CHAPTER 1

Introduction
1. Background

Most of the humanity's progress has been marked by dramatic improvements in the materials that chemists have developed, from the 'Stone Age' to the "Iron Age' to the "Bronze Age' and now to the "Polymer Age". The development of polymers is perhaps the biggest achievement. Chemistry has made and it has a significant effect on everyday life. "Polymer" is now a domestic word. Polymers are big molecules, the materials that constitute most of our natural and synthetic environment. The world would have seemed totally different without artificial fibers, plastics, elastomers etc and as economically low cost, better and stronger synthetic materials are developed, their use will undoubtedly increase further. Polymer materials, as they are constantly being modified, improved and fine-tuned for current and additional needs are readily accepted by the public, will have an ever-expanding influence on everyday life. Today, polymers are used as replacements for woods, glass and metals and for a wide variety of applications in industries such as packaging, automobiles, building and construction, electronics, aerospace, electric equipments etc. In the high technology microelectronics area, many opportunities exist for polymers to serve as improved dielectrics, improved plasma etc resistance barriers and improved lithographic resists etc.

Polymers for biomedical applications, likewise, provide a rich opportunity for synthetic innovation. Polymers are materials for the future and are versatile substances that can be tailored in an almost infinite number of ways to meet evolving needs by biomaterials as well as agro based resources. It is not surprising then that much of the high technology in future, from biotechnology to
microelectronics, will depend on our ability to synthesize and modify the existing polymers.

Syntheses of new monomers with special functionalities are greatly needed to fine-tune polymers for specific tasks. The raw materials cost, market size, energy needs, and health environmental concerns have been the important factors especially for invention / discovery and introduction of new monomers from agro based materials. There have been always constant explorations for new cost effective monomers that can be used in the synthesis of polymers for specialty applications. In this respect, the synthesis of polymers from renewable resources has attracted considerable attention of research workers throughout the world.

2. Petite Survey on Naturally Occurring Monomers

2.1 Classification

In general, naturally occurring organic polymers are classified into the following groups: Hydrocarbon polymers (natural rubber, gutta-percha etc), carbohydrates (starch, cellulose etc), polyphenolic compounds (lignin and other polyphenols), proteins and nucleic acids [1]. Monomers associated with the above polymers can be found free in nature, though it cannot be taken as a general rule (for example though natural rubber is polyisoprene, the plant does not produce isoprene, the monomer as such). However, a preliminary survey indicated the availability of innumerable number of monomers from various sources such as alkaloids, terpenes, lipids, fattyacids, amino acids etc. For the sake of clarity the naturally occurring monomers have been classified as shown in table 1.1. The
following discussions organized into subgroups and only those that are considered more potential in terms of polymerization are discussed. Compounds, whose functionality is more than one is considered as a potential monomer but actual polymerization may depend on many factors, for example, steric hindrance may inhibit a potential monomer from polymerization.

2.1.1 Terpene monomers:

Terpenes constitute one of the largest groups of natural products. They embrace a vast family of chemical compounds which are isolated from essential oils and resins of plants [2]. This class also includes naturally occurring and synthetic alcohols, aldehydes, ketones and other derivatives having same carbon skeleton as parent terpene hydrocarbon called terpenoids.

<table>
<thead>
<tr>
<th>Naturally occurring monomers</th>
<th>Hydrocarbon type compounds</th>
<th>Terpenes</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen containing compounds</td>
<td>Oxygen containing terpenes</td>
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<tr>
<td></td>
<td>Oxygen containing compounds</td>
<td>Lipids, fatty acids (unsaturated and saturated)</td>
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<td></td>
<td></td>
<td>Alkaloids</td>
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<td>Carbohydrates</td>
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<td>Steroids</td>
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<td></td>
<td></td>
<td>Phenolic and hydroxyl plant products</td>
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<tr>
<td></td>
<td></td>
<td>Furans and their derivatives</td>
</tr>
<tr>
<td>Nitrogen containing compounds</td>
<td></td>
<td>Amino acids, Nucleotide</td>
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<tr>
<td></td>
<td></td>
<td>Alkaloids containing nitrogen</td>
</tr>
</tbody>
</table>

Table 1.1: Classification of naturally occurring monomers
2.1.2 Fatty acid monomers:

The fatty acids, frequently occurring as components of natural fats and oils can be classified into several series. One is saturated fatty acid and other group is characterized by the presence of one or more double bonds.

2.1.3 Alkaloid monomers:

They constitute one of the largest groups of natural products. They occur throughout the animal and plant kingdom display a diversity of structure unmatched by any other group of naturally occurring compounds and exhibit an extraordinary assay of pharmacologic activities.

2.1.4 Monomers based on phenolic and hydroxyl compounds:

They form another major category of the natural products. Phenolic compounds and their quinones are widespread occurrence in nature [3]. They are abundant in plants and fruits as chromones, glucosides, coumarin derivatives, essential oils, lignin etc. They occur also in animals.

2.1.5 Amino acid monomers:

They are a broad class of organic compounds containing both amino and acid functional groups. Here only polymerizable amino acids containing primary or secondary amino groups and carboxylic groups will be considered.

2.1.6 Monomers based on furans and derivatives:

Furfural and its derivatives comprise an industrially significant class of heterocyclic compounds. These compounds are found in agricultural wastes such as corn cobs, bagasse, rice husks, coconut shell etc [4].
2.1.7 Steroid monomers:

Steroids are ubiquitous members of a large class of marine and terrestrial organic compounds. Included under the designation of steroids are the naturally occurring and synthetic substances [5].

