Synthesis and Characterization of Condensation Monomers
3.1 Introduction

Cashew nut shell liquid (CNSL)—a by-product of the cashew processing industry—is abundantly available worldwide (1,25,000 tpa).\(^1\) CNSL is a product of cashew tree, *Anacardium occidentale\(^2\)* and occurs as a greenish-yellow viscous liquid in the soft honeycomb of the shell of the cashew nut. Cashew nut consists of an ivory colored kernel covered by a thin brown membrane (testa) and enclosed by an outer porous shell—the mesocarp—with a honeycomb structure, where CNSL is stored (Figure 3.1).

![Figure 3.1](image)

**Figure 3.1** (a) Cross section of cashew nut (b) Cashew fruit (c) Cashew nut shell liquid

CNSL is available in many parts of the world, such as, Brazil, India, Bangladesh, Tanzania, Kenya, tropical regions of Africa and South-East and Far-East Asia. Traditionally, a number of methods are employed to extract the oil from the nuts. Hot oil bath method where raw nuts are passed through a bath of hot CNSL at 180-200°C and roasting method are commonly used ones. Reports are also available on using steam distillation, solvent extraction, supercritical extraction using a mixture of CO\(_2\) and isopropyl alcohol for extraction of CNSL.\(^1\)

Industrial grade CNSL is reddish brown in color. CNSL constitutes about 20-25% of the weight of cashew. Crude CNSL represents one of the major and cheapest sources of naturally occurring non-iso-prenoid phenolic lipids such as; anacardic acid, cardol, cardanol and 2-methyl cardol\(^1\) (Figure 3.2).

![Figure 3.2](image)

**Figure 3.2** Constituents of Cashew Nut Shell Liquid (CNSL)
Commercial grade CNSL contains hardly any anacardic acid because of decarboxylation during roasting process, which converts anacardic acid to cardanol. Unsaturated 15- carbon chain and phenolic moiety in CNSL has offered a variety of possibilities for the synthetic chemist. Many reactions of CNSL such as, hydrogenation, polymerization, sulfonation, nitration, halogenation, etherification, esterification, epoxidation, phosphorylation, etc. have been documented in various patents and published reports.\textsuperscript{1,3,5}

Considerable attention from polymer scientists throughout the world is devoted to utilize potential attributes of CNSL as a substitute for petrochemical derivatives and has found use in phenolic resins in break lining, surface coatings, adhesives, foundry resins, laminates, rubber compounding, additives, etc. Of late, CNSL has been used in the preparation of many specialty materials such as liquid crystalline polyesters, nanotubes, cross-linkable polyphenols, polyurethanes and a range of other specialty polymers and additives.\textsuperscript{1,3} The number of chemicals that have been synthesized starting from CNSL is too large to be catalogued here. Nevertheless, representative value-added chemicals synthesized from CNSL are presented in Table 3.1.

Considering special structural features of cardanol and need for finding better opportunities for an appropriate utilization of this material, new strategies can be developed to design specialty/ high performance polymers from cardanol.

One of the most important criteria that determines the final properties of a polymer is the structure of monomers and by selecting suitable monomers properties of a polymer could be tailored.\textsuperscript{4,8} Therefore, in the synthesis of polymer the first step constitutes the synthesis of desired monomers, which can give rise to polymers with expected / targeted properties.

In the area of high performance polymers such as polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyazomethines, polyetherketones and polyesters, etc., a large number of difunctional monomers have been synthesized in the past three decades with a view to overcome the traditional processing problems caused by the limited solubility and poor processability of these polymers. Efforts devoted to incorporating the structural features that improve processability have led to an outstanding enrichment of the chemistry of high performance polymers, and have allowed the opening of new investigations and application areas for these polymers.\textsuperscript{9,10}

CNSL has special structural features like phenolic moiety with an unsaturated 15- carbon side chain. Hydrogenated cardanol- a long chain alkyl phenol with an aliphatic chain in the \textit{meta} position- represents a versatile and easily available precursor to various derivatives. Taking these attractive aspects into consideration, a variety of new monomers \textit{viz.}, dihalide, diacid, diacylhydrazide, diamines, diisocyanate and bisphenols were designed and synthesized starting from cashew nut shell liquid-a cheap and commercially available raw material.
### Table 3.1 CNSL-based chemicals

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>CNSL-based Chemicals</th>
<th>Applications</th>
<th>Ref</th>
</tr>
</thead>
</table>
| 1       | ![CNSL-based Chemical](image1) | • Foundry binder  
• Novolac resins | 11, 12 |
| 2       | ![CNSL-based Chemical](image2) | Polyol for polyurethane | 13 |
| 3       | ![CNSL-based Chemical](image3) | Anionic surfactant for polypyrrole nanospheres | 14, 15, 16 |
| 4       | ![CNSL-based Chemical](image4) | Surfactant composition | 17 |
| 6       | ![CNSL-based Chemical](image5) | Quaternary ammonium salts as phase transfer catalyst | 18 |
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<table>
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<tr>
<th>R</th>
<th>Conversion of cardols (6-alkenyl resorcinols) into lasiodiplodin, a naturally occurring 12-membered orsellinic acid type macrolide, which exhibits plant growth regulating and antileukemic properties</th>
<th>Lipophilic epoxy modifier for viscosifiers in drilling fluids</th>
<th>Polybenzoxazines</th>
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<tr>
<td>—CH₃, —CH₂CH₃, —CH₂CH₂CH₃</td>
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<tr>
<td>OMeO, OAc, AcO, CisH₃i-n, OH, CHO</td>
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<td>R = C₁₅H₃₁-n</td>
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<td>Resin to modify the properties of elastomers isobutylene isoprene rubber (IIR) and natural rubber (NR).</td>
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<tr>
<td>16</td>
<td><img src="image2" alt="Structure" /></td>
<td>Monomer for synthesis of polyimides</td>
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| 17     | ![Structure](image3) | - Polyaniline-clay composite as a novel intercalating agent cum dopant.  
- Flame retardation of polyethylene |
| 18     | ![Structure](image4) | - Molecularly imprinted polymers  
- Polycardanyl acrylate |
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<td>Used as a dietary supplements with health-promoting and disease-preventive properties</td>
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<td>WxgVcHO [image]</td>
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<td>20</td>
<td>Telechelic urethane acrylate UV-curable pre-polymeric material</td>
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<td></td>
<td>[image]</td>
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<td>21</td>
<td>Cardanol-grafted natural rubber</td>
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<td>[image]</td>
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<td>22</td>
<td>Biscardanol derivatives</td>
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<td></td>
<td>[image]</td>
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<td>Monomer for novolac-type resins</td>
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<td>[image]</td>
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<td>24</td>
<td>Development of soft nanomaterials from bio-based amphiphiles</td>
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Cardanol derivatives

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<td>29</td>
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<td>Cardanol polysulfide</td>
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<td>30</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>Curing agent</td>
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<td>31</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>Use in pigment dispersions</td>
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<td>32</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>Hydrosilylation products for grafting self-assembled monolayers onto silicon surfaces</td>
<td>46</td>
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</table>
| 33  | ![Structure](image6.png) | - Hydrophobically modified poly(acrylic) acid using 3-pentadecyl cyclohexyl amine  
- α,ω-hydroxy-poly(ethylene oxide) end-capped with 1-isocyanato-3-pentadecyl cyclohexane | 47, 144 |
| 34  | ![Structure](image7.png) | Monomers for:  
- Polyether  
- Polyurethanes | 48, 49 |
### Table 3.1 Continued

<table>
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<td>Antistatic agents for polycarbonates</td>
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<td>Chromogenic azocrown ethers</td>
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<tr>
<td>47</td>
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- **OH**
- **R**
- **R'**
- **R = C15H31-n , R' = Me or Sec-butyl**

**Blocked isocyanates**

**Petroleum marker dyes**

**Antioxidant for gasoline stabilisation**

**Liquid crystalline polymer with crosslinked network structures**

**Dopant (Polyaniline)**

**Monomer for:**
- Polyimides for liquid crystal devices.
- Polyamides
Table 3.1 Continued..............................

| 48 | HO—N—N—OH | Monomer for polycarbonates | 5 |
| 49 | C_{15}H_{31-n} | Resins | 66 |
| 50 | HO—N—N—OH | Monomer for:  
- Polyesters  
- Polyurethanes | 67, 68, 69 |
| 51 | H_{2}N—O—C_{15}H_{31} | Reagent for end-capping polyimides | 70 |
| 52 | CH_{3}(CH_{2})_{4—} | Monomer for potential membrane-forming amphiphiles | 71 |
| 53 | H_{3}N—O—S—O—C_{15}H_{31} | Monomer for polyamides | 72 |
| 54 | OH—O—OH | Monomer for polyurethanes | 73 |
| 55 | R—O— | UV-curable compositions and adhesive formulations | 74 |
| 56 | OH | Polyfunctional compounds | 75 |
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<td><img src="image" alt="Diisocyanates" /></td>
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<td>59</td>
<td><img src="image" alt="Plasticiser extenders for PVC" /></td>
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<tr>
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<td><img src="image" alt="Isocyanates" /></td>
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<th>Cardanol derivatives</th>
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<td><em>R</em> = H, CH₃</td>
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3.2 Experimental

3.2.1 Materials

3-Pentadecyl phenol, bromobenzene, copper powder, copper cyanide, palladium-on-carbon, ruthenium-on-carbon, 3-mercaptopropionic acid (3-MPA) and calcium hydride (Aldrich Chemicals) were used as received. Sulfanilic acid (Fluka), bromine, ammonia solution, copper sulfate, hydrochloric acid, sulfuric acid, pyridine, triethyl amine, ethanol, acetic acid, 1-chloro-4-nitrobenzene, ammonium acetate, aluminium chloride, phenol, sodium nitrite and sodium dithionite (Merck, India and E-Merck Germany) were used as received. Potassium hydroxide, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate, potassium carbonate, magnesium metal, acetyl chloride and methanesulfonyl chloride (Loba Chemie) were used as received. Hydrazine hydrate (99%) (S.D. Fine., India) was used as received. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.\textsuperscript{80}

Pyridiniumchlorochromate (PCC) was prepared according to the procedure reported in the literature.\textsuperscript{81}

3.2.2 Measurements

Melting points were determined by open capillary method and are uncorrected.

