline{CH_2}$- CH_2), 60.3(2xCH_2-O of ester), 33.9, 33.4,32.2, 30.0,29.2, 28.9,26.2, 25.7,24.8 (CH_2), 14.3(2xCH_3), **IR(thin film)**2940-2870(CH_2-CH_3 stretch alkyl chain), 1719 (C=O of ester), 1600(C-C aromatic) 1264-1255 (C-C esters)cm^{-1}.

8.37 The Synthesis of Compound (10)



(10)

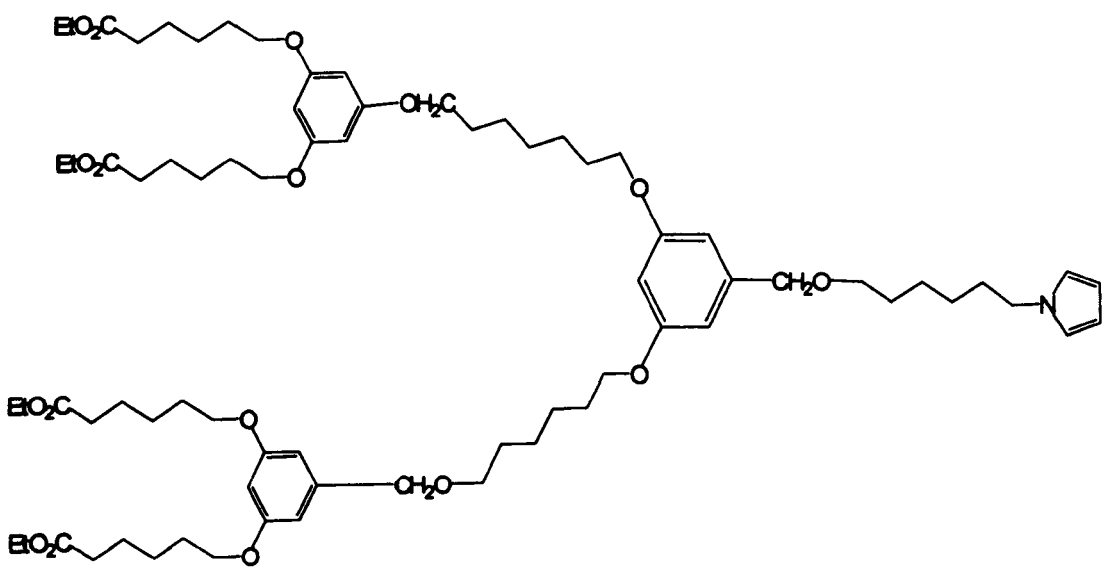
Preparation:

A mixture of 3,5-dihydroxybenzyl alcohol (0.75g, 0.005mol), and anhydrous potassium carbonate(2.4g, 0.0175mol) dissolved in 2-butanone (80ml) was refluxed gently for 10 mins before compound (9) (5.8g, 0.01mol) was added. Reflux continued for 24 hours and upon completion, as indicated by TLC (petrol 40-60/EtOAc 2:1), water (120ml) was added to the reaction mixture. DCM (3x50ml) was used to extract the crude product, and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and column chromatography using the above solvent system, was carried out to purify the compound. Characterisation of compound (10) was conducted and the following results were obtained.

Yield = 1.39g, 30% MS m/z 1157 (M^+); **H^1 NMR δ($CDCl_3$)** 6.4 (3H, t, C-H aromatic), 6.3 (6H, d,d C-H aromatic), 4.6 (1H, S, OH), 4.2 (8H, q, O-$\underline{CH_2}$-CH_3-), 4.0 (12H, t, O-$\underline{CH_2}$-), 3.5 (5H, t, O-CH_2-CH_2 & O-H), 2.3(8H, t, =O-$\underline{CH_2}$), 1.8-1.5 (28H, m, -CH_2-alkyl), 1.4-1.2 (12H, d, Ar-CH_2-$\underline{OH}$),

1.3-1.2(24H, m, -CH_2- $\underline{CH_2}$-Overlap with O-H), 1.0 (12H, t, CH_3-CH_2). **IR(thin film)** 3363-3170 (O-H alcohol), 2900-2770 (CH_2-CH_3 stretch alkyl chain), 1729 (C-O of ester), 1619(C=C aromatic) cm^{-1}.

8.38 The Synthesis of Monomer (6)



(11)

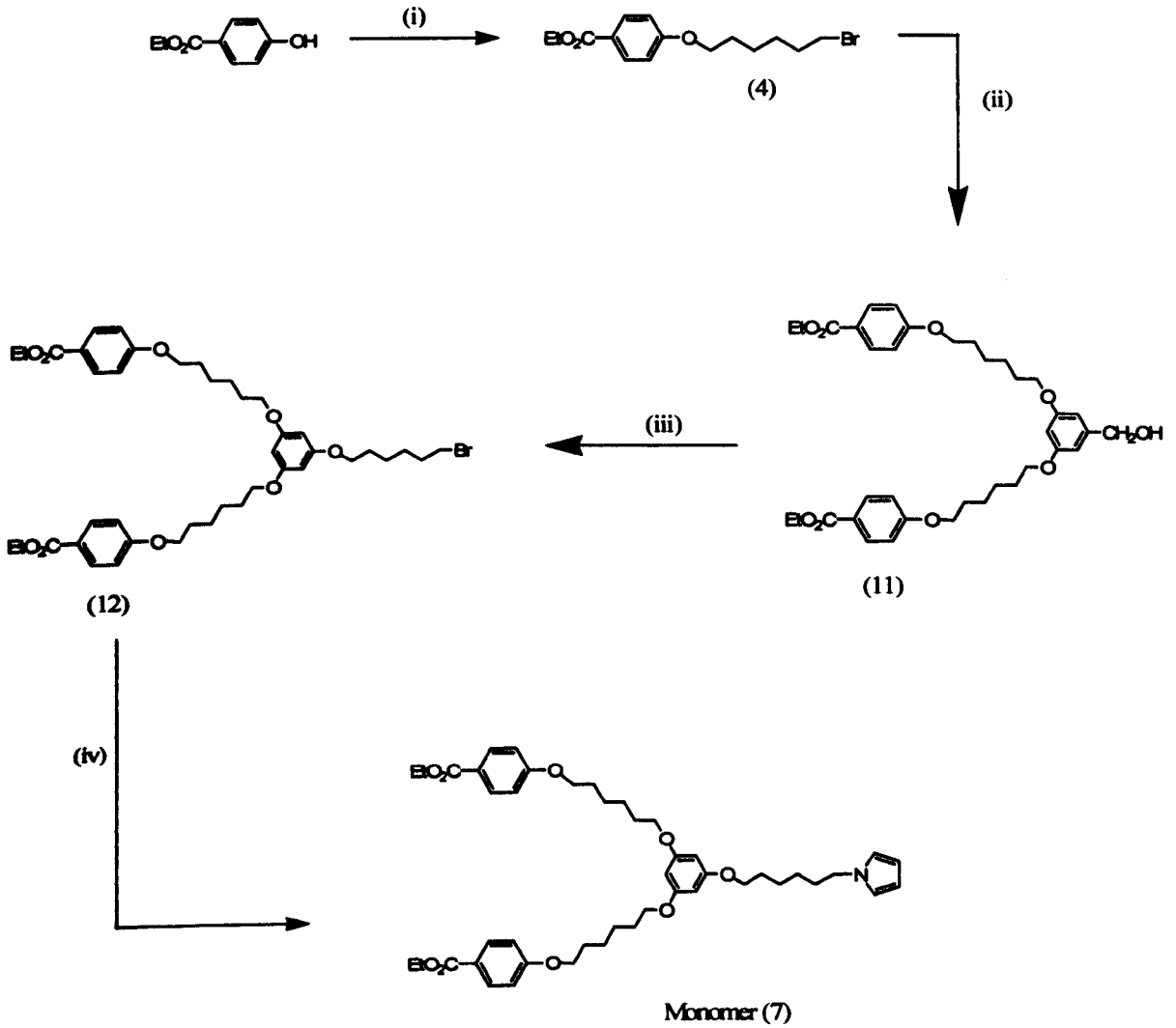
Preparation:

A mixture of 18-crown-6 (0.2g, 0.0007 mol), in diethyl ether (80ml), was stirred at room temperature and potassium *tert*-butoxide (0.2g, 0.0012mol) was added. The mixture was stirred while compound (10) (1.2g, 0.0013mol) was added in one portion. A $CaCl_2$ guard tube was fitted and stirring continued for 15 mins. Compound (3) (0.4g, 0.0012mol) dissolved in ether (20ml) was added dropwise to the reaction mixture over a period of 10 mins. The reaction was stirred for 2 days. Water (120ml) was added to the reaction mixture and the latter was extracted with dichloromethane (2x40ml). The combined organic layers were washed with saturated NaCl solution (3x50ml) and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield a dark brown semi-solid. The crude product was purified by column chromatography using a mixture of chloroform:hexane, 1:3 ratio. Yield= 0.7g, 41%. **MS m/z** 1301 (M^+); **H^1 NMR** δ(**$CDCl_3$**) 6.4 (2H, d,d, Ar-H pyrrole), 6.2 (3H, t, C-H

aromatic), 6.0 (6H, d, Ar-H), 5.7 (2H ,d, Ar-H pyrrole), 4.9 (6H, t, O-$\underline{CH_2}$-), 4.1 (20H, m, O-$\underline{CH_2}$-), 3.7 (2H, t, N-CH_2), 3.2 (6H, t, O-CH_2-CH_2), 2.5 (8H, t, =O-$\underline{CH_2}$), 1.8-1.5 (20H, m, -CH_2-$\underline{CH_2}$-CH_2), 1.4-1.2 (28H, m, -CH_2- $\underline{CH_2}$- overlapping), 1.3(12H, t, CH_3-CH_2). **IR (thin film),** 2970-27354 (CH_2-CH_3 stretch alkyl chain), 1732 (C=O of ester), 1600 (C=C aromatic), 1652,1620 (substituted pyrrole C=C, C=N vibrations), 1498,1400 (pyrrole ring vibration), 1151 (N-C aromatic stretch), 832 (meta substituted rings, 3 adjacent H's)cm^{-1}.

Elemental analysis Calculated C (69.15), H (8.90), Found C (69.11), H (8.84)

8.39 Synthetic Route for the preparation of - Monomer (7)



REAGENTS:

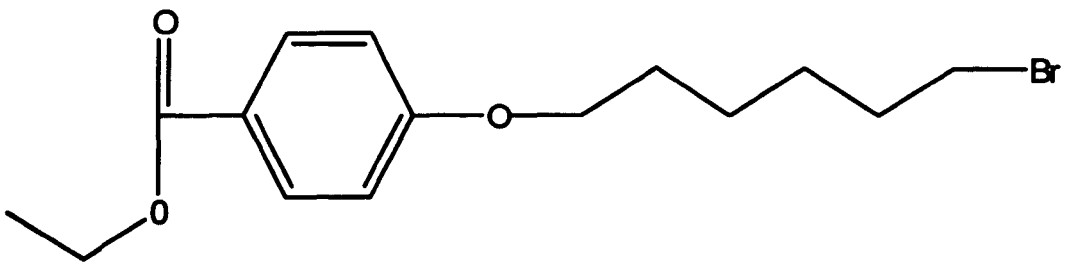
STEP (i) = 1,6-Dibromohexane, anhydrous potassium carbonate, 2-butanone.

STEP (ii) = 3,5-dihydroxy benzyl alcohol, anhydrous potassium carbonate, 2-butanone.

STEP (iii) = Potassium *tert* butoxide, 18-crown-6, DEE, 1,6-dibromohexane,

STEP (iv) = Potassium *tert* butoxide, 18-crown-6, DEE, pyrrole.

8.40 The Synthesis of Ethyl 4-(6-bromohexyloxy) benzoate - Compound (4)



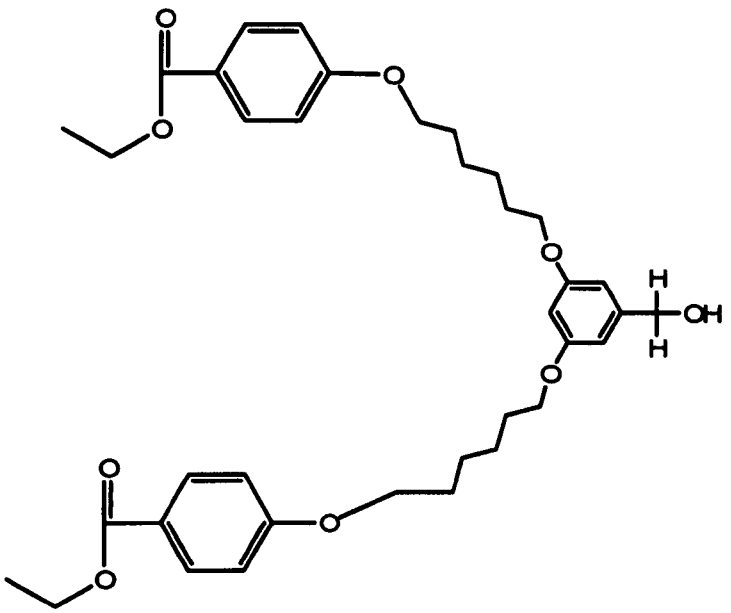
(4)

Preparation:

In a single neck conical flask, anhydrous potassium carbonate (12.42g, 0.09mol), was stirred in dried 2-butanone (30ml) for 10 minutes before ethyl 4-hydroxybenzoate (5g, 0.030mol) was added. 1,6-Dibromohexane (14.8g,0.06mol) was added dropwise over 15 minutes. The reaction was refluxed for 24 hours and TLC was used to follow the progress. Upon completion, the mixture was poured into water (50ml) and the crude product was obtained by extraction using DCM (3x50ml). The combined organic layers were dried over anhydrous magnesium sulfate for 20 minutes, and then filtered under vacuum. The filtrate was transferred to a pre-weighed round bottom flask and the solvent was removed by reduced pressure to yield a white solid with an oily residue. The crude product was then purified by high vacuum distillation to remove the excess 1,6-dibromohexane and re-crystallised using IMS. Characterisation tests were then carried out. **Yield : 6.4g, 65%.**

MS m/z 328.07, 330.01 (M^+); **H^1 NMR δ($CDCl_3$)** 7.89(2H,dd, C-H aromatic), 7.04(2H,dd,C-H aromatic), 4.30(2H,quartet,CH_2-), 4.00(2H,t,O-CH_2), 3.33(2H,t,-$\underline{CH_2}$-Br-), 1.78(2H, m, -CH_2-$\underline{CH_2}$-CH_2), 1.76,(2H,m, -CH_2-$\underline{CH_2}$-CH_2), 1.29(4H,m, -CH_2-CH_2) 1.33(3H,t,CH_3) **^{13}C NMR 100 MHz** 165.7(O-C=O), 161.1(C-O),130.0(C-H benzene),127.1(C-C=O), 116.1(C-H benzene), 67.4(O-C),59.7(O-C-C),33.2(C-Br), 32.2, 30.0, 28.9,26.2 (CH_2),14.4(C-CH_3), **IR(thin film)**2850-2570(CH_2-CH_3 stretch alkyl chain), 1740 (C=O of ester), 1574 (C-C aromatic), 640-515 (C-Br)cm^{-1}

8.41 The Synthesis of Compound (11)



(11)

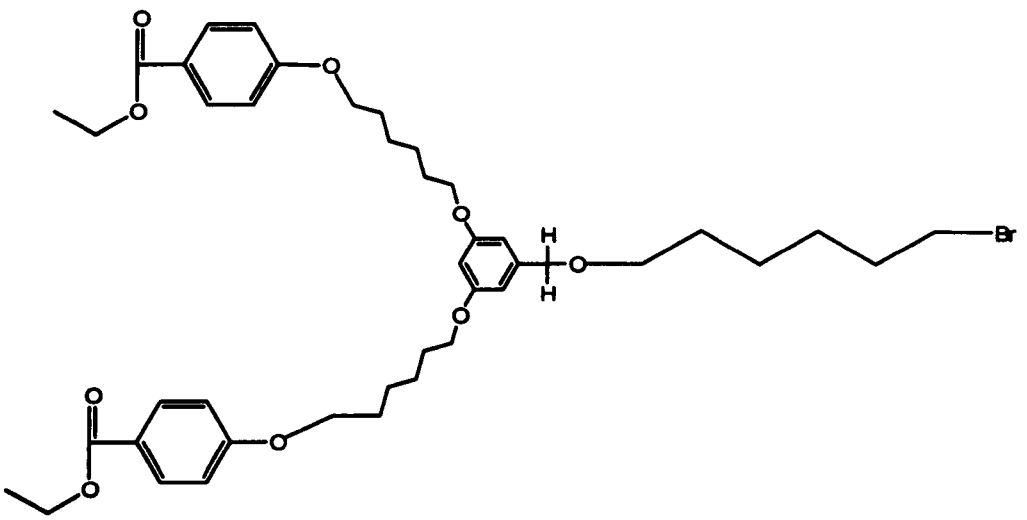
Preparation:

In a round bottom flask (150cm^3) anhydrous potassium carbonate (1.0g, 0.00304mol), compound (4) (1.0g, 0.003048mol), 3,5-dihydroxybenzyl alcohol (0.21g, 0.00152 mol) and dry butanone were refluxed for 48 hours. The progress of the reaction was followed by TLC (hexane: ethyl acetate 9.5:0.5) and upon completion water (50ml) was added. The solution was extracted with dichloromethane (3x50ml). The organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and subjected to column chromatography (SiO_2) using hexane: ethyl acetate (9.5:0.5) was carried out to purify the crude product and the final product was a light yellow oil (1.4g, 78%) .