2.1.8 Monomers based on carbohydrates or sugars:

There are a large number of sugar monomers that exist in nature. As it takes a lot of space to cover all the monomers, the relevant literature may be referred for a comprehensive understanding [6].

2.1.9 Cardanol from CNSL:

Cardanol, a bio-monomer obtained from Cashew Nut Shell Liquid (CNSL) is an industrial byproduct obtained from the cashew plant Anacardium occidentale L. The brown colored mesocarp of the nut (analogous to the peel of a citrus fruit) is processed to get the pale white kernel called the cashew nut. The CNSL (shell oil extracted from the brown mesocarp) constitutes 18–27% of the total raw nut weight. On an average, 15–20% by weight of unshelled nut in Africa and 25–30% by weight in India and 25% overall, contains CNSL. The potential of CNSL is about 4,50,000 tonnes per year [7]. As of year 2002, world-wide export of total CNSL is approximately 1900 metric tonnes with United States amounting to 737 tonnes [8].

Most of the different processes of extracting CNSL from the nut include cold pressing, roasting, or a hot oil bath. The final composition of the CNSL will depend on the extraction method. The hot oil bath process involves heating the shell in a pool of CNSL at 180°C. At this temperature, the nuts break open when the CNSL oozes out and is collected. The CNSL’s anacardic acid content is minimized in this
process as it undergoes decarboxylation at this temperature to afford cardanol [9].

The typical roasting process of extracting CNSL from a cashew apple involves the following steps (Figure 1.1) [10]. Traditionally, the dark colored nut from the cashew apple is manually/removed and soaked in water before roasting. During the roasting process, the leathery, soft shell becomes brittle and exudes the dark CNSL liquid. It is mainly composed of cardanol (60–65%), cardol (15–20%), polymeric material (10%), and traces of methylcardol.

![Figure 1.1: Cashew nut shell liquid distillates and the CNSL extraction process.](image)

3. Generalities on Cashew Nut Shell Liquid (CNSL)

3.1 CNSL Chemistries

The literature on CNSL is now enriched with hundreds of patents and reports. The Cashew Export Promotion Council (CEPC), India, had compiled lists of patents that originated form USA, UK, Japan and India upto 1962 [11, 12]. It
also brought out two other publications [13]. A few reviews have appeared emphasising the significance of CNSL and its products as versatile industrial raw materials [14-16].

CNSL occurs as a brown viscous fluid in the soft honeycomb structure of the shell of cashew nut, a plantation product obtained from the cashew tree. Many researchers have investigated its extraction [17-20] chemistry and composition. Cardanol is formed when anacardic acid is heated and can be isolated from the raw oil by double vacuum distillation, at 245 °C at 6 mm Hg [21-30].

3.1.1 Extraction
3.1.1.1 Hot oil bath process

Indian processors of cashew nuts roast them in an open perforated drum, where CNSL leaks out or is burnt in the air. The most common method of commercial extraction is the hot oil bath which extracts around 50 % of the liquid contained in the nuts. In this method, the raw nuts are heated at 180-190 °C while held on a slowly travelling conveys or belt submerged below the liquid Level. Men the outer part of the shell bursts open, CNSL are released. Another 20 % could be extracted by passing the spent shells through an expeller and the rest by solvent extraction technique [31]. This expeller oil can be upgraded by acid washing followed by centrifugation and heating. This method is largely used in some parts of India [32].
3.1.1.2 Expeller method [33]:

Another method of extraction employs manually operated cutting machines to cut shells of lightly roasted nuts, keeping the kernel intact, the shells are then fed to the expeller to recover 90% of the oil.

3.1.1.3 Kiln method [33]:

In this method nuts are shelled after sun drying or after drum roasting. The liquid obtained is crude and contaminated.

3.2 CNSL with current trend polymers

Synthetic high performance polymers are constantly being modified and improved for current and future need. This necessitates a look at the renewable natural resources that can serve as alternative feed stocks for monomers of the polymer industry. In this regard cashew nut shell liquid (CNSL), an agricultural byproduct abundantly available in the country, is one of the few major and economic sources of naturally occurring phenols and can be regarded as a versatile and valuable raw material for polymer production [34-37]. Cardanol, a natural alkyl phenol from CNSL (Anacardium occidentale L), a potential natural source for bio monomers, cannot even today be said to have found its niche in terms of an appropriate industrial applications. Considerable research works have been done by scientists all over the world to find out the multifarious uses of CNSL. Recent investigations have revealed that the constituents of CNSL possess special structural features, which can be chemically transformed into specialty and high value products / polymers.
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The literature on cardanol is replete with innumerable patents [38, 39] and reports and many reports deal with the synthesis of several futuristic products from CNSL namely melt process able liquid crystal polymers, melt / solution process able polyurethanes, cardanol grafted cellulose, multi-functional additives for natural rubber, azo benzene based cross linked network structures for liquid crystal phase stabilization etc.

By far, the greatest amount of work on polymeric materials derived from CNSL has been concerned with its use in the manufacture or modification of phenolic resins [40]. The phenolic nature of the material makes it possible to react under a variety of conditions to form both resols (condensation in presence of alkaline catalysts) and novalcs (condensation in presence of acid catalysts). Lima et al. condensed the phenolic monomers, cardol, cardanol and anacardic acid present in CNSL. Studies have shown that the phenolic resins made from a mixture of cardanol, phenol and formaldehyde have improved chemical resistance and mechanical properties such as tensile, flexural, and Izod impact strengths than those of pure phenol-formaldehyde resins [41]. The cardanol formaldehyde resins have been studied for producing protective varnishes with improved properties in food industry. Cardanol have been used for the manufacture of special phenolic resins for coatings, laminates and friction materials [42]. The phenolic resins made from cardanol can also be used for breaking crude oil emulsions and as selective ion exchangers for certain metal ions [43]. Hydroxy alkylated cardanol-formaldehyde resins have been used for the synthesis of polyurethanes with good thermal and mechanical properties [44]. Poly(vinyl
formaldehyde) was modified by phenol-cardanol-formaldehyde resins [45, 46] to improve properties of the insulating enamel varnish for copper wires. The varnish films prepared from modified poly (vinyl formaldehyde) showed better physico-mechanical properties, heat resistance and electrical properties.

