Chapter 4
Facile Green Strategy for Preparation of Advanced Structured Materials Based on Amphiphilic Cardanol

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Abstract Cashew nutshell liquid oil among different renewable resources is one of the agricultural by-products available in tropical countries such as India that is used to produce cardanol as naturally occurring fatty phenols. It has attracted great attention in advanced chemical industries to produce biopolymers, bio-surfactants, bio-composites and nanomaterials. It represents an excellent alternative feedstock for the elaboration of chemicals and polymers. Moreover, cardanol is regarded as a versatile and valuable raw material for wide applications in the form of brake linings, surface coatings, paints and varnishes as well as in polymer production. In this chapter, the possible modifications of cardanol to produce monomeric and polymeric surfactants have been discussed in different reaction schemes. It can be recommended that because of their renewable nature and structural characteristics, cardanol is likely candidates for preparing "green" surfactant species like anionic (sulfonates), non-ionic (ethoxylated and cardanol–formaldehyde ethoxylated polymers) and cationic (quaternary ammonium, pyridinium and imidazolium derivatives) to replace the petroleum based on nonylphenol surfactants. Moreover, it can be used to prepare biopolymer, polymer nanocomposites and semisynthetic processes to prepare derivatives with biological and pharmaceutical applications.

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4.1 Cardanol as Renewable Feedstock for the Chemical Industry

Significant research efforts of the academic and industrial world directed to use renewable resources to replace the petrochemicals for production of commercial materials due to the increasing prices of petrochemical products and growing environmental concerns. Cashew nutshell liquid (CNSL) is represented as an important bio-based natural material due to its availability, cheaper cost and unique structural features. Cardanol is the main phenolic component produced from the cashew nutshell liquid or oil obtained as a by-product of the cashew (*Anacardium occidentale* L.) nut processing. Figure 4.1 represents the chemical constituents of commercial-grade CNSL, in which cardanol is produced in percentages of 62.8 % due to decarboxylation of anacardic acid to cardanol [138]. 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 contain CNSL. Four constituents differing in the side chain unsaturation represented the components of CNSL (Fig. 4.1). Different methods have been used to extract CNSL from the nuts such as hot oil process and roasting process [81, 133] or solvent extraction of the oil using organic solvents [64, 134]. Oligomeric and polymeric materials have been reported by Tyman et al. [135, 136, 138].

The strategies used to modify the chemical structure of cardanol are based on the three reactive functional groups. First functional group is the reactive phenolic –OH group offering synthetic flexibility to prepare hydrophilic moieties that were used to prepare specialty polymers such as novolac or resole resins, polyurethane thermosets and liquid crystal epoxy polymers in different reaction media. The second reaction group is the meta alkyl chain with non-isoprenoic cis double bonds attributing amphiphilic and lipidic character. The presence of an unsaturated hydrocarbon chain with one to three double bonds at the meta position of the phenol group attracted great attention to produce green biopolymers. Lastly, the aromatic ring allows for π–π stacking and functionalization. Cardanol-based biomaterial polymers have been used as ionic and non-ionic surfactants in the various industrial applications due to
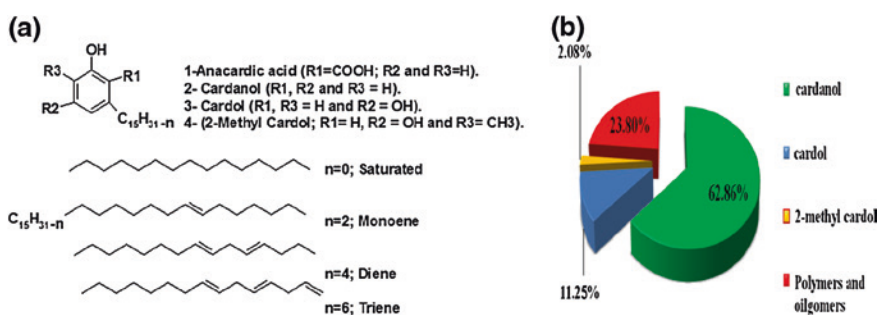