Electrospray MS; 659.3 (spiked with Na), 675.3 (spiked with K); **IR (thin film)**, 3385 (Broad O-H stretch of CH_2OH), 2940-2870 (CH_2-CH_3 stretch alkyl chain), 1739 (C-O of ester), 1601 (C-

C aromatic), 1299 (Strong O-H bending), 1060 (C-O stretch of secondary alcohols), 832 (meta substituted rings, 3 adjacent H's);cm^{-1}; **H^1 NMR δ($CDCl_3$)** 7.97 (4H,d, C-H of aromatic ring adjacent to ester group), 6.97 (4H,d,C-H of aromatic ring adjacent to ether group), 6.50 (1H,t, C-H aromatic), 6.35 (2H,d,C-H aromatic ring), 5.37 (1H, t, O-H), 4.77 (2H, d, CH_2OH), 4.35 (4H, Quartet, O- $\underline{CH_2}$-CH_3), 4.1 (8H, t, Ar-O-$\underline{CH_2}$), 1.8 (8H, m, O-CH_2-$\underline{CH_2}$], 1.5 (8H, m, CH_2-alkyl chain), 1.3 (6H, t, CH_3-CH_2-O) **^{13}C NMR 100 MHz** 14.6 ($\underline{CH_3}$-CH_2), 60.9 (CH_3-$\underline{CH_2}$), 165.9 (O-C=O), 122.3 (C-H or Ar ring position 1), 131.2 (C-Hof Ar ring position 2,6), 114.8 (C-H of Ar ring position 3,5), 162.1 (C-H of Ar position 4), 68.9(O-CH_2-CH_2), 30.1 (O-CH_2-$\underline{CH_2}$-CH_2-), 25.9 (O- CH_2-CH_2-$\underline{CH_2}$-CH_2), 160.2 (C-H Ar ring position 3,5), 99.1 (C-H Ar ring position 4), 102.2 (C-H Ar ring position 2,6), 142.8 (C-H Ar ring position 1), 68.6 (CH_2-OH).

8.42 The Synthesis of - Compound (12)



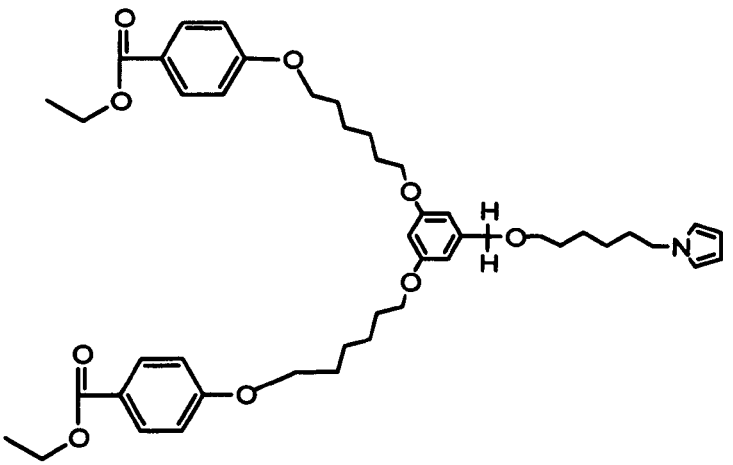
Preparation:

Compound (11) was weighed into a 100cm^3 quickfit conical flask, in which potassium *tert*-butoxide (1.23g, 0.0110 mol) and 18-crown-6 (0.166g, 0.0015mol) had been stirred in diethyl ether (50ml) for 15 minutes. Then 1,6-dibromohexane (1.2cm^3, 0.0078 mol) was added and a reflux condenser equipped with a calcium chloride guard tube was attached and the reaction proceed for 48 hours. Once the reaction had gone to completion as indicated by TLC, distilled water (50ml) was added and the reaction mixture was extracted with dichloromethane (3x50ml). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by high vacuum distillation (Kugelrohr 0.01mmHg/70^{0}C) to yield a final product that was a light brown oil. Yield = 1.2g, 58%.

Electrospray MS; 821.3(spiked with Na), **IR(thin film)**, 2870(CH_2-CH_3 stretch alkyl chain), 1732(C=O of ester), 1606(C-C aromatic), 1169(Ether aliphatic), 832(meta substituted rings, 3 adjacent H's), 500-700(C-Br); **H^1 NMR δ($CDCl_3$)** 7.97(4H,d, C-H of aromatic ring at 2,6 position), 6.97(4H,d,C-H of aromatic ring 3,5 position), 6.40(1H,t, C-H aromatic ring position

4), 6.25(2H,d,C-H aromatic ring position 2,6), 4.67(2H, t,CH_2-O-), 4.37(4H, Q, CH_3-CH_2), 4.05(8H, t, O-$\underline{CH_2}$-), 3.31(2H, m, CH_2Br), 1.8-1.30(24H, m, CH_2 of alkyl chains), 1.3(6H, t, CH_3-CH_2-). ^{13}C NMR 100 MHz 14.6($\underline{CH_3}$-CH_2), 60.9(CH_3-$\underline{CH_2}$), 165.9(O-C=O), 122.3(C-H or Ar ring position 1), 131.2(C-Hof Ar ring position 2,6), 114.8(C-H of Ar ring position 3,5), 162.1(C-H of Ar ring position 4), 68.9(O-CH_2-CH_2), 30.1(O-CH_2-$\underline{CH_2}$-CH_2-), 29.0,28.5,25.9,23.1 32.6,(CH_9-CH_2-ALKYL Chain),33.7(CH_2-Br 28.5), 158.5(C-H Ar ring position 1,3,5), 92.2(C-H Ar ring position 2,4,6), 30.0(O-CH_2-CH_2), 75.5(CH_2-O).

8.43 The Synthesis of Monomer (7)



Monomer (7)

Preparation:

Potassium *tert*-butoxide, (0.8g, 0.0077 mol), 18-crown-6 (0.205g, 0.00077 mol), and diethyl ether (50ml) were continuously stirred under the protection of a calcium choride guard tube for 15 minutes before pyrrole (0.52g, 0.0077 mol) was added. Compound (12) (1.24g, 0.00155 mol) was added to the reaction mixture and the solution was stirred at room temperature for 48 hours. The reaction mixture was poured into water (100ml). The crude product was extracted with dichloromethane (3x50ml) and washed with saturated sodium chloride solution (3x50ml). The combined organic layers were dried over magnesium sulfate, and the solvent was removed under reduced pressure. An initial attempt to purify the crude product was made by column chromatography in which the eluent was a 50:50 solvent mixture of hexane: ethyl acetate. This proved to be unsuccessful as the yield was very low and the product appeared to adhere to the stationary phase (silica gel) of the column. The only alternative was to proceed to polymerisation without further purification. The final product was a viscous dark brown oil. Yield = 49%, 0.89g.