FT-IR spectra were recorded on a Perkin-Elmer 599B spectrophotometer in chloroform or as KBr Pellets.

NMR spectra were recorded on a Bruker 200, 400 or 500 MHz spectrometer at resonance frequencies of 200, 400 or 500 MHz for $^1$H and 50, 100 or 125 MHz for $^{13}$C measurements using CDCl$_3$ or DMSO-d$_6$ as a solvent.

3.3 Preparations

3.3.1 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

3.3.1.1 Conversion of cardanol to 3-pentadecyl phenol

Cardanol (500 g, 1.64 mol) was dissolved in isopropanol (2 litres) and was hydrogenated in the presence of 5% Pd/C (1.5 g) catalyst at 70°C in a Parr autoclave under 600 psi hydrogen pressure. When no more hydrogen absorption was noticed, the hydrogenation was stopped. The reaction mixture was filtered to remove Pd/C. The solvent was evaporated to obtain crude product. Pure 3-pentadecyl phenol was obtained after recrystallization from hexane (40-60°C).

Yield: 480 g (95%); M.P: 50-51°C (Lit.\textsuperscript{119} m.p.: 50-51°C).
3.3.1.2 Synthesis of 1-pentadecyl-3-phenoxy benzene

Into a 1000 mL two necked round bottom flask fitted with a Dean and Stark assembly with a reflux condenser were taken 3-pentadecyl phenol (100.0 g, 0.33 mol), potassium hydroxide (22.06 g, 0.39 mol) N,N-dimethylacetamide (300 mL) and toluene (150 mL). The reaction mixture was refluxed for 7 h and the by-product water formed was removed from the reaction mixture azeotropically. After completion of the reaction, the solvent was distilled off and the dark sticky product was dried under reduced pressure. The compound obtained was potassium salt of 3-pentadecyl phenol.

Into a 1000 mL round bottom flask containing potassium salt of 3-pentadecyl phenol (111.0 g, 0.32 mol) was added bromobenzene (50.88 g, 0.32 mol), followed by Cu powder (2.22 g, 2 wt %) and DMAC (150 mL). The reaction mixture was heated at 150 °C for 6 h. After completion of the reaction, the obtained dark colored reaction mixture was poured into water (500 mL); the Cu salts were removed by filtration; The filtrate was extracted with ethyl acetate (2 x 300 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over sodium sulfate. Solvent evaporation yielded crude 1-pentadecyl-3-phenoxy benzene. Pure 1-pentadecyl-3-phenoxy benzene was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 70 g (57 %); M.P. 32 °C

3.3.1.3 Synthesis of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene

Into a 500 mL three necked round bottom flask equipped with a stirrer, a condenser, a dropping funnel and a thermometer containing a solution of 1-pentadecyl-3-phenoxy benzene (25.0 g, 66 mmol) in dichloromethane (150 mL) was added dropwise bromine (22.08 g, 0.14 mol) protecting from light. The top of the condenser was equipped with a trap to absorb the HBr released during the reaction. Bromine was added at a temperature between -5° to 0°C over a period of 15 minutes. After completion of the addition, the reaction mixture was stirred at the same temperature for 1 h and then refluxed overnight. After completion of reaction, excess bromine and HBr were neutralized with aqueous 10% NH₃ (100 mL). Two phases formed in the reaction mixture were separated, and the organic layer was washed with water (2 x 300 mL). After drying of dichloromethane solution over sodium sulfate and distillation, crude 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was obtained. Pure 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 30 g. (84%); M.P. 43 °C

3.3.1.4 Synthesis of 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile

Into a 250 mL three-necked round bottom flask containing 1-bromo-4-(4'-cyanophenoxy)-2-pentadecyl benzene (10.0 g, 18 mmol) was added copper cyanide (6.65 g, 74 mmol) followed by CuSO₄ (0.10 g) and DMF (50 mL). The reaction mixture was refluxed overnight. After completion of the reaction, the obtained brown colored solution was poured into concentrated hydrochloric acid
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(50 mL); and the solution was extracted with ethyl acetate (2 x 200 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over sodium sulfate. Solvent evaporation yielded crude 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile. Pure 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).
Yield: 6.7 g (83%); M.P. 64 °C

3.3.1.5 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

Into a 250 mL single necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were added 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile (5.0 g, 11 mmol), potassium hydroxide (7.81 g, 140 mmol), triethylene glycol (75 mL) and water (10 mL). The reaction mixture was refluxed for 72 h. Next, the temperature of the reaction mixture was lowered to 120 °C and water (50 mL) was added and the reaction mixture was heated at 100°C for additional 48 h. After completion of the reaction time, the reaction mixture was diluted with water (50 mL) and poured into excess concentrated hydrochloric acid. Crude 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid precipitated as a grey solid which was filtered and thoroughly washed with water. The obtained solid was dissolved in aqueous potassium hydroxide solution and was precipitated by addition of concentrated hydrochloric acid (pH 2). The solid was filtered up and washed repeatedly with water and dried. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid was purified by column chromatography (eluent: pet ether).
Yield: 3.7 g (68%); M.P. 130 °C

3.3.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

3.3.2.1 Synthesis of methyl 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecylbenzoate

Into a 250 mL two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid (14.0 g, 29.9 mmol) and 3 drops of DMF. Thionyl chloride (100 mL) was added dropwise over a period of 30 minutes and the reaction mixture was refluxed for 6 h. Excess thionyl chloride was removed by distillation under reduced pressure and to the residue was added dry toluene (25 mL). Toluene was distilled off under reduced pressure to remove the traces of thionyl chloride. This procedure was repeated twice to get 4-[4'-(chlorocarbonyl)phenoxy]-2-pentadecylbenzoyl chloride.

Into a 250 mL three necked round bottom flask equipped with a magnetic stirrer, a reflux condenser and two dropping funnels was placed 4-[4'-(chlorocarbonyl)phenoxy]-2-pentadecyl benzoyl chloride (15.10 g, 29.9 mmol). Pyridine (4.73 g, 59.8 mmol) and methanol (75 mL) were added dropwise to the reaction mixture over a period of 10 minutes and the reaction mixture was refluxed for 5 h. Excess methanol was removed by distillation under reduced pressure. The obtained brown colored solution was extracted with ethyl acetate (2 x 200 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over
sodium sulfate. Solvent evaporation yielded crude methyl 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate. Pure 4-(4'-methoxy carbonyl)phenoxy)-2-pentadecyl benzoate was obtained as a viscous liquid after silica gel (60-120 mesh) column chromatography (eluent: pet ether).
Yield: 12.6 g (85%, based on 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid)

3.3.2.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

Into a 250 mL two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed methyl 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate (11.5 g, 23.1 mmol) and ethanol (100 mL). Hydrazine hydrate (99%) (23.21 g, 464 mmol) was added dropwise to the reaction mixture over a period of 15 minutes and reaction mixture was refluxed overnight. The solid that separated out was filtered and dried. Crude 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide was purified by crystallization from ethanol.
Yield: 9.77 g (85%); M.P. 62 °C

3.3.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

3.3.3.1 Synthesis of 4-amino-3-pentadecyl phenol

Into a 500 mL three necked round bottom flask equipped with a reflux condenser, a thermowell, and a magnetic stirrer were placed 3-pentadecyl phenol (30.4 g, 0.10 mol), potassium hydroxide (28.0 g, 0.50 mol), and ethyl alcohol (200 mL). The reaction mixture was stirred and to the reaction mixture was added diazonium chloride prepared from sulphanilic acid dihydrate (21.0 g, 0.10 mol) at -5 °C. The resulting red dye solution was stirred for 2 h and then heated at 75 °C on a water bath. At this temperature, a saturated solution of sodium dithionite (53.0 g, 0.30 mol) was added to the dye solution over a period of 10 min and the reaction mixture was stirred for 30 min (color of reaction mixture changed from dark red to orange). To the reaction mixture was then added acetic acid (18.0 g, 0.30 mol) dissolved in water (20 mL) and was refluxed for 1 h (color changed to pale tan). The reaction mixture was poured into water (2 L), the product was filtered and dried under reduced pressure at 50 °C for 2 h. The crude product was purified by recrystallisation using toluene.
Yield: 25.0 g (79%); M.P. 104°C (lit.56 M.P. 105-106 °C).