CNSL can be used to manufacture epoxy by reacting with glycidyl ethers and phenol (followed by epoxidation); Tan et al [47] reported the synthesis of cardanol-lignin based epoxy resins. A study of their mechanical properties indicated that an increase of the cardanol content increases the tensile strength and Young’s modulus of the film products. Cardanol was treated with phenol using boron trifluoride as catalyst to give 1, 8-bis(hydroxyphenyl) pentadecane, which was polymerized with epichlorohydrin to give epoxy resins useful for the preparation of baked coatings having comparable corrosion and chemical resistance and better flexibility to conventional epoxy resins prepared from bisphenol-A [48]. The cardanol epoxy resin could be further modified with vinyl monomers to give air drying components which were economically low cost than the conventional epoxy coatings. Cardanol based epoxy resins are also used as binders for cathodic electro depositions and in automated bonding processes in electronics industry [49]. Phosphate ester-terminated epoxy novolac / phenolic resins having higher thermal stability than the conventional epoxy resins were also synthesized from cardanol and used in interpenetrating network coatings. There are patent reports on the use of cardanol for the synthesis of modified epoxy resins [50].
Cardanol functionalized with methacrylate was found to have application in the synthesis of several heat-resistant resins. Copolymers of MMA (methyl methacrylate) and cardinyl acrylate having a small fraction of cardinyl acrylate showed better thermal stability than the PMMA homopolymer [51].

An analysis of literature on cardanol shows that the important structural factor that makes cardanol suitable for a variety of applications is its pendant long alkyl group [52, 53]. Pendant alkyl groups and alkoxy groups are known to improve the solubility and processability of polyamides. These alkyl groups can be attached directly to the main chain or can be substituent's of the side chain, which in turn is connected to the main chain through some flexible connecting groups. In both these cases literature are mainly based on the incorporation of small and bulky alkyl groups like methyl and t-butyl and there are only very few reports on the incorporation of long pendant alkyl groups because of the difficulty in synthesizing monomers containing them. Phenols containing alkyl group substituents are useful starting materials for the synthesis of these monomers and the corresponding polymers. Most of the phenols reaction with alkyl halides, which usually give ortho, and para alkylated products. The position and length of pendant alkyl group can affect the final properties of the polymers and therefore it will be interesting to study the properties and applications of polyamides and polyimides synthesized from phenols having long alkyl groups in the meta position. In this regard cashew nut shell liquid can be considered as a potential natural resource of long chain alkyl phenol like cardanol, where the substitution is at the meta position, which is very difficult to obtain by any synthetic method and can be used in the synthesis of
monomers and polymers having pentadecyl groups directly attached to the main chain [54] or as a meta substituents of the pendant phenyl group.

3.3 Production and export of CNSL in India

The average annual production of CNSL in India is of the order of 10,000 to 14,000 tonnes; through the potential availability of the liquid is about 37,000 tonnes. Due to the adoption of the expeller method another 30% could be added. The export of CNSL from India which was 14,000 tonnes in 1963-64 is only 7,011 tonnes in 1975-76 and 10,699 tonnes in 1980 [33]. The price of CNSL registered a rise in 1978-79 and it began dropping in 1980. The potential availability of CNSL in the world is around 1,25,000 tonnes/year of which only a fraction is, in fact, used [33]. India used to be the major exporter of CNSL with a peak export of 14,400 tonnes in 1964 and lost her first position to Mozambique in 1971 which exported 11,500 tonnes followed by Brazil with 6,500 tonnes, India coming third with 5,500 tonnes [55, 56].

3.4 Chemical Composition

CNSL is said to be the most widely distributed and abundant natural phenolic lipids source. The phenolic lipids present in CNSL are (1) phenolic acid – anacardic acid [57, 58], (2) dihydric phenol – cardol [57, 59] (3) monohydric phenol-cardanol [60], and (4) 2-methyl cardol [61] figure 1.2 shows the components of CNSL [42]. Anacardic acid is the major component of natural CNSL but during the hot oil bath process it gets decarboxylated to cardanol. Cardol and 2-methyl cardol are the most widely distributed dihydric phenols.
through their presence in natural and technical CNSL. Cardanol is the minor component of natural CNSL and the major one in technical CNSL [62].

\[
\text{C}_{15}\text{H}_{31-n} - \text{Unsaturated side chain with one or two or sometimes three double bonds. The substituent chain present in anacardic acid, cardol and cardanol is not a homogeneous, diolefin but is a mixture of olefins of different degree of unsaturation.}
\]

Anacardic acid - 82 ± 1.06%,
Cardanol - 13.8 ± 0.79%,
2 methyl cardol - 2.6 ± 0.16%
Cardol - 1.6 ± 0.17%

**Figure 1.2: Structure and composition of natural CNSL**

3.5 CNSL: Present and Future Trends

Stadeler in 1847, first investigated CNSL systematically and separated cardol from anacardic acid and decarboxylated anacardic acid [57]. But the correct formula for the acid, \(\text{C}_{22}\text{H}_{32}\text{O}_3\) (this is the molecular formula for the diene which is
the average unsaturation) was not established till 40 years [63]. A.J.H. Smit, in 1931 recognised the presence of salicylic acid system and a penta decadienyl side chain [64] and P. Von Rornburg put forward the structure of anacardic acid and anacardol (Figure 1.3) (the name anacardol was used for cardanol in the early years but changed into cardanol by M.T. Harvey) by analogy with work on pelandjauic acid and pelandjauol [65].