Electrospray MS; 824.3(spiked with Potassium), **IR (thin film),** 2870-2534 (CH_2-CH_3 stretch alkyl chain), 1722 (C=O of ester), 1606 (C-C aromatic), 1662,1630 (substituted pyrrole C=C, C=N vibrations), 1498,1400 (pyrrole ring vibration), 1151 (N-C aromatic stretch), 832 (meta substituted rings, 3 adjacent H's)cm^{-1}; **H^1NMR δ($CDCl_3$)** 8.1 (4H,d, C-H of aromatic), 7.5 (4H, t, C-H of aromatic), 6.9 (2H,d,d, C-H aromatic of py), 6.4 (1H, t, C-H aromatic ring position 2), 5.8 (2H, d,CH-Ar py), 4.7 (2H, t, C-H or py), 4.4 (4H,q, CH_2-O,), 4.0 (8H, m, Ar-O-CH_2), 3.7 (2H, t, N-$\underline{CH_2}$-), 3.3 (2H, t, CH_2 O-CH_2), 1.8-1.5 (24H, m, CH_2-alkyl), 1.3 (6H, q, CH_3-CH_2) **^{13}C NMR 100 MHz** 14.6($\underline{CH_3}$-CH_2), 60.9 (CH_3-$\underline{CH_2}$), 165.9 (O-C=O), 122.3 (C-H or Ar ring position 1), 131.2 (C-Hof Ar ring position 2,6), 114.8 (C-H of Ar ring position 3,5), 162.1 (C-H of Ar ring position 4), 68.9 (O-C H_2-CH_2), 30.1 (O-CH_2-$\underline{CH_2}$-CH_2-), 29.0,28.5,29.9,25.1 32.6, (CH_9-CH_2-alkyl Chain), 158.5(C-H Ar ring position 1,3,5), 92.2 (C-H Ar ring position 2,4,6), 30.0 (O-CH_2-CH_2), 75.5 (CH_2-O), 108.1 (C-H ar pyrrole 3,4 position), 122.1 (C-H or pyrrole 2,5 position); **Elemental analysis** Calculated C (71.57), H (7.96). Found (71.47), H (7.95)

8.44 Polymerisation of Monomers

Two main types of polymerisation methods were used in this project

1. Electrochemical Polymerisation

Potentiostatic sweep, oxidation of a monomer in a supporting electrolyte solution

2. Chemical Polymerisation

General method used was based on Sugimoto *et al* using anhydrous $FeCl_3$ as the oxidant.

Monomers 1-7 were all attempted to be polymerised using the above 2 methods; however not all monomers were successfully polymerised by both methods. Generally monomers showed a preference to one method of polymerisation over the other. This will be discussed in more detail, in the results and discussion section.

8.44.1 Electrochemical Polymerisation

Electrochemical polymerisation involves a cell with 3 electrodes, an electrolyte salt and a solvent.

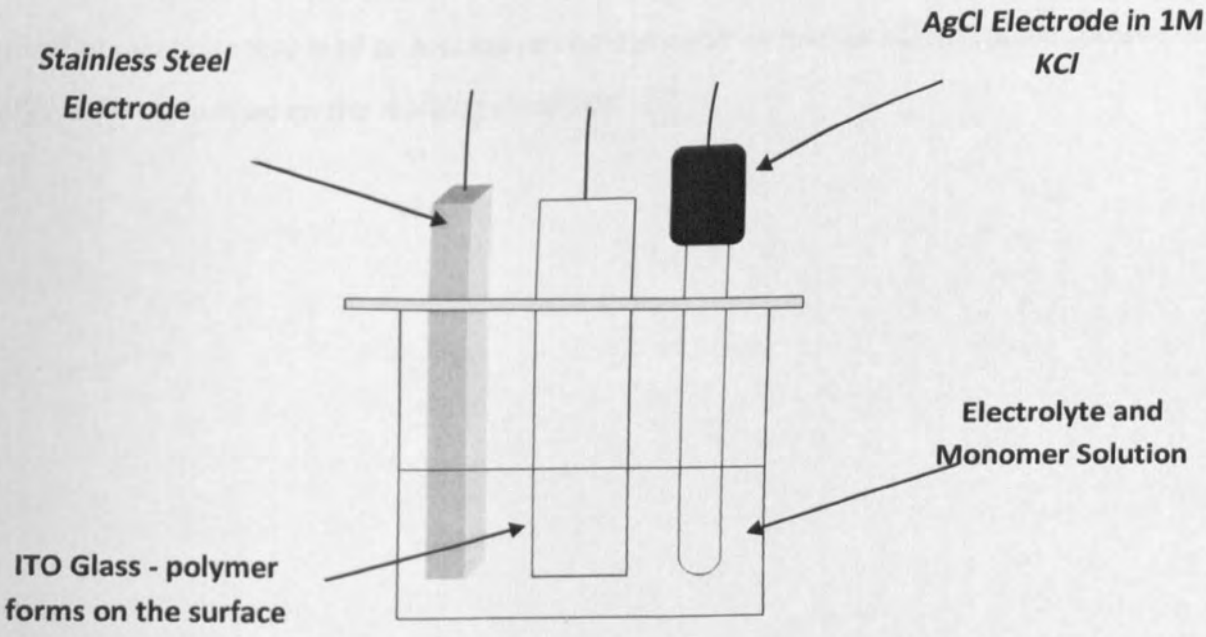


Figure 8.1 Typical Apparatus for Electrochemical Polymerisation

Figure 8.1 illustrates a typical set up of electrochemical polymerisation equipment in which:

1. Working electrode (ITO Glass)

2. Counter electrode (Stainless Steel)

3. Reference Electrode (AgCl)

4. Electrolyte Salt ($Et_4N.BF_4$)

5. Solvent (Propylene Carbonate)

Although the yield of the polymer obtained from electrochemical polymerisation is not always very good, it provides useful information about the pattern of formation, and the

properties of the polymer. The process involves the passage of current through a solution, which is always accompanied by chemical changes in the electrodes. Electrons are gained at the cathode, and chemical compounds reduced; electrons are lost at the anode where oxidation occurs. During this exchange, reactive intermediates may be produced, which can initiate chain polymerisation. Free radical or ionic polymerisation may thus be initiated by one electron transfer per chain. Alternatively, the initial electron transfer may facilitate coupling reactions that lead to successive chain growth as further electrons are transferred. Lastly, a film is formed on the working electrode.

8.45 Chemical Polymerisation

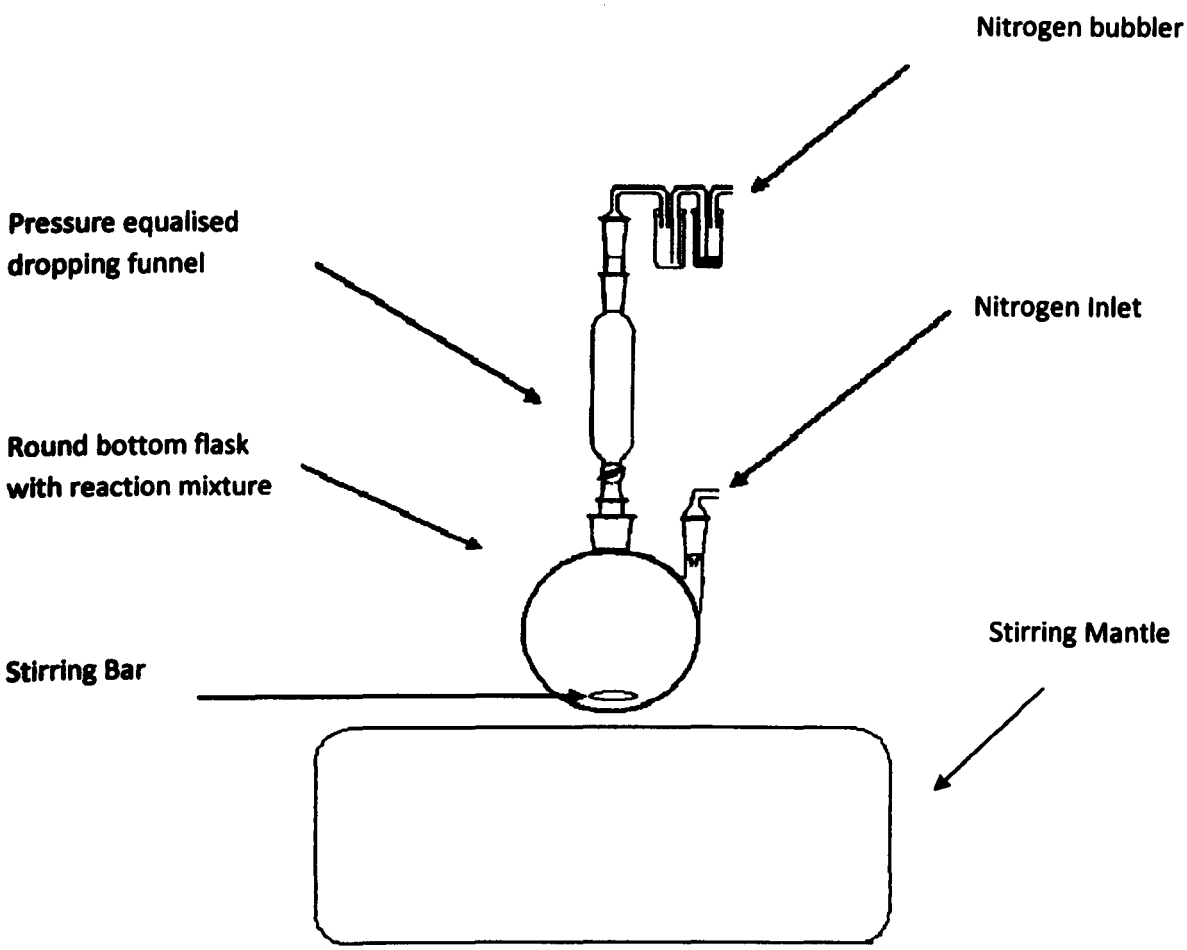


Figure 8.2 Typical Apparatus for Chemical polymerisation

8.45.1 Oxidative Polymerisation

Most aromatic rings such as pyrrole and thiophene can be oxidised to form a radical cation which can then initiate polymerisation. A variety of oxidising agents can be used, such as copper (II) chloride [Samuelsen], molybdenum (V) chloride [Sugimoto], iron (III) chloride and many others. However the most commonly used oxidising agent is iron (III) chloride as it is cheap and produces good yields of polymer material.