Fig. 4.1 Chemical compositions of CNSL

its antibacterial and chemically modifiable properties. Cardanol-based surfactants are just emerging as green alternative to conventional petroleum-derived nonylphenols for the preparation of surfactants. Cardanol has naturally an ideal chemical structure for the synthesis of amphiphilic derivatives and surfactants. The alkyl $C_{15}H_{27}$ alkyl side chain provides an essential hydrophobicity, while the slightly polar phenoxy group allows a wide variety of chemical modifications. This section aims to report the conversion of cardanol to polymeric and monomeric amphiphilic surfactants to produce advanced materials based on polymers, nanomaterials and composites.

The preparation of new molecules based on natural materials by environmental friendly and cost-effective means is the target for advanced researches. Cardanol as one of the renewable bio-resource feedstocks attracted great attention to produce different types of amphiphiles that can be used to produce advanced materials such as biopolymers and nanomaterials [67, 68, 111, 132]. Further, it is assumed that an increased fraction of natural building blocks in the chemical structure will be beneficial for reducing aquatic toxicity and increasing the rate of biodegradation. In this section, we represent two decades of research focused on turning cardanol into value-added materials due to inherent 'programmed,' or 'built-in' functionalities. We highlight the efficient conversion of cardanol into a wide array of surfactant monomers, polymers and self-assembled systems to produce nanomaterials and polymer composite materials. The presence of different functional groups became target for different chemical modifications to generate a library of amphiphiles and functional monomers that remained a vital building block for the synthesis of different chemicals that find applications as described in Fig. 4.2 [80].
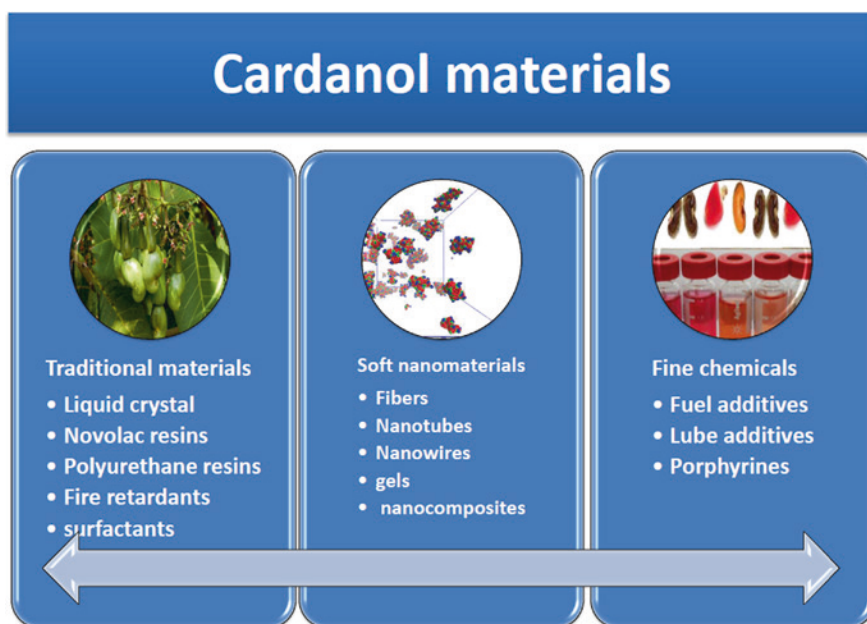