3.3.3.2 Synthesis of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine

Into a 500 mL three necked round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirrer were placed 4-amino-3-pentadecyl phenol (20.0 g, 62 mmol), 1-chloro-4-nitrobenzene (9.87 g, 62 mmol), potassium carbonate (9.53 g, 68 mmol) and DMF (100 mL). The reaction mixture was refluxed for 3 h under dry nitrogen gas stream. After completion of the reaction time, reaction mixture was cooled to room temperature and poured into water. The precipitated product was filtered, dried and recrystallised from ethyl alcohol.
Yield: 18.9 g (90%); M.P. 67°C
3.3.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

Into a 250 mL three necked round bottom flask equipped with a dropping funnel and a reflux condenser were placed 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine (10.0 g, 22 mmol), palladium-on-charcoal (3 wt%) and ethyl alcohol (100 mL). To the reaction mixture, hydrazine hydrate (34.13 g, 0.68 mol) was added dropwise over a period of 15 min at 80 °C. After the addition was complete, the reaction mixture was refluxed for 3 h. The reaction mixture was filtered to remove palladium-on-charcoal. The product precipitated on cooling was isolated by filtration and was recrystallised twice from ethanol.

Yield: 8.38 g (90%); M.P. 81°C

3.3.4 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

3.3.4.1 Synthesis of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine

Into a 500 mL three necked round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirrer were charged 4-amino-3-pentadecyl phenol (7.0 g, 21.9 mmol), 1-chloro-2-nitrobenzene (3.45 g, 21.9 mmol), potassium carbonate (3.33 g, 24.1 mmol) and N,N-dimethylformamide (75 mL). The reaction mixture was refluxed for 3 h under dry nitrogen gas stream. The reaction mixture was then cooled to room temperature and poured into water. The precipitated viscous product was filtered, dried and purified by column chromatography (Eluent: pet ether).

Yield: 7.7 g (80%)

3.3.4.2 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

Into a 250 mL three necked round bottom flask equipped with a dropping funnel and a reflux condenser were charged 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine (5.0 g, 11.3 mmol), palladium-on-charcoal (3 wt%) and ethyl alcohol (70 mL). To the reaction mixture, hydrazine hydrate (17.06 g, 0.3 mol) was added dropwise over a period of 15 min at 80 °C. After the addition was complete, the reaction mixture was refluxed for 3 h. The reaction mixture was filtered to remove palladium-on-charcoal. The product precipitated on cooling was isolated by filtration and was recrystallised twice from ethanol.

Yield 3.96 g (85%); M.P. 70°C

3.3.5 Synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

Into a 250 mL three necked round bottom flask equipped with a stirrer, a reflux condenser, a pressure equalizing dropping funnel and a nitrogen inlet were placed 4-(4'-aminophenoxy)-2-pentadecylbenzenamine (1.0 g, 2.40 mmol) and dry toluene (50 mL). The reaction mixture was flushed with nitrogen gas and the solution was stirred at 0 °C. In another 100 mL single-necked flask, bis(trichloromethyl) carbonate (triphosgene) (4.38 g, 14.7 mmol) was weighed and dissolved in dry toluene (50 mL). The solution of triphosgene was transferred to the dropping funnel under
nitrogen atmosphere and was slowly added to the solution containing 4-(4'-aminophenoxy)-2-pentadecyl benzenamine with constant stirring over a period of 15 minutes at 0 °C. After completion of the addition, the reaction mixture was stirred at room temperature for 2 h and then refluxed for 6 h. Finally, excess phosgene was removed by flushing the stream of nitrogen through the solution and toluene was distilled off under reduced pressure to yield 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene.

Yield: 0.84 g (75%)

3.3.6 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

3.3.6.1 Synthesis of 1-methane sulfonyloxy-3-pentadecyl benzene

Into a 250 mL two necked round bottom flask equipped with an addition funnel and an air condenser were added 3-pentadecylphenol (5.0 g, 16.4 mmol), triethyl amine (1.8 g, 18 mol) and dichloromethane (50 mL). To the reaction mixture, methanesulfonyl chloride (2.06 g, 18 mol) was added dropwise at 0 °C. After complete addition of methanesulfonyl chloride, the reaction mixture was stirred for 2 days. After completion of the reaction, the reaction mixture was extracted with dichloromethane (2 x 100 mL). The organic layer was washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL). The organic layer was dried over sodium sulfate and filtered. The evaporation of solvent afforded 1-methane sulfonyloxy-3-pentadecyl benzene.

Yield: 4 g (95.4%); M.P. 58°C

3.3.6.2 Synthesis of pentadecyl benzene

Into a 250 mL two necked round bottom flask were taken 1-methane sulfonyloxy-3-pentadecyl benzene (5 g, 13.6 mmol), palladium on charcoal (0.5 g), magnesium metal (0.39 g, 16.3 mmol), ammonium acetate (14.7 g, 191 mmol) and methanol (50 mL) and the reaction mixture was degassed by three vaccum/N₂ cycles. The reaction mixture was stirred under nitrogen atmosphere at room temperature. After completion of the reaction, the reaction mixture was filtered and the filtrate was extracted with dichloromethane (500 mL). The organic layer was washed with saturated aqueous sodium chloride solution (2 x 100 mL), followed by water (3 x 100 mL). The organic layer was dried over sodium sulfate and filtered. The evaporation of solvent afforded pentadecyl benzene as a yellow liquid. The purification was done by column chromatography (eluent: pet ether).

Yield: 2.3 g (62 %)

3.3.6.3 Synthesis of 4-acetyl pentadecyl benzene

Into a 500 mL three necked round bottom flask fitted with a magnetic stirrer, a reflux condenser and a dropping funnel were charged aluminium chloride (5.82 g, 43.67 mmol) and dichloromethane (100 mL). Acetyl chloride (3.42 g, 43.67 mmol) was added to the vigorously stirred reaction mixture over a period of 15 minutes at 0°C. Pentadecyl benzene (10 g, 34.66 mmol) was added over a period of 30 minutes; the reaction mixture was stirred at 0 °C for 2 h and then
allowed to attain room temperature. The reaction mixture was poured into ice and extracted with dichloromethane (3 x 100 mL). The dichloromethane solution was washed with 1 N hydrochloric acid (2 x 30 mL) and water (3 x 50 mL), dried over sodium sulfate and the solvent was evaporated to obtain 4-acetyl pentadecyl benzene as a faint yellow solid. Pure compound was obtained after column chromatography. (eluent: pet ether)

Yield: 10 g (87%); M.P. 34°C

3.3.6.4 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

Into a 250 mL three necked round bottom flask fitted with a magnetic stirrer and a gas dip tube were charged 4-acetyl pentadecyl benzene (5.0 g, 15.15 mmol), phenol (8.54 g, 90.90 mmol) and 3-mercaptopropionic acid (0.13 mL). The reaction mixture was stirred at room temperature for 15 minutes, after which anhydrous hydrogen chloride gas was bubbled into the reaction mixture for 4 days at 50 °C, where upon the reaction mixture solidified. The reaction mixture was dissolved in ethyl acetate (500 mL), washed with aqueous sodium bicarbonate solution (3 x 100 mL) and water (3 x 100 mL). The organic layer was separated and dried over sodium sulfate. The vacuum stripping of solvent afforded a pink solid, which was purified by column chromatography (eluent: pet ether: ethyl acetate, 80:20 v/v) to obtain 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane in the pure form.

Yield: 4 g (52%); M.P. 114 °C

3.3.7 Synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane

3.3.7.1 Synthesis of 3-pentadecylcyclohexanol

3-Pentadecylphenol (80 g, 0.26 mol) dissolved in isopropanol (300 mL) was hydrogenated using 5% Ru/C (2.4 g) as the catalyst in a Parr reactor at 125 °C and at hydrogen pressure of 1000 psi. After the completion of the reaction, the catalyst was filtered off and isopropanol was distilled off to obtain 3-pentadecyl cyclohexanol.

Yield: 79.90 g (98%); M.P. 46-49°C (Lit. m.p. 45-48°C)

3.3.7.2 Synthesis of 3-pentadecylcyclohexanone

Into a 1 liter round bottom flask equipped with a mechanical stirrer was added a finely ground mixture of pyridinium chlorochromate (97 g, 0.45 mol) and silica gel (97 g, 100-200 mesh). To this mixture, dichloromethane (600 mL) was added, the suspension was stirred and 3-pentadecylcyclohexanol (50 g, 0.22 mol) was added in small portions at room temperature. The reaction mixture darkened (30 min) and the stirring was continued for 4 h. The reaction mixture was filtered through a short column of Celite and silica gel. The filtrate was concentrated under reduced pressure to obtain crude 3-pentadecylcyclohexanone. The crude 3-pentadecylcyclohexanone was dissolved in ethyl acetate (300 mL) and washed with saturated aqueous sodium chloride (2 x 200 mL) followed by washing with water (2 x 200 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and ethyl acetate was removed on a rotary evaporator. The residue obtained
was recrystallized from methanol.
Yield: 46.68 g (94%); M.P. 44°C (Lit.\textsuperscript{142} m.p. 43°C)

3.3.7.3 Synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecyclohexane

Into a 250 mL three necked round bottom flask fitted with a magnetic stirrer bar, a HCl dip tube and a reflux condenser connected to a scrubber were placed 3-pentadecyclohexanone (20 g, 0.06 mol), phenol (36.62 g, 0.38 mol) and 3-mercaptopropionic acid (0.1 mL). Dry HCl was bubbled into the reaction mixture at room temperature. The reaction mixture became solid at the end of 1 h. The reaction mixture was dissolved in ethyl acetate (600 mL) and neutralized by washing with aqueous sodium bicarbonate solution (3 x 200 mL) followed by washing with water (2 x 200 mL). The organic layer was dried over sodium sulfate, filtered and ethyl acetate was distilled off. The excess phenol was removed by washing with hexane. The product was crystallized twice from a mixture of hexane and toluene (9:1, v/v).
Yield: 21.72 g (70%); M.P. 104°C (Lit.\textsuperscript{142} m.p. 104°C)

3.4 Results and discussion

One of the approaches to improve solubility and processability of high temperature/high performance polymers is the attachment of flexible chains as pendant groups. It is reported that the use of monomers bearing pendant flexible groups greatly reduces strong intermolecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect. In general, such pendant groups not only bring about improved solubility but also help lower the melting and glass transition temperatures. Thus, our synthetic research effort was directed towards designing monomers with features that disturb structural regularity and chain packing hence imparting improved processability characteristics to the polymers. The approach involved making use of 3-pentadecyl phenol, which in turn is obtained from cashew nut shell liquid. A range of difunctional monomers such as aromatic dibromide, diacid, diacylhydrazide, diamines, diisocyanate, and bisphenols were designed and synthesized.