![Figure 1.3: Structure of anacardic acid and anacardol](image)

Backer and Haack isolated 3-methoxyphthalic acid and 3-methoxybenzoic acid together with palmitic acid by the oxidative degradation of hydrogenated and methylated anacardic acid and anacardol respectively and synthesized anacardol [66]. A. A. Dusrani and J.H.P. Tyman synthesized anacardic acid by two different methods [67].

Stadeler first isolated cardol from natural CNSL and examined its structure. Then Backer and Haack reinvestigated the structure and the molecular formula, \( \text{C}_{15}\text{H}_{27}\text{C}_6\text{H}_3(\text{OH})_2 \) was put forward for what they considered to be penta decadienyl resorcinol [66]. The hydrogenated material was assigned the following structure.
since the oxidation of methyl ether gave 3,5-dimethoxybenzoic acid and palmitic
acid (Figure 1.4).

![Structure of Hydrogenated cardol](image)

**Figure 1.4**: Structure of Hydrogenated cardol

Later D. Wasserman and C.R. Dawson confirmed the structure in 1948 by
synthesis [68].

2-methyl homologues of cardol were separated by argentation TLC and are
structurally investigated by mass spectrometry and $^1$H NMR [61].

Dawson and Wasserman [69] examined the structure of cardanol and
showed that it is identical except for the degree of unsaturation with the product of
solvent extraction of natural CNSL followed by thermal decarboxylation. In the
early structural work, it was universally believed that a penta decadienyl side chain
was present in the phenols [42]. Later cardanol was shown to consist of a mono-
and a di-olefin which formed crystalline glycols separable by fractional
crystallization [42]. B.G.K. Murthy et al in 1968 had reported the separation of
cardanol and cardo1 from technical cardanol using silica gel thin layer
chromatography and silica gel column chromatography. They also separated
cardanol into 4 components viz. saturated, mono-, di- and tri-olefins using silver
nitrate impregnated silica gel TLC and column chromatographic techniques. The 4
components were characterized by consideration of their properties and hydrogenation [70] values. In 1953, William F. Symes and C.R Dawson found that methyl ether derivative of cardanol can be separated by chromatography on alumina into 4 components which vary only in their degree of unsaturation in the side chain. They established the structure of 4 components by oxidative degradation. The saturated component was proven to be identical with the catalytically reduced methyl cardanol. The olefins were subjected to ozonization and the products were analysed.

Table 1.2: Chemical Composition of Cardanol

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular weight</th>
<th>%</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardanol with saturated side chain</td>
<td>304</td>
<td>5.4</td>
<td><img src="image1" alt="Molecular structure image" /></td>
</tr>
<tr>
<td>Cardanol with one double bond in the side chain (Monoolefine)</td>
<td>302</td>
<td>48.5</td>
<td><img src="image2" alt="Molecular structure image" /></td>
</tr>
<tr>
<td>Cardanol with two double bonds in the side chain (diolefine)</td>
<td>300</td>
<td>16.8</td>
<td><img src="image3" alt="Molecular structure image" /></td>
</tr>
</tbody>
</table>
Cardanol with three double bonds in the side chain (triolefine)

The aromatic fragment resulting from ozonolysis was oxidized. Again the pure olefin was oxidized with potassium permanganate and all the products were analyzed. The formation of the degradation products indicated the monoolefine to be 3- (pentadecenyl- 8') anisole, diolefin to be 1-methoxy-3- (pentadecadienyl4, 11') benzene and triolefin to be 1-methoxy-3- (pentadecatrienyl- 8', 11', 14') benzene [71] (Table 1.2).

J.H.P. Tyman and J, Caplin synthesized menoene, diene and triene constituents of cardanol [72]. Paul and Yeddanappalli isolated the mono-,di- and triene constituents of anacardic acid by low temperature crystallization (from acetone at -80 °C) followed by potassium permanganate oxidation and showed the unsaturation to be present at 8'-11' and 14' [71].

In the early years trans configuration was assigned to the 8', 11" unsaturation in the constituents of cardanol, anacardic acid and cardol. The synthetic 3-(8'-pentadecenyl) anisole [73] which was considered to be the cis-isomer because of the final hydrogenation step, was converted into a glycol different in melting point from that derived from cardanol monoene methyl ether. From this it was concluded that natural monoene had the trans configuration, Fourier Transform Infra Red (FTIR) spectroscopy of the natural product revealed a
band at 960 cm⁻¹ characteristic of the C-H band in a cis olefin which is also present in the diene and triene. Dihydroxylation of natural (cis) cardanol monoene methyl ether with osmic acid gave the same glycol as the dihydroxylation with performic acid of trans cardanol monoene methyl ether, itself obtained by the isomerization of cis isomer with selenium [74]. The existence of unsaturated constituents in the cis configuration had been shown in the ¹H nmr by the coupling constant value of the olefinic hydrogen [75-76].