Fig. 4.2 Cardanol-modified materials including traditional polymer, fine chemical synthesis and soft nanomaterial synthesis
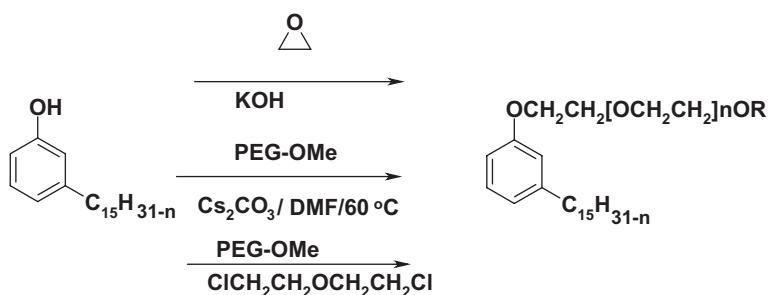
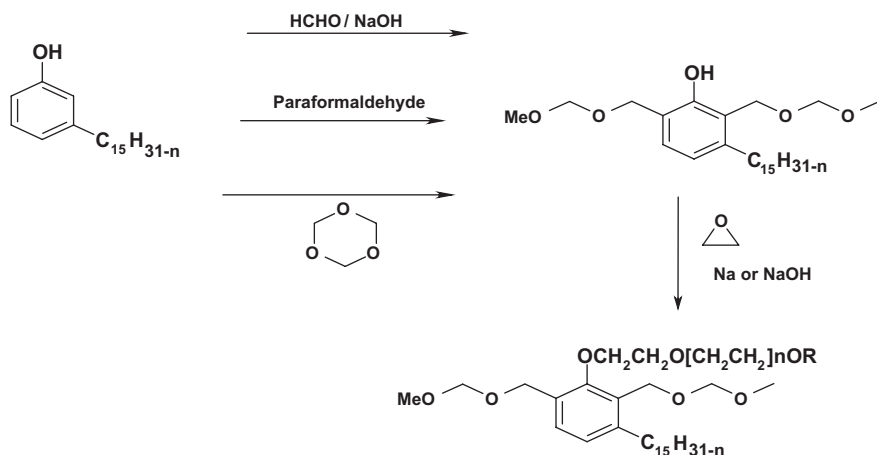## 4.2 Cardanol Surfactants

4.2.1 Non-ionic Surfactants

Cardanol resembles in its chemical structure alkyl phenol surfactants that ethoxylated to produce non-ionic surfactants that attracted great attentions in the petroleum and chemicals industries as emulsifier, demulsifier, dispersant and wetting agents [28, 29, 101, 102]. Different routes can be used to obtain non-ionic surfactants as illustrated in Scheme 4.1. Route 1 is based on the preparation of polyethylene glycol derivatives as described by Tocco et al. [131]. The monomethyl ether of poly-(ethylene glycols), MPEG, was selected because it can be easily reacted with cardinal and it is soluble in a wide range of solvents, non-toxic, inexpensive, commercially available, easy to functionalize and also resistant to drastic operative conditions [39]. Moreover, PEG chemistry has shown wide applications as a large part used to deliver drugs, oligonucleotides or enzymes [49].