The following difunctional monomers were synthesized starting from CNSL:

- a. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene,
- b. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid,
- c. 4-[4'-(Hydrazinocarbonyl)phenoxyl]-2-pentadecyl benzoic hydrazide,
- d. 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine,
- e. 4-(2'-Aminophenoxy)-2-pentadecylbenzenamine,
- f. 1-Isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecyl benzene,
- g. 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane, and
- h. 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane.
3.4.1 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

Aromatic dicarboxylic acids are an important class of monomers for the preparation of industrially useful polyesters, polyamides, polyhydrazides, poly(amideimide)s, polyimides, etc. There are several routes available to synthesize carboxylic acids. The oxidation of alkyl benzenes, oxidation of ketones or aldehydes, hydrolysis of esters, hydrolysis of nitriles, using carbon monoxide as a co-reagent, etc. are some of the routes generally adapted for synthesis of carboxylic acids.

The starting material used for the synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid was 3-pentadecyl phenol, which was obtained from side chain hydrogenation of cardanol.

Scheme 3.1 depicts route for the synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid.

A new dicarboxylic acid monomer containing pendant alkyl chain, viz, 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid was designed and synthesized starting from 3-pentadecyl phenol making use of simple organic transformations like Ullmann etherification, electrophilic aromatic substitution such as bromination, cyanation followed by alkaline hydrolysis.

In the first step, 1-pentadecyl-3-phenoxy benzene was prepared by reaction of 3-pentadecyl phenol with bromobenzene in the presence of potassium hydroxide and Cu as a catalyst under classical Ullmann etherification reaction conditions. Typical Ullmann etherification reaction uses Cu-powder/ Cu salts as catalyst. There are several other reagents available for Ullmann etherification reaction such as use of Pd (DBA)2/dppf, Pd(OAc)2/aryldialkyl phosphines as a ligand, (CuOTf)2,PhH/ EtOAc/Cs2CO3/ArCOOH, CuI/ N,N-dimethyl glycine, HCl salt/Cs2CO3, CuCl/Cs2CO3/2,2,6,6- tetramethylheptane-3,5-dione, phosphazene P4-t-Bu base/CuBr, CuI/K2CO3/Raney Ni-Al alloy, etc. In the present study, Cu-powder was used as the catalyst.

The product obtained was purified using column chromatography and was characterized by FTIR, 1H-NMR and 13C-NMR spectroscopy.

FTIR spectrum of 1-pentadecyl-3-phenoxy benzene displayed absorption band at 1267 cm⁻¹ corresponding to -C-O-C- stretching. (Figure 3.3)
Figure 3.3 FTIR spectrum of 1-pentadecyl-3-phenoxy benzene

$^1$H-NMR spectrum of 1-pentadecyl-3-phenoxy benzene is shown in Figure 3.4.

A multiplet in the region 6.80-7.38 δ ppm corresponds to aromatic protons. A triplet at 2.57 δ ppm is assigned to benzylic –CH$_2$. A triplet at 1.55 and a multiplet in the range 1.22-1.27 δ ppm corresponds to the methylene protons of the pendant alkyl chain. The –CH$_3$ protons of pentadecyl chain appeared as a triplet at 0.88 δ ppm.

$^{13}$C-NMR spectrum of 1-pentadecyl-3-phenoxy benzene with assignments is presented in Figure 3.5.
In the second step, 1-pentadecyl-3-phenoxy benzene was selectively brominated at para position to obtain 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene. Various methods of bromination of diphenyl ether have been described in the literature. Preferred brominating agents include, e.g., Br₂, or bromine may be generated in-situ e.g., by employing HBr together with an oxidizing agent such as H₂O₂ or NaBrO₃ or the like known oxidizing agents. The reaction can be carried out in a solvent or without solvent but the presence or absence of a solvent may affect the selectivity of the bromination. When a solvent is employed, it is preferred to employ such a solvent which is unreactive under the reaction conditions such as halocarbons e.g., dichloromethane, carbon tetrachloride, and 1,2-dichloroethane.

The formation of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was confirmed by FTIR, ¹H-NMR and ¹³C-NMR spectroscopy.

In the FTIR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene (Figure 3.6) the band at 796 cm⁻¹ is assigned to C-Br stretching.
Figure 3.6 FTIR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene

In $^1$H-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene, (Figure 3.7) aromatic protons ortho to bromine atom on both aromatic rings exhibited a multiplet in the range 7.38-7.49 ppm, while two aromatic protons 'b' ortho to ether linkage and one proton ortho to pentadecyl chain, displayed a multiplet in the range 6.85-6.90 ppm. A proton meta to bromine atom on pentadecyl-substituted aromatic ring appeared at 6.69 ppm as doublet of doublet. Due to the electron withdrawing nature of bromine atom, the benzylic –CH$_2$ in pentadecyl chain shifted to 2.66 ppm. The methylene protons $\beta$ to aromatic ring exhibited a triplet 1.58 ppm and a multiplet in the range 1.23-1.27 ppm could be assigned to methylene protons in the pendant alkyl chain. The –CH$_3$ protons of pentadecyl chain appeared as a triplet at 0.87 ppm.

Figure 3.7 $^1$H-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene in CDCl$_3$. 

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**13C-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene** with assignments is presented in **Figure 3.8**. Carbons 'a' and 'b' appeared as two signals at 156.23 and 155.93 δ ppm due to the asymmetric nature of the monomer. Carbon bearing pentadecyl chain and unsubstituted carbons both ortho to bromine appeared at 143.96 and 133.67 δ ppm, respectively. The peak at 132.71 and 120.30 δ ppm refers to carbons ortho and meta to bromine on unsubstituted ring, respectively. Carbons bearing bromine atom appeared at 118.30 and 115.86 ppm. Aliphatic carbons were observed in the upfield region and their assignments are shown in **Figure 3.8**.

![Figure 3.8](image.png)

**Figure 3.8** 13C-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene in CDCl3

In the third step, 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was treated with copper cyanide in the presence of copper sulfate in N,N-dimethyl formamide as a solvent to obtain 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile. A variety of methods for the preparation of aryl nitriles have been developed. The direct cyanation of aryl halides by copper(I) cyanide is known as Rosenmund-von Braun reaction. Recently, several palladium- or nickel-catalyzed aryl cyanation approaches were reported. However, many of these methods require special reagents such as expensive and toxic phosphines as ligands, etc. Rosenmund-von Braun reaction remains one of most practicable approaches for the synthesis of aryl nitriles because of its cost efficiency and easy operation.

4-(4'-Cyanophenoxy)-2-pentadecyl benzonitrile was characterized by FTIR, 1H-NMR and 13C-NMR spectroscopy.

FTIR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile (Fig. 3.9) exhibited the characteristic stretching band for the -CN at 2225 cm⁻¹.
**Figure 3.9** FTIR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile

$^1$H NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile is reproduced in Figure 3.10. It was observed that after substitution of Br with $-\text{CN}$ group, the peaks shifted to downfield, due to more electron-withdrawing nature of $-\text{CN}$. The protons ortho to $-\text{CN}$ group appeared in the range 7.57-7.71 δ ppm as a multiplet. Two protons meta to $-\text{CN}$ group on unsubstituted ring appeared as a doublet at 7.07 δ ppm. Two protons meta to $-\text{CN}$ group on pentadecyl-substituted ring showed a multiplet in the range 6.86-6.98 δ ppm. The benzylic $-\text{CH}_2$ in pentadecyl chain appeared as a triplet at 2.80 δ ppm due to electron-withdrawing nature of $-\text{CN}$ group. The methylene protons β to aromatic ring appeared as a triplet at 1.64 δ ppm and a multiplet in the region 1.22-1.26 δ ppm could be attributed to remaining methylene protons. The terminal $-\text{CH}_3$ showed a triplet at 0.86 δ ppm.

**Figure 3.10** $^1$H-NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile in CDCl$_3$
$^{13}$C-NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile is presented in Figure 3.11, along with assignments.