One drawback of oxidative polymerisation is that the polymer is not very region-specific and it is difficult to remove the excess oxidant from the polymer. On the other hand, some of the advantages include:

- Generally a simple one step process
- Requires the use of cheap chemicals that can be easily scaled up to industrial production
- The molecular weight of the product can be reasonably high.

8. 46 Electrochemical Polymerisation of Monomer (I)

Preparation:

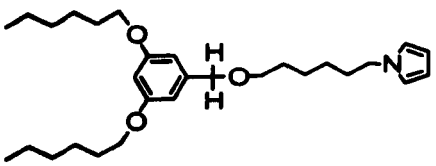
Monomer (I) was electrochemically polymerised from an electrolyte solution containing tetrabutylammonium tetrafluoroborate (TBAF) (0.25g, 0.00075mol) dissolved in propylene carbonate (20cm^3), to which a solution of monomer (I) (0.3g, 0.00075mol) dissolved in propylene carbonate (5cm^3) was added. The mixture was purged with nitrogen to remove oxygen. The cell consisted of a stainless steel counter electrode, an indium tin oxide (ITO) glass working electrode and a self-contained saturated calomel reference electrode. The electrode potential was cycled 50 times from -500 to 1500 mV vs SCE, at a scan rate of 50mVs^{-1}. A very thin homogenous brown film was formed. The film was very thin and we were unable to peel a substantial amount from the ITO glass therefore no IR or ^{1}HNMR of polymer (1) could be carried out at this stage.

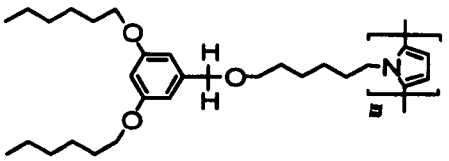
8.47 Electrochemical Polymerisation of Monomer (3) - 1st attempt

Preparation:

The first attempt at electrochemical polymerisation was carried out by preparing an electrolyte solution containing tetraethylammonium tetrafluoroborate (TEATFB) (0.2g, 0.0013mol) dissolved in acetonitrile (25cm^3), to which a solution of monomer (3) (0.3g, 0.00067mol) dissolved in propylene acetonitrile (5cm^3) was added. The mixture was purged with nitrogen to remove oxygen. The cell consisted of a stainless steel counter electrode, an indium tin oxide (ITO) glass working electrode and a self-contained saturated calomel reference electrode. The electrode potential was cycled 50 times from -500 to 1500 mV vs SCE, at a scan rate of 50mVs^{-1}. A very thin film was yielded which had a speckles of polymer randomly distributed on the surface. As the film quality was poor it was decided that the polymerisation should be attempted again, but this time with a smaller amount of solvent to make the mixture more concentrated. (See 4.2.1)

8.48 Electrochemical Polymerisation of Monomer (3) – 2nd Attempt

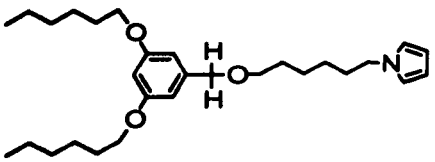


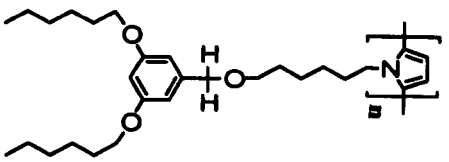


Preparation:

The second attempt of EC polymerisation of Monomer (3) was carried out by preparing an electrolyte solution containing tetraethylammonium tetrafluroborate (TEATFB) (0.2g, 0.0013mol) dissolved in acetonitrile (15cm^3), to which a solution of monomer (3) (0.3g, 0.00067mol) dissolved in propylene acetonitrile (5cm^3) was added. The mixture was purged with nitrogen to remove oxygen. The cell consisted of a stainless steel counter electrode, an indium tin oxide (ITO) glass working electrode and a self-contained saturated calomel reference electrode. The electrode potential was cycled 50 times from -500 to 1500 mV vs SCE, at a scan rate of 50mVs^{-1}. Reducing the volume of solvent did improve the quality of the polymer film, as a very thin homogenous dark brown film was yielded which had only a few speckles on the surface. However the layer of film was still too thin. So it was decided that a 3rd approach to EC polymerise monomer (3) would be to use an alternative electrolyte salt tetrabutylammonium perchlorate (TBAP), and to try a 1:1 ratio electrolyte salt : monomer instead of the 2:1 electrolyte salt : monomer used previously.

8.49 Electrochemical Polymerisation of Monomer (3) – 3rd Attempt

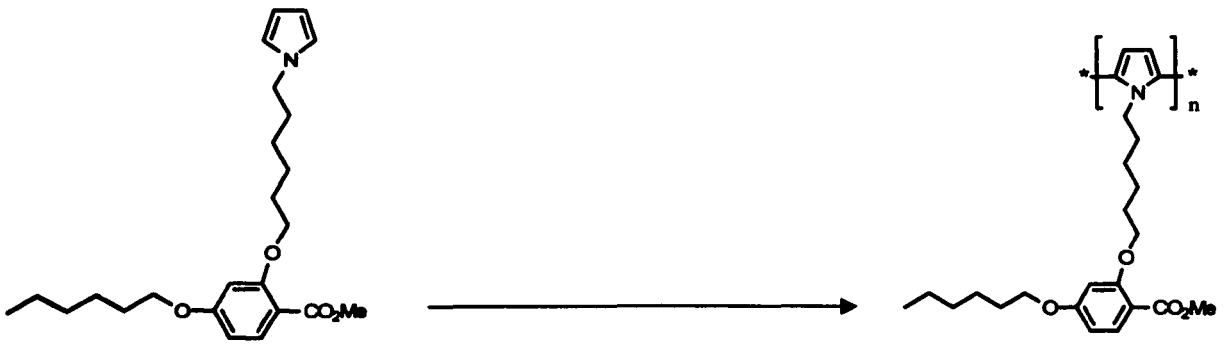




Preparation:

The third attempt to EC polymerise monomer (3) was carried out by preparing an electrolyte solution containing tetrabutylammonium perchlorate (TBAP) (0.4g, 0.0010mol) dissolved in acetonitrile (15cm^3), to which a solution of monomer (3) (0.5g, 0.0010mol) dissolved in propylene acetonitrile (5cm^3) was added. The mixture was purged with nitrogen to remove oxygen. The cell consisted of a stainless steel counter electrode, an indium tin oxide (ITO) glass working electrode and a self-contained saturated calomel reference electrode. The electrode potential was cycled 50 times from -500 to 1500 mV vs SCE, at a scan rate of 50mVs^{-1}. This method yielded a very thin homogenous dark brown film, without any speckles. The film was very thin and we were unable to peel a substantial amount from the ITO glass therefore IR or ^{1}HNMR of polymer (3) could not be carried out at this stage.