Many tutorial reviews [77-79] could serve as an introduction of cardanol into the world of soft nano materials; it is a biobased lipid-mixture obtained from the plant *Anacardium occidentale* L. Cardanol is a renewable raw material derived from a byproduct of cashew nut processing industry; Cashew Nut Shell Liquid (CNSL). Cardanol is a rich mixture of non-isoprenoic phenolic compounds that is a valuable raw material for generating a variety of soft nano materials such as nanotubes, nanofibers, gels and surfactants. These nanostructures may then serve as templates for the synthesis of additional nano materials. The wealth and diversity of cardanol-derived functional nanomaterials has urged us to present an article that will give readers a taste of a new class of cardanol-derived functional amphiphiles, along with their ability to generate hierarchical functional nano materials through non-covalent soft-chemical routes. In this concise review, we discuss selected examples of novel biobased surfactants, glycolipids, and polymers derived from cardanol, and their subsequent self-assembly into functional soft materials.
Cardanol is then separated from other components by double vacuum distillation (at 3-4 mm torr) in which the fraction boiling at 220 °C is collected as a clear to pale yellow liquid. It is composed of four different meta-alkyl phenols differing in the degree of unsaturation in the side chain: 5% of 3-(pentadecyl)-phenol, 49% of 3-(8Z-pentadecenyl)-phenol, 17% of 3-(8Z, 11Z-pentadecadienyl)-phenol, and 29% of 3-(8Z, 11Z, 14-pentadecatrienyl)-phenol (Table 1.2). These mono/di/tri unsaturated components possess exciting functional flexibility due to three main structural and chemical features. First is the reactive phenolic -OH group offering synthetic flexibility, and second is the meta alkyl chain with non-isoprenoic cis double bonds attributing amphiphilic and lipidic character. Lastly, the aromatic ring allows for p–p stacking and functionalization. These features make cardanol a tenable precursor for chemical modifications to generate a library of amphiphiles and functional monomers.

Figure 1.5: Cardanol as a renewable resource and the spectrum of applications including polymers, fine chemical synthesis and soft nanomaterial synthesis.

A variety of functional groups can be attached to the reactive phenoxy group of cardanol for further derivatization. Therefore, cardanol has remained a
vital building block for the synthesis of various chemicals that find applications in fine chemicals, as well as in synthesis of functional materials and polymers [80] (Figure 1.5).

Cardanol based polymers and polymeric materials are both well documented in the literature [80] and the focus of continuing research. We choose to restrict the present discussion exclusively to self-assembled soft-nano materials such as liquid crystals, nano/micro fibers, tubes and gels. Despite this, we would like to emphasize that the wide array of potential applications of cardanol as a valuable starting material is not restricted to the examples included in this tutorial review. Unfortunately the intention to discuss every example of cardanol-based materials in a review would not be possible. The authors would also like to direct readers towards the pioneering work by the eminent research groups of J.H. Tyman, C.K.S. Pillai, O. Attanasi, G. Vasapollo and others who continue to be inspired by this wonder molecule.

4. Generalities on Cardanol

Cardanol is a phenolic derivative with a C15-side chain in the meta position [81-84] and is obtained from cashewnut shell liquid (CNSL) by vacuum distillation at 3.4 mm Hg (RP. 228 –235°C) [85]. CNSL contains about 90% of its weight cardanol. The physical properties of cardanol are tabulated in table 1.3.

Cardanol is a mixture of four components differing in the degree of unsaturation at the side chain table 1.2 shows the structure, molecular weight, and
% composition of each component of cardanol [86]. The % composition, however, may vary depending upon the source, method of extraction, etc.

Table 1.3: Physical properties of cardanol

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point °C</td>
<td>228-235 °C (3.4 mm Hg)</td>
</tr>
<tr>
<td>Color (Lovibond, 1 cm cell)</td>
<td>Red (1.0-3.0)</td>
</tr>
<tr>
<td>Freshly distilled</td>
<td>Yellow (1.5-3.5)</td>
</tr>
<tr>
<td>Viscosity 30 °CcP</td>
<td>45-52</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.509 µ</td>
</tr>
</tbody>
</table>

Cardanol is a monohydric phenol having an unsaturated aliphatic side chain at the meta position (see table 1.2 for its properties). Being phenolic in nature, it has been used in the manufacture of special surface coatings, brakelining resins, epoxy resins etc. [86-90]. The literature on cardanol is replete with innumerable patents [90-92] and reports [89, 90], but its industrial utilization has been lagging behind. Actual commercial ventures have been limited to a few industries and in most of the applications, the inherent properties of cardanol has not been properly utilized. Moreover, an analysis of the literature on cardanol indicates that most of the work is product oriented without much concern for basic studies such as fundamental aspects of polymerization, structure-property correlations etc. It is well known that information on these aspects is essential for the design and development of advanced polymers to meet specific requirements. The reasons for this lacuna in the case of CNSL polymers may be many, but in the case of cardanol the inherent problems associated with it is the fact that it is a mixture of
four components (see table 1.2) differing in their degree of unsaturation [95-97]. Although separation of these components has been worked out by many groups [98, 99]. It was difficult to get polymerisable quantities. Being an inexpensive raw material, large scale manufacturers still prefer cardanol and would not resort to separation [93] into its components on economic grounds. The scarcity of data on the polymerization characteristics of cardanol and structure-property correlations of its polymers has been an impediment in the development of speciality polymers from cardanol.

The lower thermal stability of cardanol is in comparison to phenolics was explained on the basis of the presence of the labile aliphatic side chain of cardanol.