![Figure 3.11 $^{13}$C-NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile in CDCl$_3$](image)

In the final step, 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile was hydrolyzed under alkaline conditions to yield 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid. Nitriles can be hydrolyzed using both strong acidic or alkaline conditions. (Figure 3.12)

![Figure 3.12 Hydrolysis of nitrile](image)

The hydrolysis of nitriles proceeds in the distinct steps under acid or alkali treatment to achieve carboxamides [RC(=O)NH$_2$] and then carboxylic acids [RCOOH]. The hydrolysis of nitriles is generally considered to be one of the best methods for the preparation of carboxylic acids. There are various methods available for hydrolysis of nitriles. To name a few, the Mathew's reaction, a 'dry' hydrolysis procedure of nitriles,$^{90}$ alkaline or acid hydrolysis, metal-mediated and metal-catalyzed hydrolysis of nitriles,$^{91}$ biocatalysis$^{92}$ are some of the methods adapted for nitrile hydrolysis.

The hydrolysis reaction of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile was carried out in triethylene glycol/water in the presence of KOH.

4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid was characterized by FTIR, $^1$H-NMR and $^{13}$C-NMR spectroscopy.

Figure 3.13, depicts FTIR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid. FTIR spectrum exhibited absorption bands at 1689 cm$^{-1}$ and 1244 cm$^{-1}$ corresponding to C=O stretching and C-O-C stretching, respectively.
Figure 3.13 FTIR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

$^1$H NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid along with assignments is presented in Figure 3.14.

Figure 3.14 $^1$H-NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid in DMSO-d$_6$

Two hydroxyl protons of carboxyl groups appeared as a broad peak at 12.82 δ ppm confirming the formation of carboxylic acid. Three aromatic protons ortho to carboxyl group appeared as two doublets at 7.97 and 7.87 δ ppm, while rest of the aromatic protons appeared as a multiplet in the region 6.89-7.13 δ ppm. The benzylic –CH$_2$ appeared as a triplet at 2.90 δ ppm. The methylene protons β to aromatic ring appeared as a triplet at 1.50 δ ppm. The other methylene protons exhibited a multiplet over the range 1.18-1.22 δ ppm. The terminal –CH$_3$ showed a triplet at 0.83 δ ppm.

In $^{13}$C-NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid, (Figure 3.15)
carbonyl carbons of the carboxyl group resonated at 188.09 and 188.14 δ ppm. Carbons adjacent to carboxylic moiety appeared as two signals at 126.11 and 126.30 δ ppm. Spectral data corresponding to other carbon atoms was in good agreement with the proposed structure.

![13C-NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid in DMSO-d6](image)

Figure 3.15 13C-NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid in DMSO-d6

### 3.4.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide

Scheme 3.2, outlines route for the synthesis of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide.

![Scheme 3.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide](image)

The synthesis of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide involved three steps. In the first step, 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid was treated with thionyl chloride in the presence of DMF to yield 4-[4'-(chlorocarbonyl)phenoxy]-2-pentadecylbenzyol chloride, which was converted into diester viz, 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate. The obtained diester after hydrazinolysis with hydrazine hydrate gave the desired diacyl hydrazide viz, 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide.

In the first step, the diacid was treated with thionyl chloride to obtain 4-[4'-(chlorocarbonyl) phenoxy]-2-pentadecylbenzyol chloride. It was not isolated but directly transformed into diester.
The obtained diester is a viscous liquid and it was purified by column chromatography.

The diester viz, 4-(4'-methoxy carbonyl)phenoxy)-2-pentadecyl benzoate was characterized by FTIR, $^1$H and $^{13}$C NMR spectroscopy.

In the FTIR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate (Figure 3.16) a band at 1720 cm$^{-1}$ was observed which corresponds to the carbonyl of the ester group.

![Figure 3.16 FTIR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate](image)

$^1$H-NMR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate is shown in Figure 3.17.

![Figure 3.17 $^1$H-NMR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate in CDC$\text{Cl}_3$](image)

The protons ortho to ester group appeared as two doublets at 8.03 and 7.90 $\delta$ ppm. The protons meta to ester group appeared as a doublet at 7.03 $\delta$ ppm and a multiplet in the range 6.80-6.91 $\delta$ ppm. Methyl protons of methyl ester exhibited two singlets at 3.87 and 3.90 $\delta$ ppm. The benzylic $-\text{CH}_2$ appeared as a triplet at 2.92 $\delta$ ppm while remaining methylene protons appeared as a
triplet at 1.56 δ ppm and a multiplet in the range 1.22-1.26 δ ppm. Terminal –CH₃ appeared as a triplet at 0.86 δ ppm.

¹³C-NMR spectrum of 4-(4’-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate along with assignments of the carbon atoms is shown in Figure 3.18

The carbonyl carbons of the ester groups gave rise to two distinct resonances at 167.21 and 166.36 δ ppm. Carbons (c,d) adjacent to oxygen resonated at 160.41 and 158.70. Aromatic carbon attached to benzylic –CH₂ appeared at 148.07 δ ppm. Methyl carbons of methyl ester appeared as two separate peaks at 52.0 and 51.78 δ ppm.

The diester was converted to diacyl hydrazide viz, 4-[4’-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide. The hydrazinolysis of diester was carried out with hydrazine hydrate (99%) in ethanol and the product was crystallized twice from ethanol.

4-[4’-(Hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide was characterized by FTIR, ¹H-NMR and ¹³C-NMR spectroscopy.

FTIR spectrum of 4-[4’-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide is shown in Figure 3.19. Absorption band at 3289 cm⁻¹ is assignable to -NH₂ and -NH- functions. Absorption band at 1662 cm⁻¹ is attributed to the carbonyl of the acid hydrazide group.
Figure 3.19 FTIR spectrum of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

Figure 3.20 ¹H-NMR spectrum of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide in DMSO-d₆.

Two broad singlet peaks observed at 9.70 and 9.42 δ ppm were assignable to the –NH- of the acid hydrazide group. The aromatic protons ortho to acid hydrazide group exhibited two doublets at 7.86 and 7.30 δ ppm. The remaining aromatic protons appeared as a multiplet in the range 6.83-7.06 δ ppm. A broad singlet at 4.49 δ ppm is due to the –NH₂ of the acid hydrazide group. The benzylic –CH₂ appeared as a triplet at 2.67 δ ppm; while, methylene –CH₂ appeared as a triplet at 1.49 δ ppm and a multiplet over the range 1.19-1.24 δ ppm. The terminal –CH₃ appeared as a triplet at 0.84 δ ppm.
13C-NMR spectrum of 4-[4’-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide along with assignments is presented in Figure 3.21.

![Figure 3.21 13C-NMR spectrum of 4-[4’-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide in DMSO-d6](image)

3.4.3 Synthesis of 4-(4’-aminophenoxy)-2-pentadecylbenzenamine

Diamines constitute a highly important class of starting materials for the manufacture of a variety of polymers such as polyimides, polyamides, polyazomethines, polyurethanes, polyureas, etc. Various methods have been developed for the preparations of amines such as replacement of halogen, reduction of nitro compounds, alkaline hydrolysis of isocyanates, etc. Other methods used in the synthesis of diamines include (i) Hofmann degradation (ii) Schmidt reaction (iii) condensation of sodium salt of aminophenol with dihalo diphenyl sulfone and (iv) condensation of amine or its hydrochloride with a ketone or an aldehyde.

The diamines used in the synthesis of polymers are mainly synthesized by the catalytic hydrogenation of the respective dinitro compounds. This is due to the fact that many substituted dinitro compounds can be readily prepared by simple substitution reactions of dinitro or mononitro halides and acid chlorides with compounds having an active hydrogen atom like bisphenols, phenols or amines. The most widely used catalysts for these reductions include palladium and platinum catalysts. Ruthenium and rhodium catalysts have also been used, but they have only limited and specialized use.

Scheme 3.3 depicts route for synthesis of 4-(4’-aminophenoxy)-2-pentadecylbenzenamine. The synthesis of 4-(4’-aminophenoxy)-2-pentadecylbenzenamine comprised of three steps; diazotization, condensation and reduction.
In the first step, 4-amino-3-pentadecyl phenol was obtained by reaction of 3-pentadecyl phenol with diazotized sulfanilic acid and sodium dithionite. The structure of 4-amino-3-pentadecyl phenol was confirmed by FTIR, $^1$H-NMR and $^{13}$C-NMR spectroscopy and the data was in good agreement with the expected structure.

FTIR spectrum of 4-amino-3-pentadecyl phenol showed absorption bands at 3400 and 3350 cm$^{-1}$ indicating the presence of primary amino group.

$^1$H-NMR spectrum (Figure 3.22) of 4-amino-3-pentadecyl phenol showed the presence of a multiplet in the range of 6.51-6.62 $\delta$ ppm which could be assigned to three aromatic protons. A broad peak at 3.65 $\delta$ ppm could be assigned to $-\text{NH}_2$. The benzylic $-\text{CH}_2$ appeared as a triplet at 2.43 $\delta$ ppm. The methylene protons $\beta$ to aromatic ring appeared as a triplet at 1.57 $\delta$ ppm. The other methylene protons exhibited a multiplet over the range 1.22-1.26 $\delta$ ppm. The terminal $-\text{CH}_3$ exhibited a triplet at 0.87 $\delta$ ppm.

![Figure 3.22 $^1$H-NMR spectrum of 4-amino-3-pentadecyl phenol in CDCl$_3$](image)
$^{13}$C-NMR spectrum of 4-amino-3-pentadecyl phenol along with assignments of the carbon atoms is shown in Figure 3.23.