Route 2 (Scheme 4.2) shows the preparation of polymeric non-ionic surfactants that can be prepared by forming cardanol–formaldehyde polymers by reaction of cardanol with formalin or trioxane as described by Atta et al. for preparing rosin formaldehyde resins [9, 10, 13, 17]. The produced rosin formaldehyde resins can be reacted with MPEG or ethylene oxide to produce non-ionic polymeric surfactants as reported on conversion of rosin to polymeric surfactants [9, 10, 13, 17]. The phenolic nature of resulting cardanol makes it possible to react with formaldehyde under a variety of conditions to form novolac or resole resins [38, 98, 146]. Compared with conventional alkyl phenol ethoxylated surfactants, ethoxylated cardanol–formaldehyde surfactants have improved flexibility. Moreover, the side chain imparts a hydrophobic nature to the polymer, making it water repellent and resistant to biodegradation. Non-ionic surfactants have also been synthesized by reacting cardanol with alkylene oxide (ethylene or propylene oxides), polyalkylene glycol or halohydrin [30, 120].
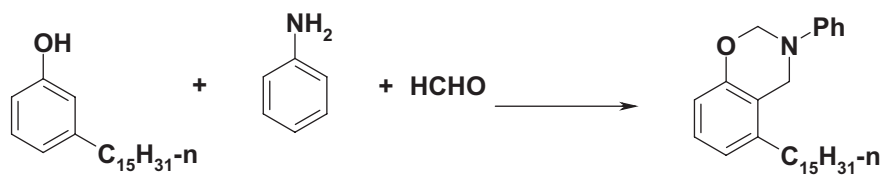
Scheme 4.3 is used to prepare a benzoxazine surfactant based on cardanol as a renewable resource's ability to perform its functions as non-ionic surfactants. The synthesis procedure was described as solventless method to react aniline,
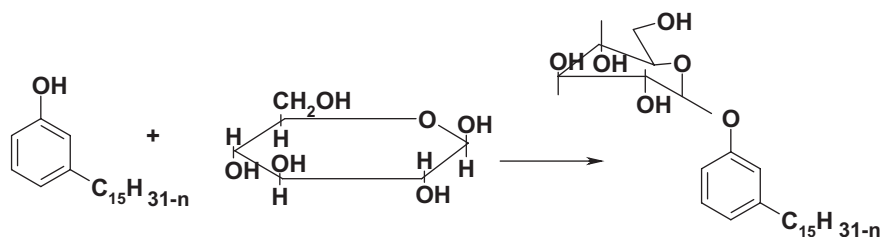

Scheme 4.1 Preparation of ethoxylated cardanol

**Scheme 4.2** Preparation of cardanol–formaldehyde condensates

Scheme 4.3 Preparation of cardanol–benzoxazine surfactant

Scheme 4.4 Preparation of cardanol glycosides

formaldehyde and cardanol to prepare non-ionic surfactants that have wide application to prepare composites [31, 79, 103].

Cardanol glycosides are special type of glycolipids that can be prepared by reacting phenol group with sugar or by attaching glucopyranose to cardanol (Scheme 4.4). The presence of sugar moiety adds non-ionic polar head group to cardanol and bestows chirality to the molecule. These materials have a tendency to
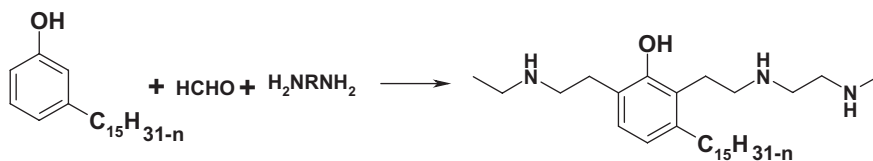
Scheme 4.5 Mannich reaction of cardanol to produce non-ionic surfactants

Table 4.1 Surface activity and application of non-ionic surfactants based on cardanol

| Cardanol surfactants	Surface properties		Applications	References
	Critical micelle concentrations (CMC) (mM)	Surface tension at CMC (mN m^{-1})		
Ethoxylated cardanol acrylate copolymers	0.08–0.22	35.4–38.2	Biological and pharmaceutical applications	[34–36]
Ethoxylated cardanol phenol–formaldehyde	0.03–0.53	32.3–38.5	Petroleum demulsifiers and dispersants	[37]
Cardanyl-b-D-glucopyranoside	0.23	38.13	Nanotube architectures	[38]

form self-assembled layers to surround the colloidal particles to produce soft materials, such as twisted fibers, helical coils and high-axial-ratio nanotubes [21, 66].

The modification of CNSL with polyamines is used to produce non-ionic surfactants as represented in Scheme 4.5. This technique is based on Mannich reaction that involves the reaction of the CNSL with formaldehyde and diethylenetriamine, triethylenetetramine, tetraethylenepentamine, or pentaethylenehexamine in methanol solution. Under these conditions, the dihydric phenol, cardol, forms high molecular weight polymeric non-ionic surfactants, while the cardanol remains substantially unreacted [40].