4.1 Isolation

Cardol and cardanol were isolated from the technical cashew nut shell liquid according to the procedures described by Paramashivappa et al. (2001) [100] and Kumar et al. (2002). Technical CNSL was dissolved in methanol, ammonium hydroxide (25%) was added, and the solution was stirred for 15min. The cardanol was extracted by adding hexane (4 times), followed by a 5% HCl wash of the organic layer. The hexane fraction was then dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure to obtain pure cardanol. The methanolic ammonia solution was extracted with ethyl acetate/hexane (4:1), followed by a 5% HCl wash of the resulting organic layer, and a distilled water wash. The remaining fraction was dried over anhydrous
sodium sulfate and the solvent was evaporated under reduced pressure to obtain pure cardol.

The dependence of chemical industry on petroleum resources could be reduced by the full utilization of the renewable natural biomass resources whenever it is possible. Ranging from algae to wood its availability is limited only by the photosynthetic efficiency of the plant [101]. It is renewable; availability is flexible through crop switching and is also adaptable through genetic manipulations [102]. Cellulose, starch, sugar, lignin, oils, fatty acids, etc, provide a variety of naturally occurring starting materials from which a host of chemicals like alcohol, ethylene, glycerol, hydrocarbons, etc could be synthesized [102]. The biomass system presents opportunities to continue the production of chemicals that are needed at reasonable prices while conserving fossil resources and it could be grown to satisfy changing end use chemicals on both quantitative and qualitative basis.

4.2 Surfactants from cardanol

Cardanol possesses a similar structure to linear alkyl benzenes (LABs), which are the most commonly used as industrial and household surfactants. Cardanol based surfactants offer a green alternative to petroleum-products derived LAB surfactants. Fittingly, chemically unmodified cardanol does have inherent surfactant-like properties due to its slightly polar phenolic ring and long hydrophobic hydrocarbon chain. An extracted pure form of cardanol was able to stabilize the phospholipid liposomes akin to cholesterol, a well-known liposome/membrane/lamellar stabilizer. The ability to stabilize liposomes is an
important characteristic requirement of drug-delivery vehicles. Increased stability prevents the non-specific leakage of drugs from the interior compartment of liposomes. This stability relates to the retained structural integrity of the drug loaded liposomal membranes over a long time inside the body, allowing for circulation through the blood system. Doping of cardanol into 1-palmitoyl-2-oleylphosphatidylcholine (POPC) liposomes at the mole ratio of 9:1 enhanced the stability of the POPC vesicles. Furthermore, a direct comparison study on the release of carboxy fluorescein dye from POPC liposomes revealed that liposome-stabilizing ability of pristine cardanol was similar to the widely used cholesterol liposome-stabilizer.33 This study also suggested that cardanol could be interdigitated in the bilayers of POPC lipids similar to cholesterol doped POPC liposomes.

One of the most interesting aspects of the structure of cardanol is its ability to undergo polymerization by both step reaction and chain reaction mechanisms. Added to this is its amenability to manipulations through chemical modifications. Being phenolic in nature, cardanol undergoes the conventional aldehyde condensation reactions to give novolaks and resols depending on the conditions of polymerization. The kinetics of formaldehyde condensation of cardanol has been reported only very recently. In the case of chain reaction polymerization, few systematic studies are reported except that of dimerization studies of cardanol by Tyman. However, many of the patents cite a cationic polymerization involving acid catalysts such as sulphuric acid, phosphoric acid, diethyl sulphate etc. There are also examples of Lewis acids such as aluminium chloride in the polymerization of
cardanol. Even metals and metallic powders are reported to be used in the polymerization of cardanol. In this perspective, Manjula et al undertook a systematic study of the polymerization of cardanol using catalysts.

CNSL is chemically constituted from 3-n-pentadecyl-phenol (cardanol) and its derivatives with in saturation on the alkylic chain. The latter could be easily reconverted in 3-npentadecyl-phenol by simple catalytic hydrogenation. In smaller amount there are cardol, methylcardol and anacardic acid. CNSL is a cheap and renewable substance which can be employed for making of a multitude of useful products; infact it is widely employed in more fields of manufacture of resins and plastics, surface coatings, adhesives, laminates, rubber compounding. Greater utilization of CNSL for industrial polymer products can be an attractive proposal in view of its low cost, abundant availability and chemically reactive nature.

The cashew (AnacardiumoccidentaleL.) is a well-known member of the anacardiacea family and is commonly found in northeast Brazil. The cashew nut has been commercially exploited since colonization. Brazil, India and Mozambique, are the leading cashew nut producers in the world (Paramashivappa et al. 2001) [100].

The process of the improvement of the cashew involves four basic stages: stockpiling, structuring of the chestnut for use, extraction of the almond, and refinement (Moura et al. 2005). The technical cashew nut shell liquid (CNSL), containing the phenolic compounds, cardanol (60-65 %), cardol (15-20 %), polymeric material (10 %), and traces of methyl-cardol, is the most abundant by-
product of cashew improvement (Paramashivappa et al. 2001 [100], Kumar et al. 2002, Trevisan et al. 2006). CNSL is used for industrial technological applications, biological/pharmaceutical applications, friction dust production by the automobile industry, and in certain polymeric/surface coating applications (Stasiuk et al. 2008).

5. Methods of polymerization and applications

It should be noted that some of the naturally occurring monomers have already found applications in the polymer field. The monomer can either be modified to other suitable monomers or can be polymerized directly into a useful polymer, an example for the latter is furfural which acts as a precursor to hexamethylene diamine and adipic acid, the latter two utilized to form nylon - 6, 6. Furfural or its derivatives are known to be utilized for the production of phenolic resins.