![C-NMR spectrum of 4-amino-3-pentadecyl phenol](image)

The second step involved condensation of 4-amino-3-pentadecyl phenol with 1-chloro-4-nitrobenzene in the presence of potassium carbonate to yield 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine. The pure product was obtained after recrystallisation from ethanol. The formation of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine was confirmed by FTIR, $^1$H-NMR and $^{13}$C-NMR spectroscopy.

![FTIR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine](image)

In FTIR spectrum (Figure 3.24) of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine, a strong absorption band at 3350 cm$^{-1}$ appeared due to the $\text{\text{-NH}_2}$ group. The absorption bands characteristic of the nitro group were observed at 1534 cm$^{-1}$ (asymmetric stretching) and 1340 cm$^{-1}$ (symmetric
stretches). The peak at 1250 cm\(^{-1}\) was assigned to \(-\text{C-O-C-}\) stretching.

\(^1\)H-NMR spectrum (Figure 3.25) of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine exhibited the presence of a doublet at 8.15 \(\delta\) ppm which corresponds to protons ortho to \(-\text{NO}_2\) group. The doublet at 6.93 \(\delta\) ppm is assigned to aromatic protons meta to \(-\text{NO}_2\) group. The protons on pentadecyl-substituted ring exhibited multiplet in the region 6.66-6.81 \(\delta\) ppm. A broad peak at 3.62 \(\delta\) ppm is attributed to \(-\text{NH}_2\) group. The benzylic \(-\text{CH}_2\) appeared as a triplet at 2.45 \(\delta\) ppm; while, methylene protons appeared as triplet at 1.60 \(\delta\) ppm and a multiplet in the region 1.24-1.26 \(\delta\) ppm. The terminal \(-\text{CH}_3\) appeared as a triplet at 0.86 \(\delta\) ppm.

![1H-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine in CDCl\(_3\)](image)

**Figure 3.25** \(^1\)H-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine in CDCl\(_3\)

\(^{13}\)C-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine along with assignments of the carbon atoms is shown in **Figure 3.26**.

![13C-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine in CDCl\(_3\)](image)

**Figure 3.26** \(^{13}\)C-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine in CDCl\(_3\)
In the next step, conversion of 4-(4'-nitrophenoxy)-2-pentadecylbenzeneamine to 4-(4'-aminophenoxy)-2-pentadecylbenzeneamine was accomplished using Pd/C as catalyst and hydrazine hydrate. The synthesized diamine was characterized by FTIR, $^1$H-NMR and $^{13}$C-NMR spectroscopy.

FT-IR spectrum (Figure 3.27) of 4-(4'-aminophenoxy)-2-pentadecylbenzeneamine showed broad band in the region 3300-3400 cm$^{-1}$ (-N-H stretching).

![FT-IR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzeneamine](image)

Figure 3.27 FTIR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzeneamine

In the $^1$H NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzeneamine (Figure 3.28), the multiplet in the region 6.60-6.82 δ ppm corresponds to seven aromatic protons. A broad signal at 3.12 δ ppm was due to -NH$_2$ group. The triplet at 2.43 δ ppm corresponds to benzylic -CH$_2$ of pentadecyl group. The methylene protons β to aromatic ring exhibited a triplet 1.57 δ ppm and a multiplet in the range 1.23-1.27 δ ppm could be assigned to the remaining methylene protons in the pentadecyl chain. The -CH$_3$ protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.

![$^1$H-NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzeneamine in CDCl$_3$](image)

Figure 3.28 $^1$H-NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzeneamine in CDCl$_3$
\(^{13}\)C-NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine along with assignments of the carbon atoms is shown in Figure 3.29 and is in good agreement with the structure.

![Figure 3.29](image-url)

**Figure 3.29** \(^{13}\)C-NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine in CDCl₃

3.4.4 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

Aromatic polyamides and polyimides are well accepted as advanced materials for thin-film application in microelectronic devices and liquid crystal displays due to their outstanding mechanical, chemical, thermal, and physical properties. However, the technological applications of most of these polymers are limited by processing difficulties because of high melting or glass transition temperatures and limited solubility in most organic solvents due to their rigid backbones. One of the common approaches for increasing solubility and processability of polyamides and polyimides without sacrificing high thermal stability is the use of asymmetric monomer. It is generally recognized that aryl-ether linkage and asymmetric structure impart properties such as better solubility and melt-processing characteristics and improved toughness to the polymers. The introduction of asymmetric ether-diamine moieties decreases the chain-to-chain interactions, which interrupts the close packing of polymer chains, thereby leading to an enhancement in solubility and decrease in crystallinity.

In this work, a new aromatic asymmetrical ether diamine, 4-(2-aminophenoxy)-2'-pentadecylbenzenamine was synthesized as shown in Scheme 3.4. In the first step, 4-amino-3-pentadecyl phenol was synthesized as reported in previous section (3.4.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine).
Scheme 3.4 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

In the second step, 4-amino-3-pentadecyl phenol was reacted with 1-chloro-2-nitrobenzene in the presence of K₂CO₃ to obtain 4-(4'-nitrophenoxy)-2'-pentadecylbenzenamine. The pure product was obtained by column chromatographic purification and was characterized by FTIR, ¹H-NMR and ¹³C-NMR spectroscopy.

FTIR spectrum of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine exhibited the bands at 1532 and 1346 cm⁻¹ due to asymmetric and symmetric –NO₂ stretching vibrations. The band at 1280 is due to –C-O-C- stretching vibration. A broad band at 3400-3456 cm⁻¹ corresponds to –N-H stretching.

¹H NMR spectrum of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine is presented in Figure 3.30.

Figure 3.30 ¹H-NMR spectrum of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine in CDCl₃

In the aromatic region, proton ortho to –NO₂ group exhibited doublet of doublet at 7.89 δ ppm. The rest of the aromatic protons exhibited multiplet over the range 6.66-7.46 δ ppm. In the aliphatic region, the triplet at 2.45 δ ppm corresponds to benzylic –CH₂ of pentadecyl group. The
methylene protons $\beta$ to aromatic ring exhibited a triplet 1.58 $\delta$ ppm and a multiplet in the range 1.22-1.26 $\delta$ ppm could be assigned to the remaining methylene protons in the pentadecyl chain. The $\text{-CH}_3$ protons of pentadecyl chain appeared as a triplet at 0.87 $\delta$ ppm.

In the next step, 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine was hydrogenated with hydrazine hydrate and Pd/C to the corresponding diamine, viz, 4-(2-aminophenoxy)-2'-pentadecyl benzenamine. FTIR, $^1$H-NMR and $^{13}$C-NMR spectroscopy confirmed the structure of the desired compound.

FTIR spectrum of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine showed a broad band at 3366-3456 cm$^{-1}$ due to $\text{-N-H}$ stretching vibration.

$^1$H-NMR spectrum of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine is represented in Figure 3.31. Aromatic protons exhibited a multiplet over the range 6.62-6.96 $\delta$ ppm. A broad signal at 3.88 $\delta$ ppm was observed due to the $\text{-NH}_2$ group. The triplet at 2.47 $\delta$ ppm was due to benzylic $\text{-CH}_2$ of pentadecyl group. The methylene protons $\beta$ to aromatic ring exhibited a triplet 1.59 $\delta$ ppm and a multiplet in the range 1.22-1.26 $\delta$ ppm could be assigned to the methylene protons in the pendant alkyl chain. The $\text{-CH}_3$ protons of pentadecyl chain appeared as a triplet at 0.87 $\delta$ ppm.

![Figure 3.31](image)

Figure 3.31 $^1$H-NMR spectrum of 4-(2-aminophenoxy)-2'-pentadecyl benzenamine in CDCl$_3$.

$^{13}$C-NMR spectrum of 4-(2-aminophenoxy)-2'-pentadecyl benzenamine alongwith assignment is presented in Figure 3.32 and was in good agreement with the proposed structure.
3.4.5 Synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

Aromatic diisocyanates are important raw materials in polymer chemistry as they are valuable precursors for the synthesis of polyurethanes, polyureas, polyimides, polyamides, etc. Various methods are available for the preparation of diisocyanates.\textsuperscript{105} The phosgenation of an amine or its salt is the method of great importance.\textsuperscript{106} The reaction of a nitro compound with carbon monoxide,\textsuperscript{107} the reaction of isocyanic acid with an olefin,\textsuperscript{108} Curtius rearrangement,\textsuperscript{109} Loosen rearrangement\textsuperscript{110} are some of the methods generally employed for synthesis of diisocyanates.

Scheme 3.5 depicts route for synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene starting from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine.

\begin{center}
\begin{equation}
\text{H}_2\text{N} \quad \text{O} \quad \text{NH}_2
\end{equation}
\text{C}_{15}\text{H}_{31}
\end{center}

\begin{center}
\text{Bis(trichloromethyl) carbonate}
\text{Toluene/\Delta (75%)}
\end{center}

\begin{center}
\begin{equation}
\text{O} \equiv \text{C} \equiv \text{N} \quad \text{O} \equiv \text{C} \equiv \text{N}
\end{equation}
\text{C}_{15}\text{H}_{31}
\end{center}

Scheme 3.5 Synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

The synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene was carried out starting from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine in a single step reaction using a well-known method, i.e. phosgenation of an amine with bis(trichloromethyl) carbonate (triphosgene). The phosgenation reaction of diamine was carried out in an inert atmosphere with excess bis(trichloromethyl) carbonate. The structure of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene was confirmed by FTIR, \textsuperscript{1}H-NMR and \textsuperscript{13}C-NMR spectroscopy.