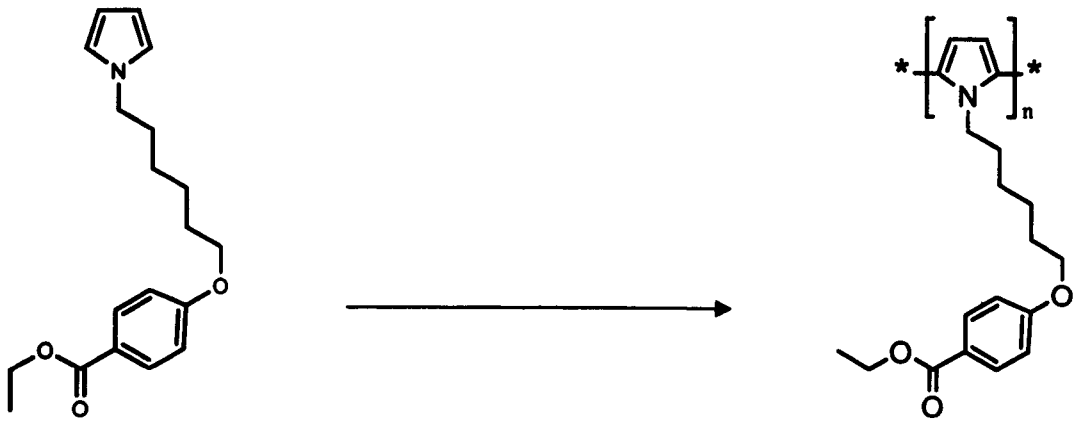
8.50 Chemical Polymerisation of Monomer (1)



Preparation:

Chemical polymerisation of Monomer (1) was carried out by dissolving $FeCl_3$ (0.17g, 0.001mol) in the minimum amount of chloroform (10ml) in a two necked round bottom flask (50ml) fitted with a pressure equalized dropping funnel and nitrogen inlet. The mixture was stirred vigorously, and purged with N_2(g) until dissolved. In a separate beaker (50ml), monomer (1) (0.2(g), 0.0005mol) was dissolved in chloroform (10ml) and then slowly poured into the dropping funnel and added to the reaction mixture over 10 mins. The mixture was heated gently (30^{0}C), with vigorous stirring under a nitrogen atmosphere. After 24h the reaction was stopped, and the mixture as poured into methanol. A precipitate formed and the solid residue was filtered off. The crude product was washed with methanol several times to remove all traces of $FeCl_3$. Finaly column chromatography (DCM:Hexane 2:1)was required to remove a small trace of the starting materials. The final product was collected and placed in the vacuum oven overnight to dry. Characterisation tests were carried out to determine the structure of polymer (1). **Yield = 0.21g IR(KBr disc)** 2900-2840(CH_2-CH_3 stretch alkyl chain), 1711.8(C=O of ester), 1674-1597 (C=C stretch pyrrole), 1590(C=C aromatic), 1596 (N-H bending), , 1254 (C-O stretch of ester) cm^{-1}.

8.51 Chemical Polymerisation of Monomer (2)

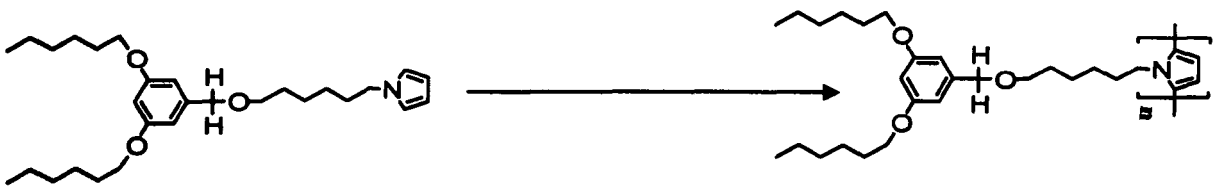


Preparation:

Monomer (2) is related to monomer (1), with the exception being that it has a terminally attached LC group instead of a laterally attached LC group. It was therefore decided that he same method of chemical polymerisation should be used. Chemical polymerisation of Monomer (2) was carried out by dissolving $FeCl_3$ (1.1g, 0.0069mol) in the minimum amount of chloroform (10ml) in a two necked round bottom flask (50ml) fitted with a pressure equalized dropping funnel and nitrogen inlet. The mixture was stirred vigorously, and purged with N_2(g) until dissolved. In a separate beaker (50ml), monomer (2) (1.0(g), 0.0031mol) was dissolved in chloroform (15ml) and then slowly poured into the dropping funnel and added to the reaction mixture over 10 mins. The mixture was heated (30^0C), with vigorous stirring under a nitrogen atmosphere. After 24h the reaction was stopped, and the mixture as poured into methanol. A precipitate formed and the solid residue was filtered and washed with methanol several times to remove all traces of $FeCl_3$. Column chromatography (DCM:Hexane 2:1)was required to remove a small trace of the starting materials The final product was collected and placed in the vacuum oven overnight to dry. Characterisation tests were carried out to determine the structure of Polymer (2) Yield = 0.39g.

IR(KBr disc) 2940-2870(CH_2-CH_3 stretch alkyl chain), 1732(C=O of ester), 1677-1657 (C=C stretch pyrrole), 1600(C=C aromatic), 1596 (N-H bending), cm^{-1}, (1108 & 1254 C-O stretch of ester).

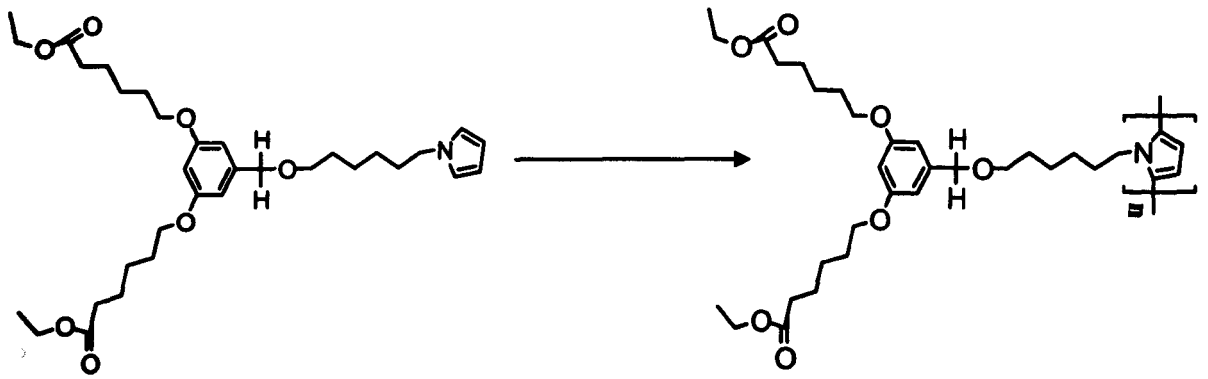
8.52 Chemical Polymerisation of Monomer (3)



Preparation:

Monomer (3) was chemically polymerised by dissolving $FeCl_3$ (0.4g, 0.002mol) in the minimum amount of chloroform (10ml) in a two necked round bottom flask (50ml) fitted with a pressure equalized dropping funnel and nitrogen inlet. The mixture was stirred vigorously, and purged with N_2(g) until dissolved. In a separate beaker (50ml), monomer (3) (0.5(g), 0.001mol) was dissolved in chloroform (10ml) and then slowly poured into the dropping funnel and added to the reaction mixture over 10 mins. The mixture was heated gently (30^0C), with vigorous stirring under a nitrogen atmosphere. After 24h the reaction was stopped, and the mixture as poured into methanol. A precipitate formed and the solid residue was filtered and washed with methanol several times to remove all traces of $FeCl_3$. Column chromatography (DCM:Hexane 2:1) was carried out to remove the impurities arising from the starting materials, however the product appered to partially adher to the stationary phase, which may have reduced the product yield. The final product was collected and placed in the vacuum oven overnight to dry. Characterisation tests were carried out to determine the structure of polymer (3). Yield = 0.13g **IR (KBr)** 2931-2558(CH_2-CH_3 alkyl chain), 1611-1665 (C=C stretch pyrrole), 1600 (C=C aromatic ring), 1500(pyrrole C=C), 1254 (C-N Stretch)), 1040(C-H in plane bending) 776 (C-H out of plane bending) cm^{-1}

8.53 Chemical Polymerisation of Monomer (5)

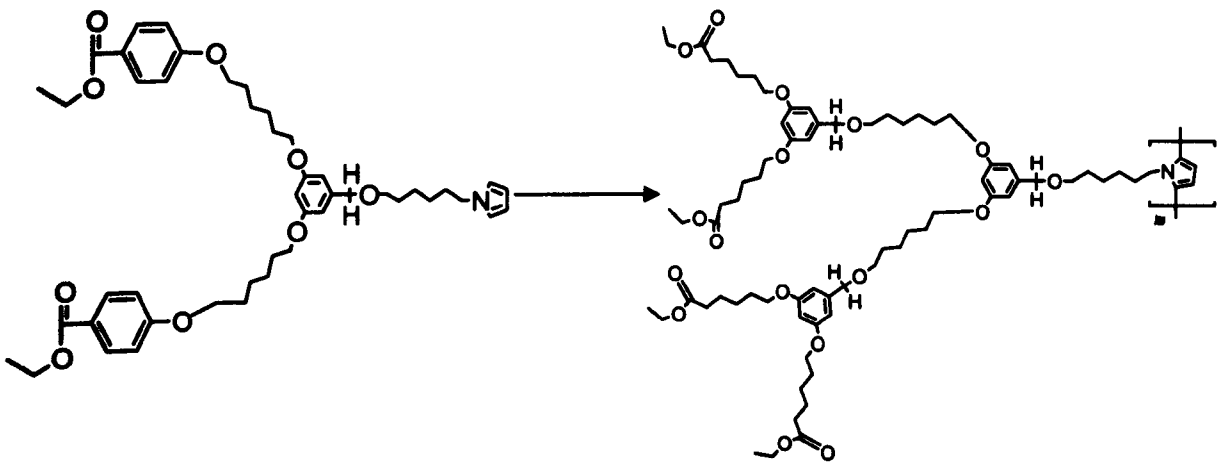


Preparation:

Monomer (5) was chemically polymerised by dissolving $FeCl_3$ (0.3g, 0.0019mol) in the minimum amount of chloroform (10ml) in a two necked round bottom flask (50ml) fitted with a pressure equalized dropping funnel and nitrogen inlet. The mixture was stirred vigorously, and purged with $N_2(g)$ until dissolved. In a separate beaker (50ml), monomer (5) (0.5(g), 0.00087mol) was dissolved in chloroform (10ml) and then slowly poured into the dropping funnel and added to the reaction mixture over 10 mins. The mixture was heated gently (30^0C), with vigorous stirring under a nitrogen atmosphere. After 24h the reaction was stopped, and the mixture as poured into methanol. A precipitate formed and the solid residue was filtered and washed with methanol several times to remove all traces of $FeCl_3$. The crude product was subjected to column chromatography, using (ethyl acetate: hexane 2:1). The final product was collected and placed in the vacuum oven overnight to dry. Characterisation tests were carried out to determine the structure of Polymer (5) .

Yield = 0.18g **IR(KBr disc)** 2530-2830(CH_2-CH_3 stretch alkyl chain), 1740(C=O of ester), 1644-1667 (C=C stretch pyrrole), 1601(C=C aromatic), 1516 (N-H bending), 1018 & 1224 (C-O of ester), 800-724(meta substituted benzene ring) cm^{-1}. Yield = 0.2 g

8.54 Chemical Polymerisation of Monomer (7)

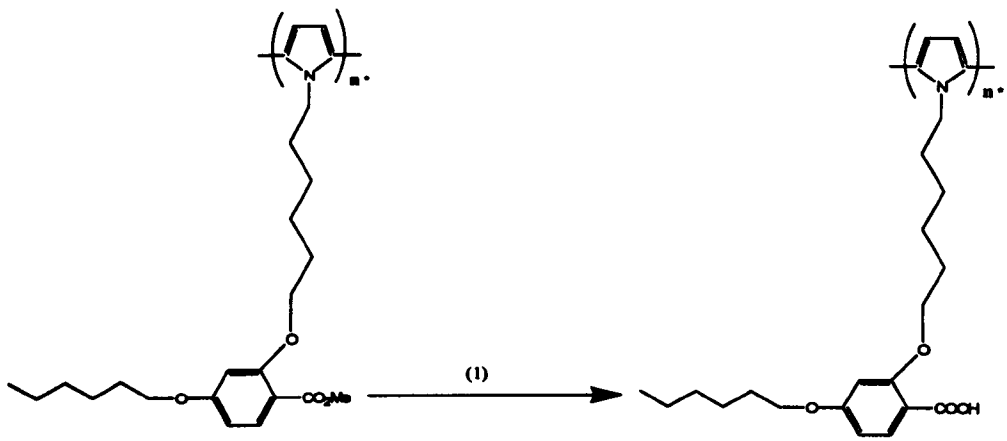


Preparation:

Monomer (7) was chemically polymerised by dissolving $FeCl_3$ (0.09g, 0.00056mol) in the minimum amount of chloroform (10ml) in a two necked round bottom flask (50ml) fitted with a pressure equalized dropping funnel and nitrogen inlet. The mixture was stirred vigorously, and purged with N_2(g) until dissolved. In a separate beaker (50ml), monomer (7) (0.2(g), 0.00025mol) was dissolved in chloroform (10ml) and then slowly poured into the dropping funnel and added to the reaction mixture over 10 mins. The mixture was heated gently (30^0C), with vigorous stirring under a nitrogen atmosphere. After 24h the reaction was stopped, and the mixture as poured into methanol. A precipitate formed and the solid residue was filtered and washed with methanol several times to remove all traces of $FeCl_3$. The crude product was subjected to column chromatography using (ethyl acetate: hexane 2:1). The final product was collected and placed in the vacuum oven overnight to dry. Characterisation tests were carried out to determine the structure of polymer (7).

Yield = 0.24g **IR(KBr disc)** 2940-2870(CH_2-CH_3 stretch alkyl chain), 1739(C=O of ester), 1644-1667 (C=C stretch pyrrole), 1600(C=C aromatic), 1596 (N-H bending), 1254(C-O of ester), (800-724(meta substituted benzene ring) cm^{-1}.

8.55 Hydrolysis of Poly-1-(N-pyrrole)-6-(methyl 4-n-hexyloxy-2-oxybenzoate)hexane - Polymer (I)



Step (1) = Potassium hydroxide, Ethanol, THF Distilled water H_3O^+

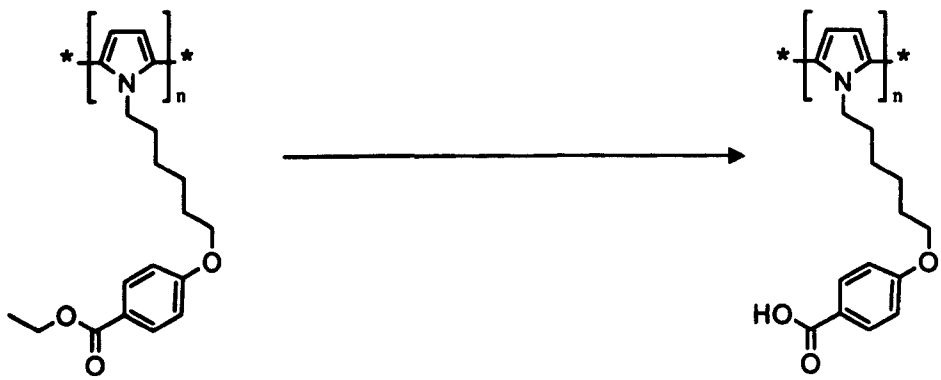
Preparation:

To a round bottom flask (100ml) equipped with a reflux condenser, polymer (1) (1g) was added to a mixture of KOH(0.4g) in 80% aqueous ethanol (50cm^3). The mixture was heated under reflux for 12 hours. Upon completion the reaction mixture was cooled, and poured into distilled water (50ml). Next hydrochloric acid was added dropwise until an acidic pH was achieved. The precipitate was filtered off and the polymer product was washed several times with distilled water (20cm^3) and extracted with dichloromethane (3x50cm^3). The organic layer was collected and dried over magnesium sulphate and the solvent was removed under reduced pressure. The final product was placed in the vacuum oven overnight. The final carboxylic acid polymer (1a) was a dark brown granular solid. Yield = 0.69g

IR(KBr disc) 2940-2870(CH_2-CH_3 stretch alkyl chain), 2500(OH of carboxylic acid), 1705(C=O of acid), 1644-1667 (C=C stretch pyrrole), 1600(C=C aromatic), 1596 (N-H bending), 1285 (C-O of COOH) cm^{-1}

IR Spectroscopic characterisation of the carboxylic acid forms of polymers 1,2,5,6 & 7 are broadly similar to their related ester polymers. The most noticeable difference being the carbonyl of each acid polymer appears lower at 1700 cm^{-1} than that of the ester carbonyl at 1732 cm^{1} due to hydrogen bonding lowering the strength of the carbonyl bond. In addition a very broad OH band at approximately 3500-2500cm^{-1} can be seen for the COOH polymers whereas the esters did not show any presence of OH bonding in this region.