Another example of modification is the dry distillation of castor oil to get sebacic acid, a monomer for the production of nylon. Another example is that of terpene resins polymerized from terpenes such as β-pinene. Terpene resins have found use as pressure sensitive adhesive, coating etc. Natural oils such as linseed oil, tung oil etc., have formed the basis for paints (drying involves an oxidative polymerization at the double bonds leading to a crass-linked network). The alkyd resins can also be considered in this case, although they are partly synthetic.

Since the methods of polymerization and characterization of polymers are now well established, a detailed discussion on it is out of place here. The application of a particular polymerization technique generally depend upon the
structure of the monomer. For example, a monomer having two or more functional
groups such as hydroxyl-, carboxyl-, etc., can undergo what is generally known as
condensation polymerization. When unsaturated bonds are available, chain
reactions can be initiated by appropriate catalysts called initiators. Table 1.1
provides the list of naturally occurring monomers which have already been
polymerized and used commercially.

6. Selection of naturally existing monomers for the present study

The preceding section dealt with monomers of natural origin that had been
polymerized or that have potential for polymerization. Among these monomers,
unsaturated long chain hydrocarbon phenols occupy a very important position.

Cashewnut shell liquid (CNSL), obtained as a byproduct of cashew
industry, is a rich source of unsaturated long chain hydrocarbon phenols. CNSL is
one of the monomeric systems selected for the present work because of its ready
availability in large quantities, its regional importance, and its ability to polymerize
through double bonds as well as through the phenol-formaldehyde type
condensation. CNSL occurs as a reddish brown viscous liquid in the soft honey
comb structure of the shell of the cashew nut which is a plantation product
obtained from cashew tree, *Anacardium occidentale.* L which is cultivated in a
large number of tropical and subtropical countries. The tree is native to Brazil and
the coastal areas of Asia and Africa. Cashewnut production has increased
worldwide and it holds a share (20%) almost the same as the almond and the
hazel. Cashewnut attached to a cashew apple is a grey colored kidney shaped
structure and is 2.5 - 4 cm long. The cashewnut consists of an ivory colored kernel covered by a thin brown membrane (testa) and enclosed by an outer brown porous shell that is the mesocarp which is around 3 mm thick and contains CNSL. The nut thus consists of the kernel (20-25 %), the shell liquid (CNSL) (20-25 %) and the testa (2 %), the rest being the shell. The kernels freed from testa contains 1.6 % water, 10 % protein, 57.4 % fat, 5.3 % carbohydrate, 2.4 % ash and 0.9 % fiber. The CNSL is present to 18-27 % of the total raw nut weight, kernel is approximately 20-25 % and the balance is the shell weight and the testa (2 %).

7. Polymerization of Derivatives

7.1 Addition Polymerization at the Side Chain Unsaturation:

Polymerization could be carried out through the double bonds of the side chain employing either free-radical or ionic initiators. CNSL responds easily to acidic catalysts like H₂SO₄, HCl, diethyl sulfate, and the like, which induce polymerization through the formation of an allylic carbonium ion from the more reactive double bonds of the triene.

7.2 Oxidation Polymerization:

When CNSL or derivatives are oxidized, its iodine number may be reduced quickly to zero, and the reaction product dries very quickly at ordinary and elevated temperatures. The product, when dissolved in solvents such as turpentine, naphtha, or kerosene, gives an excellent coating material useful for making paints, varnishes, and such for impregnating paper and woven fabrics.
7.3 Condensation Polymerization:

CNSL or derivatives could be condensed with active methylene compounds such as formaldehyde, furfural, and others, at the ortho or para positions of the phenolic moiety to produce many varieties of novolac or resole polymers. Condensation polymers are now finding use as coatings materials, adhesives, plastic and rubber compositions, and automobile brakes.

Manjula, Pillai, and Kumar [103] have reported on the thermal characterization of cardanol-formaldehyde resins and cardanol-formaldehyde/PMMA semi-IPNs. Cardanol formaldehyde products decompose at a faster rate and hence have lower thermal stability. Between cardanol-formaldehyde (resol) and cardanol-formaldehyde (novolac) products, the former decomposes at a faster rate. The TGA of semi-IPNs indicates that thermal degradation of PMMA is slowed by the formation of IPNs. PMMA is known to degrade to show 50% weight loss at 350°C, whereas cardanol-formaldehyde (resol)–based semi-IPNs show only 15% weight loss at this temperature. The PMMA stabilization is greater in the case of a novolac resin–based semi-IPN system. The activation energies for the first stage of decomposition for the cardanol-formaldehyde (resol)/PMMA semi-IPNs range from 40 to 55 kJ mol⁻¹, whereas the corresponding values for semi-IPNs based on a novolac system are between 44 and 65 kJ mol⁻¹. The second stage of decomposition, which is between 400 °C and 500 °C, has activation energy between 90 and 110 kJ mol⁻¹ for semi-IPNs, whereas it is 139 kJ mol⁻¹ for the cardanol-formaldehyde resin. The differences are attributed to the structure of the resins.
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John and Pillai [104] have reported a self-cross-linkable monomer and the polymer from cardanol. Cardanol was reacted with acryloyl chloride to obtain cardanyl acrylate, a new bio-based vinyl monomer. This vinyl monomer was polymerized in solution and suspension medium using benzoyl peroxide as the initiator. In the case of solution polymerization, a linear poly(cardanyl acrylate) was obtained, whereas in the case of suspension polymerization, a cross-linked bead was obtained. These polymers were characterized using an FTIR technique. The morphology of the cross-linked bead was obtained using scanning electron microscopy.