FTIR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene is shown in Figure 3.33. A strong absorption band at 2256 cm\textsuperscript{-1} characteristic of the asymmetric stretching vibration of the isocyanate group was observed.
Figure 3.33 FTIR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

$^1$H-NMR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene is shown in Figure 3.34.

Aromatic protons ortho to the -NCO group appeared as a multiplet in the range 7.0-7.08 δ ppm. Other four aromatic protons exhibited a multiplet in the region 6.72-6.95 δ ppm. Benzylic -CH$_2$ appeared as a triplet at 2.58 δ ppm. The other methylene protons appeared as a triplet at 1.55 δ ppm and a multiplet in the region 1.22-1.26 δ ppm. Terminal methyl protons of the aliphatic chain appeared as a triplet at 0.87 δ ppm.

$^{13}$C-NMR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene along with assignments of the carbon atoms is shown in Figure 3.35.
Figure 3.35 $^{13}$C-NMR spectrum 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene in CDCl$_3$

In $^{13}$C-NMR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene the peaks at 127.23 and 128.51 were assigned to the carbon atoms of the -NCO group. The carbons 'a' and 'b' adjacent to ether linkage appeared at 154.45 and 154.58 $\delta$ ppm.

3.4.6 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyphenyl] ethane

Bisphenols are an important class of monomers useful for the preparation of industrially useful epoxy resins, polycarbonates, polyesters, poly(ether sulfone)s, poly(ether ketone)s, etc. Bisphenols are usually synthesized by the acid-catalyzed condensation of aldehydes or ketones with phenols. A variety of aldehydes or ketones have been used for synthesis of bisphenols.

A new bisphenol monomer containing pendant pentadecyl chain was designed and synthesized starting from 3-pentadecyl phenol.

Scheme 3.6 depicts route for the synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyphenyl] ethane. The synthesis of bisphenol involved four steps.

The synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyphenyl] ethane proceeded through dehydroxylation of 3-pentadecyl phenol to obtain pentadecyl benzene. Since phenolic group is quite poor leaving group, it should be activated prior to deoxygenation. Several methods are available in the literature for dehydroxylation of phenol.$^{111}$ The conversion of the phenolic hydroxyl group to the corresponding sulfonate,$^{112}$ isourea,$^{113}$ dimethyl thiocarbamate,$^{112}$ aryl ether,$^{114}$ 5-phenyltetrazolyl ether,$^{115}$ and phosphate ester,$^{116}$ etc. are generally employed for activation as a substrate of reductive deoxygenation.
Scheme 3.6 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

In the first step, 3-pentadecyl phenol was converted into 1-methane sulfonyloxy-3-pentadecyl benzene. The obtained mesyl ester was characterized by FTIR, $^1$H-NMR and $^{13}$C-NMR spectroscopy.

FTIR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene is presented in Figure 3.36. The absence of band at 3300 cm$^{-1}$ corresponding to hydroxyl group confirmed the replacement of–H of hydroxyl group by mesyl group.

Figure 3.36 FTIR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene

$^1$H-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene is reproduced in Figure 3.37. Proton meta to mesyl group exhibited a triplet at 7.34 $\delta$ ppm. Protons ortho and para to mesyl group appeared as multiplet in the range 7.05-7.16 $\delta$ ppm. The singlet for methyl protons of mesyl ester appeared at 3.12 $\delta$ ppm. The triplet at 2.62 $\delta$ ppm was due to benzylic $-\text{CH}_2$ of pentadecyl group. The methylene protons $\beta$ to aromatic ring exhibited a triplet 1.60 $\delta$ ppm and a multiplet in the
region 1.22-1.26 δ ppm could be assigned to the methylene protons in the pendant alkyl chain. The –CH₃ protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.

**Figure 3.37** ¹H-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene in CDCl₃

¹³C-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene along with assignments is presented in **Figure 3.38**.

**Figure 3.38** ¹³C-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene in CDCl₃

Further, the mesyl ester of 3-pentadecyl phenol was converted into pentadecyl benzene using Mg metal and ammonium acetate with Pd/C as catalyst. The obtained pentadecyl benzene was purified by column chromatography. The product was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

In ¹H-NMR spectrum (**Figure 3.39**) of pentadecyl benzene aromatic protons appeared as a multiplet in the range 7.13-7.33 δ ppm. Benzylic –CH₂ splitted as a triplet at 2.60 δ ppm. The
methylene protons β to aromatic ring exhibited a triplet at 1.61 δ ppm, while rest of the methylene protons appeared as multiplet over the range 1.23-1.27 δ ppm. A triplet at 0.88 δ ppm could be attributed to the terminal –CH₃.

Figure 3.39 ¹H-NMR spectrum of pentadecyl benzene in CDCl₃

¹³C-NMR spectrum of pentadecyl benzene along with assignments of the carbon atoms is shown in Figure 3.40.

Figure 3.40 ¹³C-NMR spectrum of pentadecyl benzene in CDCl₃

In the next step, monoacylation of pentadecyl benzene was carried out using acetyl chloride as acylating agent and aluminium chloride as catalyst. The pure monoacylated product was obtained after column chromatography.

4-Acetyl pentadecyl benzene was characterized by FTIR, ¹H-NMR and ¹³C-NMR spectroscopy.
FTIR spectrum of 4-acetyl pentadecyl benzene (Figure 3.41) showed the presence of C=O stretching band at 1690 cm\(^{-1}\) confirming the presence of a ketone.

![FTIR spectrum of 4-acetyl pentadecyl benzene](image)

**Figure 3.41** FTIR spectrum of 4-acetyl pentadecyl benzene

\(^1\text{H-NMR}^\text{spectroscopy of 4-acetyl pentadecyl benzene is reproduced in Figure 3.42. Downfield shift was observed for protons ortho to acetyl group. These two protons appeared as a doublet at 7.88 \(\delta\) ppm. Protons meta to acetyl group exhibited a doublet at 7.26 \(\delta\) ppm. Methyl protons of acetyl group appeared as a singlet at 2.58 \(\delta\) ppm. Benzylic \(-\text{CH}_2\) appeared as a triplet at 2.66 \(\delta\) ppm. The methylene protons exhibited a triplet at 1.61 \(\delta\) ppm and a multiplet over the range 1.22-1.27 \(\delta\) ppm. The terminal \(-\text{CH}_3\) appeared as a triplet at 0.88 \(\delta\) ppm.

![\(^1\text{H-NMR}^\text{spectroscopy of 4-acetyl pentadecyl benzene in CDCl}_3\)](image)

**Figure 3.42** \(^1\text{H-NMR}^\text{spectroscopy of 4-acetyl pentadecyl benzene in CDCl}_3\)

In \(^{13}\text{C-NMR}^\text{spectroscopy (Figure 3.43) of 4-acetyl pentadecyl benzene, the signal corresponding to acetyl carbon appeared at 197.68 and methyl carbon of acetyl group appeared at 29.33 \(\delta\) ppm.}
In the fourth step, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane was prepared by condensation of 4-acetyl pentadecyl benzene with phenol using hydrogen chloride/3-mercapto propionic acid catalyst system. The role of 3-mercapto propionic acid for this reaction has been investigated in detail by various researchers.\textsuperscript{117,118} When 3-mercapto propionic acid is used for the condensation in combination with other strong acids, the rate and the selectivity for the formation of desired bisphenol (p,p'-isomer) is increased. The crude bisphenol was purified by column chromatography.

1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane was characterized by FTIR, \textsuperscript{1}H-NMR and \textsuperscript{13}C-NMR spectroscopy.

FTIR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane (Figure 3.44) showed a broad band at 3490 cm\textsuperscript{-1} corresponding to –OH stretching.
In $^1$H-NMR spectrum (Figure 3.45) of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane, aromatic protons ortho to –OH group appeared as a doublet at 6.70 δ ppm. Rest of the aromatic protons exhibited a multiplet in the region 6.91-7.10 δ ppm. Two proton of hydroxyl group appeared as a single peak at 4.82 δ ppm. The peak at 2.09 δ ppm is assigned to methyl protons attached to quaternary carbon. Benzylic –CH$_2$ appeared as a triplet at 2.56 δ ppm. The methylene protons β to aromatic ring appeared as a triplet at 1.59 δ ppm, while rest of the methylene protons appeared as a multiplet in the region 1.23-1.27 δ ppm. A triplet at 0.87 δ ppm could be attributed to the terminal –CH$_3$.

Figure 3.45 $^1$H-NMR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane in CDCl$_3$

$^{13}$C NMR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane along with the assignments is presented in Figure 3.46.

Figure 3.46 $^{13}$C-NMR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane in CDCl$_3$
Carbons 'a' next to –OH group appeared at 153.35 δ ppm. A peak at 50.92 δ ppm could be assigned to quaternary carbon 'i', while the aliphatic carbon 'j' and aromatic carbon 'b' appeared at 22.67 and 146.65 δ ppm, respectively. In aromatic region, the most upfield shift is observed in case of carbons ortho to –OH group. These four carbons appeared at 114.55 δ ppm.