8.56 Hydrolysis of Polymer (2)



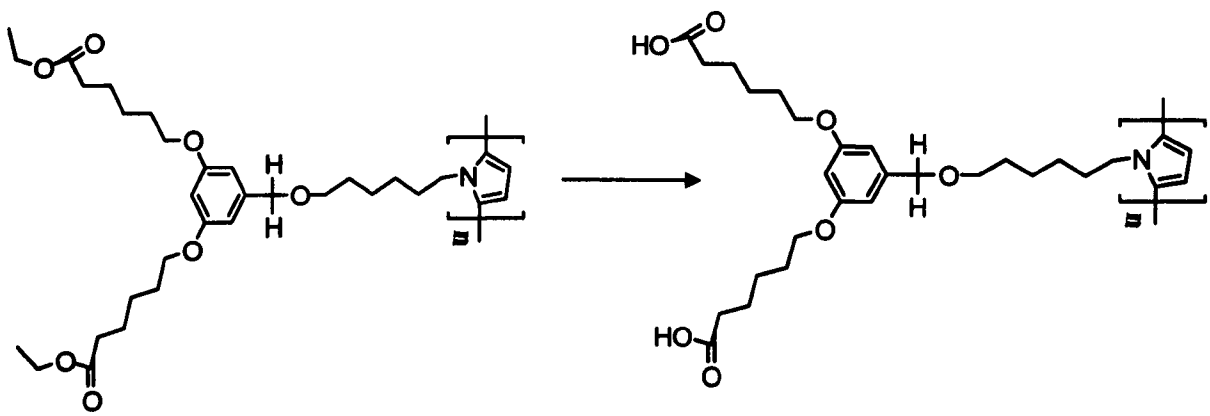
Step (1) = Potassium hydroxide, Ethanol, THF Distilled water H_3O^+

Preparation:

To a round bottom flask (100ml) equipped with a reflux condenser, polymer (2) (1g,) was added to a mixture of KOH(0.5g) in 80% aqueous ethanol ($50cm^3$). The mixture was heated under reflux for 12 hours. Upon completion the reaction mixture was cooled, and poured into distilled water (50ml). Next hydrochloric acid was added dropwise until an acidic pH was achieved. The precipitate was filtered off and the polymer product was washed several times with distilled water ($20cm^3$) and extracted with dichloromethane ($3x50cm^3$). The organic layer was collected and dried over magnesium sulphate and the solvent was removed under reduced pressure. The final product was placed in the vacuum oven overnight. The final carboxylic acid polymer (2a) was a black granular solid. Yield = 0.76g

IR(KBr disc) 2940-2870(CH_2-CH_3 stretch alkyl chain), 3417(OH of carboxylic acid), 1705(C=O of acid), 1644-1667 (C=C stretch pyrrole), 1600(C=C aromatic), 1596 (N-H bending), 1293 (C-O of COOH) cm^{-1}.

8.57 Hydrolysis of Polymer (5)



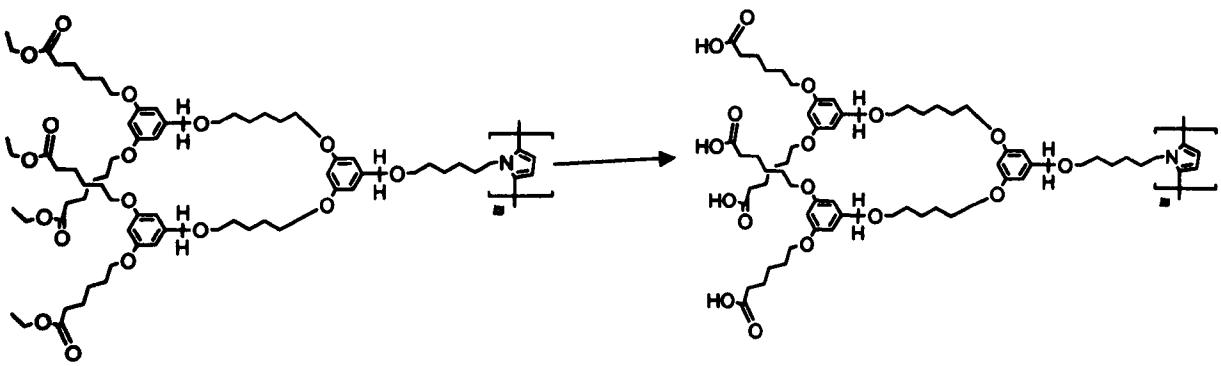
Step (1) = Potassium hydroxide, Ethanol, THF Distilled water H_3O^+

Preparation:

To a round bottom flask (100ml) equipped with a reflux condenser, polymer (1) (1g,) was added to a mixture of KOH(0.5g) in 80% aqueous ethanol (50cm^3). The mixture was heated under reflux for 12 hours. Upon completion the reaction mixture was cooled, and poured into distilled water (50ml). Next hydrochloric acid was added dropwise until an acidic pH was achieved. The precipitate was filtered off and the polymer product was washed several times with distilled water (20cm^3) and extracted with dichloromethane (3x50cm^3). The organic layer was collected and dried over magnesium sulphate and the solvent was removed under reduced pressure. The final product was placed in the vacuum oven overnight. The final carboxylic acid polymer (5a) was a dark brown powdery solid. Yield = 0.4g

IR(KBr disc) 2940-2870(CH_2-CH_3 stretch alkyl chain), 2875(OH of carboxylic acid), 1700.5(C=O of acid), 1644-1667 (C=C stretch pyrrole), 1592 (C=C aromatic), 1596 (N-H bending), 1224 (C-O of COOH)cm^{-1}.

8.58 Hydrolysis of Polymer (6)



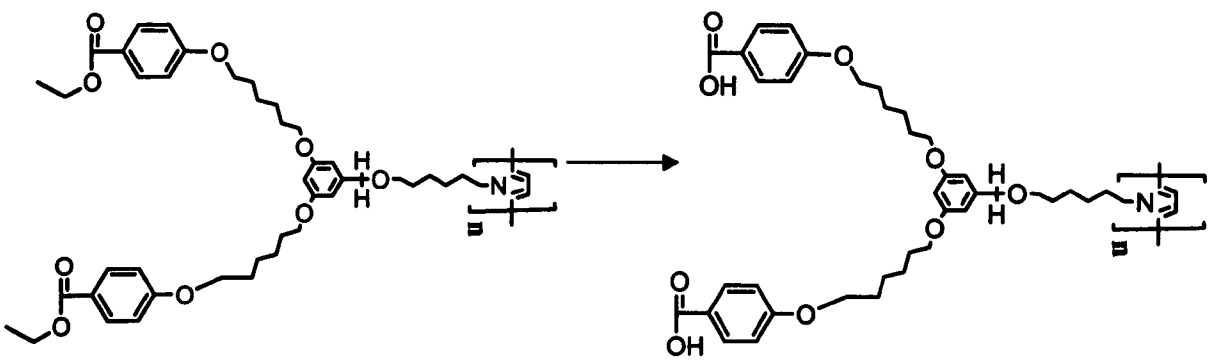
Step (1) = Potassium hydroxide, Ethanol, THF Distilled water H_3O^+

Preparation:

To a round bottom flask (100ml) equipped with a reflux condenser, polymer (6) (1g) was added to a mixture of KOH(0.5g) in 80% aqueous ethanol (50cm^3). The mixture was heated under reflux for 12 hours. Upon completion the reaction mixture was cooled, and poured into distilled water (50ml). Hydrochloric acid was added dropwise until an acidic pH was achieved. The precipitate was filtered off and the polymer product was washed several times with distilled water (20cm^3) and extracted with dichloromethane (3x50cm^3). The organic layer was collected and dried over magnesium sulphate and the solvent was removed under reduced pressure. The final product was placed in the vacuum oven overnight. The final carboxylic acid polymer (6a) was a black granular solid. Yield = 0.37g

IR(KBr disc) 2654-2718(CH_2-CH_3 stretch alkyl chain), 2570(OH of carboxylic acid), 1700(C=O of acid), 1612-1654 (C=C stretch pyrrole), 1602 (C=C aromatic), 1596 (N-H bending), 1300 (C-O of COOH) cm^{-1}.

8.59 Hydrolysis of Polymer (7)



Step (1) = Potassium hydroxide, Ethanol, THF Distilled water H_3O^+

Preparation:

To a round bottom flask (100ml) equipped with a reflux condenser, polymer (7) (1g) was added to a mixture of KOH(0.5g) in 80% aqueous ethanol (50cm^3). The mixture was heated under reflux for 12 hours. Upon completion the reaction mixture was cooled, and poured into distilled water (50ml). Next hydrochloric acid was added dropwise until an acidic pH was achieved. The precipitate was filtered off and the polymer product was washed several times with distilled water (20cm^3) and extracted with dichloromethane (3x50cm^3). The organic layer was collected and dried over magnesium sulphate and the solvent was removed under reduced pressure. The final product was placed in the vacuum oven overnight. The final carboxylic acid polymer (7a) was a black granular solid. Yield = 0.41g

IR(KBr disc) 2940-2870(CH_2-CH_3 stretch alkyl chain), 2600(OH of carboxylic acid), 1728.0(C=O of acid), 1644-1667 (C=C stretch pyrrole), 1605(C-C aromatic), 1596 (N-H bending), 1305 (C-O of COOH) cm^{-1}.

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