One of the interesting aspects of the chemistry of polymerization of cardanol is that it does not undergo polymerization by conventional free-radical initiators such as benzoyl peroxide or AIBN. The phenolic moiety of cardanol, because of its antioxidant nature, can act as a radical scavenger during the initiation step. However, it is well known that cardanol is susceptible to auto oxidation, leading to polymerization, giving rise finally to cross-linked products. Cardanol, with its hydrophobic moiety, can be considered an unsaturated non-conjugated lipid. It is well known that non-conjugated lipids undergo oxidation polymerization through the formation of hydro peroxide groups as intermediate reactive species, which can give rise to active centres for further reaction and polymerization. Similar mechanisms are operating in the drying of oils such as triglyceride of linoleic acid and in the auto oxidation of non-conjugated cyclic dienes. Tyman [105] suggested that cardanol can undergo hydro peroxidation through the triene double bonds, giving rise to allylic radical centers that would
combine to form conjugated intermediates, leading to propagation reactions and cross-linking.

8. Utility of CNSL and Cardanol

When studies were initiated to develop speciality polymers from cardanol it became apparent that there exists a wide gap between the technology and scientific understanding. CNSL and its polymeric products find a wide variety of applications in industry. Polymeric products include friction-lining materials, surface coatings, paints and primers, varnishes, lacquer, specialty coatings, adhesives, and binders. CNSL also has been used as a basic raw material for a vast number of industrially important chemical and chemical intermediates. A few include fungicides, bactericides, and insecticides. Cardolite corporation, a company based on CNSL, has been set up in New Jersey, and is engaged in manufacturing many polymers and oligomers for various industrial applications.

The structural difference between phenol and cardanol is only the C15 unsaturated side chain and hence cardanol undergoes most of the reactions of phenol. Thus cardanol can be polymerised with formaldehyde to give resols and novolaks [106]. The presence of the side chain gives it an added advantage that it can be polymerised by chain reaction methods as well. This gives rise to opportunities for selection and control on polymerisation techniques for a particular product. For example, the preparation of resins for brakelining is reportedly made by making use of an acid catalysed side chain polymerization followed by the conventional formaldehyde condensation. Apart from the variety in polymerisation
reactions cardanol can also undergo chemical modifications at the hydroxyl ring and the side chain. Moreover, the hydrocarbon side chain itself by its very presence imparts new properties such as internal plasticization, flexibility etc. [107]. A study by Pillai et al [108] have shown that high performance and speciality polymers could be produced from cardanol by a variety of synthetic methods.

9. **Scope and Objectives:**

Aromatic poly(ether–ketone)s, PEK; and Aromatic poly(ether–ether–ketone)s, PEEK, are an important class of thermoplastic high performance polymers having excellent mechanical and dielectric properties are well known for their high chemical and heat resistance. Glycidyl polymers employed for the preparation of protein arrays). These excellent properties make them potentially suitable for a wide range of applications, such as structural adhesives and matrix resins for composites in aerospace applications. However, their aromatic structure and semi-crystallinity result into high melting points (around 340–360 °C), high glass transition temperatures and low solubility in organic solvents often restricting the use of these resins for some application.

Thus, new novel polymers containing preferred flexible linkages, pendant C–15 long alkyl substituents, were synthesized and their structural proof was provided by FT-IR, $^1$H-NMR, $^{13}$C-NMR, mass spectrometry and Elemental Analysis.

The general goal of the research conducted for this thesis is to (i) develop new thermally stable polymers with free ionic pendants for technological fields,
research targets includes that (a) to develop mild and efficient protocols to achieve the modification reactions of the prime polymers. (b) The dielectric constant and dielectric loss of the ionomers at room temperature needs to be preferable for the practical applications. (c) The developed ionomers has good thermo and chemical stability, and durability.

The solubility of polymers containing bulky pendant phenyl / C-15 alkyl substituent's tended to be improved with increase in content of such units; and copolymers become soluble in organic solvent, whereas PEEK (of biphenyl / BPA) is soluble only in conc. H₂SO₄. The unsymmetrical and kink structures of the polymer chains, randomness due to copolymer formation, could disturb interchain and intrachain interactions and make them amorphous and readily soluble in polar, aprotic solvents. Thus the effect of the order and ratio of aromatic ether ether ketone linkage, unsymmetrical and kink, m/p – phenyl substitution, pendant alkyl / pendant phenyl groups, amide / imide linkages, and overall effect of the co-monomer structures has been analyzed.

DSC-TGA analysis were performed to study glass transition temperature and temperature withstanding ability of these polymers; and effect of introduction of the pendant phenyl/pendant C-15 long chain alkyl groups.

Consequently, new engineering materials, with excellent properties and improved solubility / processability for high performance applications, as materials for films, coating for optical devices and electronics, gas separation membranes, aerospace, as fuel cell and nuclear industries, are developed.
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The relevance of an integrated effort to utilize the biomass resource for the synthesis of new polymers or substitution of existing polymeric materials is, no doubt, important. In this thesis an effort is made to collect and codify the available data on various monomeric constituents of biomass, especially CNSL oil and chemical modification of prime high performance polymers with these active monomers. The following studies are also included in this thesis (1) to synthesize cardanol derivatives (obtained from cashew nut shell liquid) by diverse chemical routes, (2) to synthesize and study the thermal properties of high performance polymers in addition to synthesized poly glycidyl methacrylate and chemical modification of these by cardanol and related synthetics in comparison, (3) thermo gravimetric and differential scanning calorimetric studies of chemically modified polymers and, (4) studies on physical properties of cardanol sulfonates and related derivative salts of the same.
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