3.4.7 Synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane

Scheme 3.7 depicts route for the synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane. The synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane involved three steps: hydrogenation, oxidation and condensation.

In the first step, 3-pentadecylphenol was prepared by the catalytic hydrogenation of freshly distilled cardanol in the presence of 5% Pd/C catalyst. The product obtained was recrystallized from petroleum ether (60-80°C) and was characterized by FTIR and 1H NMR spectroscopy. FTIR spectrum showed absorption band at 3342 cm⁻¹, corresponding to –OH stretching.

Several researchers have studied the catalytic hydrogenation of cardanol at normal and elevated temperatures with different catalysts like nickel, Raney nickel, etc. Effect of hydrazine hydrate on the reduction of cardanol was studied by Bhople et al and the products were compared to those obtained by catalytic hydrogenation. It was observed that increase in the molar ratio of hydrazine hydrate to cardanol (more than 1:15) gave better reduction of cardanol. In the present study, Pd/C was used for high yields and reusability of the catalyst.

In the second step, 3-pentadecylphenol was hydrogenated using 5% Ru/C to get 3-pentadecylcyclohexanol. Transition metal catalysts such as Ni, Pd, Co, Rh, Pt, Ru, etc can also be used for the hydrogenation of phenols. After complete reduction, reaction mixture was filtered and the catalyst was recovered. The filtrate was passed through short column of silica gel (100-200 mesh) to obtain colorless solution. The evaporation of solvent under reduced pressure yielded 3-pentadecylcyclohexanol as white solid.

The reduction of 3-pentadecyl phenol gives cis- and trans-3-pentadecylcyclohexanols. 3-
Pentadecylcyclohexanol was characterized by FTIR, $^1$H-NMR and $^{13}$C-NMR spectroscopy.

The disappearance of the band around 1600 cm$^{-1}$ corresponding to aromatic C=C stretching indicates the reduction of aromatic ring. The O-H stretching vibration was observed at 3334 cm$^{-1}$.

The complete reduction of aromatic ring was further indicated by the disappearance of peaks corresponding to aromatic protons in the region 6.65-7.18 ppm in $^1$H NMR spectrum (Figure 3.47). The two isomers can be distinguished by $^1$H-NMR spectroscopy as proton ‘a’ and ‘e’ appear at 3.56 and 4.04 δ ppm, respectively.

![Figure 3.47 $^1$H-NMR spectrum of 3-pentadecylcyclohexanol in CDCl$_3$](image)

$^{13}$C-NMR spectrum of 3-pentadecylcyclohexanol with partial assignments is presented in Figure 3.48.

![Figure 3.48 $^{13}$C-NMR spectrum of 3-pentadecylcyclohexanol in CDCl$_3$](image)

The assignment for the pentadecyl chain is not given because of the complexity of the system. The spectrum indicates the presence of cis and trans isomers. The carbon number 1 from cis isomer was observed at 70.94 ppm, where as carbon 1’ from trans isomer was observed at 66.90 ppm. Carbon 3 and 3’ were observed at same chemical shift value (31.56 ppm). The terminal CH$_3$ from pentadecyl chain appeared at 14.05 ppm. However, isomer separation and detailed spectral analysis was not carried out as it was outside the scope of present work.
The oxidation of alcohols to aldehydes and ketones is fundamental reaction in organic synthesis. Since the first experiment in 1820 by Davy who oxidized ethanol with air over a platinum catalyst, various reagents have been reported which include high valent chromium, and manganese compounds, hypervalent iodine compounds, m-chloroperbenzoic acid or sodium hypochlorite with 2,2,6,6-tetramethyl-1-piperidinyloxy, etc. From the standpoint of the green and sustainable chemistry cleaner catalytic systems for oxidations have been in demand. Recently metal-catalyzed oxidations of alcohols using clean and cheap oxidants such as $\text{H}_2\text{O}_2$, $\text{O}_2$, and/or air have been investigated.

In the present study, pyridinium chlorochromate (PCC) was used for oxidation of 3-pentadecylcyclohexanol because of the easy preparation as well as its demonstrated utility for moderate to large scale oxidations. In the second step, 3-pentadecyl cyclohexanol was oxidized to 3-pentadecyl cyclohexanone using PCC. After the completion of reaction, the reaction mixture was filtered through short column of Celite and silica gel to obtain colorless filtrate. The solvent was distilled off and solid was dissolved in ethyl acetate and washed with brine solution followed by water. 3-Pentadecylcyclohexanone was crystallized from methanol to obtain white solid.

3-Pentadecylcyclohexanone was characterized by FTIR and $^1\text{H}$-NMR spectroscopy. FTIR spectrum showed the absence of band at 3300 cm$^{-1}$ corresponding to hydroxyl group and appearance of characteristic band for the carbonyl stretch at 1705 cm$^{-1}$.

$^1\text{H}$ NMR spectrum of 3-pentadecylcyclohexanone is reproduced in Figure 3.49, which shows absence of peaks at 3.56 and 4.04 ppm, corresponding to ‘a’ and ‘e’ protons of 3-pentadecylcyclohexanol.

In the fourth step, 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane was prepared by condensation of 3-pentadecyl cyclohexanone with phenol using hydrogen chloride/3-mercaptopropionic acid catalyst system. Under these conditions, the reaction was complete within one hour. The pink colored solid mass was dissolved in ethyl acetate and was washed with sodium
bicarbonate solution and water. Ethyl acetate was removed under reduced pressure to get resinous mass. The excess phenol was removed by washing with hexane and crude 1,1-bis(4-hydroxyphenyl)-3-pentadecylocyclohexane was crystallized two times from hexane:toluene mixture (9:1, v/v).

1,1-Bis(4-hydroxyphenyl)-3-pentadecylocyclohexane was characterized by FTIR, $^1$H-NMR and $^{13}$C NMR spectroscopy.

FTIR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylocyclohexane (Figure 3.50) showed broad band at 3291 cm$^{-1}$ corresponding to –OH group.

![Figure 3.50 FTIR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylocyclohexane](image)

$^1$H NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylocyclohexane along with assignments is presented in Figure 3.51.

![Figure 3.51 $^1$H-NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylocyclohexane in CDCl3](image)

$^1$H and $^{13}$C NMR spectra of 1,1-bis(4-hydroxyphenyl)-3-pentadecylocyclohexane showed the presence of distereotopic phenyl rings, which are magnetically non-equivalent. 1,1-Bis(4-hydroxyphenyl)-3-pentadecylocyclohexane is not symmetrical about a C$_2$ axis between the two phenyl rings and this results in different environments for two phenyl rings. Because of this, the
aromatic rings showed four doublets in $^1$H NMR spectrum and two sets of four aromatic shifts in $^{13}$C spectrum as compared to only one set for symmetrical bis-phenols. The substituent on the cyclohexyl ring prevents the ring inversion of cyclohexyl ring and axial and equatorial phenyl groups can hence be distinguished.

The protons of axial and equatorial phenyl rings can be distinguished. Two sets of doublets are observed in the region of 6.57 – 7.12 ppm. Protons meta to hydroxyl of equatorial phenyl ring appeared at 7.11 ppm, while those for axial ring appeared at 6.92 ppm. Protons ortho to hydroxyl of equatorial phenyl ring appeared at 6.70 ppm while those of axial ring appeared at 6.58 ppm.

$^{13}$C NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane along with assignments is presented in Figure 3.52. Equatorial phenyl ring carbons appeared downfield compared to their axial phenyl ring partners. Carbons attached to hydroxyl group appeared as two peaks at 153.07 and 153.01 ppm for equatorial and axial phenyl rings, respectively. Carbons para to hydroxyl group appeared at 144.78 and 138.19 ppm. Carbons meta to hydroxyl group appeared at 129.15 and 127.35 ppm, whereas carbons ortho to hydroxyl group showed signals at 115.20 and 114.78 ppm. Aliphatic carbons were observed at higher field. Carbon 1, 2, 6, 3, 4 and 5 appeared at 45.59, 44.46, 37.73, 33.56, 33.35 and 22.85 ppm, respectively. Terminal CH$_3$ of alkyl chain showed signal at 14.07 ppm.

![Figure 3.52 $^{13}$C-NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane in CDCl$_3$](image)
3.5 Conclusions

1. The potential of using a renewable resource material like Cashew Nut Shell Liquid (CNSL); as a raw material for the synthesis of variety of value-added condensation monomers viz; dihalide, diacid, diacylhydrazide, diamines, diisocyanate and bisphenols was explored.

2. Six novel difunctional monomers viz;
   1. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene
   2. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid
   3. 4-[4’-(Hydrazinecarbonyl)phenoxy]-2-pentadecyl benzohydrazide
   4. 4-(4’-Aminophenoxy)-2-pentadecylbenzenamine
   5. 4-(2-Aminophenoxy)-2'-pentadecylbenzenamine
   6. 1-Isocyanato-4-(4’-isocyanatophenoxy)-2-pentadecylbenzene containing ether moiety and pendant linear pentadecyl chain were synthesized starting from CNSL.

3. Two bisphenols viz; 1,1,1-[bis(4-hydroxyphenyl)-4’-pentadecylphenyl] ethane containing pendant pentadecyl chain and 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane containing cyclohexylidene moiety with flexible pentadecyl substituent were synthesized starting from CNSL.

4. Difunctional monomers are potentially useful for the synthesis of a host of high performance polymers.
References

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