The surface activity parameters of the non-ionic surfactants produced from modified cardanol and their industrial applications in the preparation of polymers, nanocomposites and nanomaterials are represented in Table 4.1.

4.2.2 Anionic Surfactants

It is well established that anionic surfactants based on dodecyl benzene sulfonate have greater applications as detergents in the household and chemical industries. As previously discussed, the structure of cardanol is similar to dodecyl benzene which can easily be sulfonated to produce surfactants that have similar properties to dodecyl benzene sulfonate [21, 97, 129]. The surfactant from cardanol can be
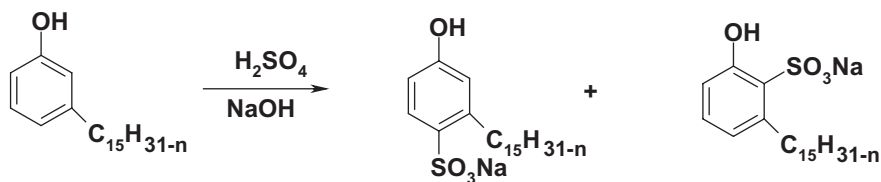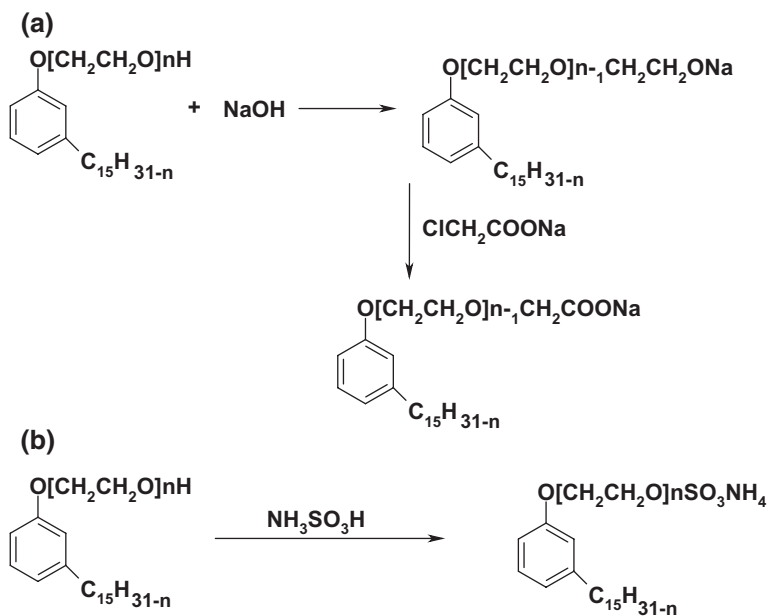
Scheme 4.6 Sulfonation of cardanol

prepared as illustrated in Scheme 4.6. The physicochemical properties such as surface activity, solubility in sea water and detergency indicated the superior properties when it was compared to dodecyl benzene sulfonate [97]. PDPSA surfactants that have sulfonate group within in O– or P– position (Scheme 4.6) have reduced the surface tension of water to be 32.25 mN m^{-1} at 20 % w/v and 28.00 mN m^{-1} for dodecylbenzene sulfonate at 15 % w/v. Critical micelle concentrations (CMC) of dodecyl benzene sulfonate and cardanol sulfonate were found to be 0.435 and 0.372 M, respectively [97]. The results confirmed that cardanol sulfonate can be applied as an alternative bio-based anionic surfactant. The bio-based surfactant produced from sulfonation of cardanol commonly known as 3-pentadecylphenol 4-sulfonic acid (PDPSA) is having amphiphilic character and can act as stabilizing and capping agents to control the shape, size and stabilization of the nanomaterials [121, 122].
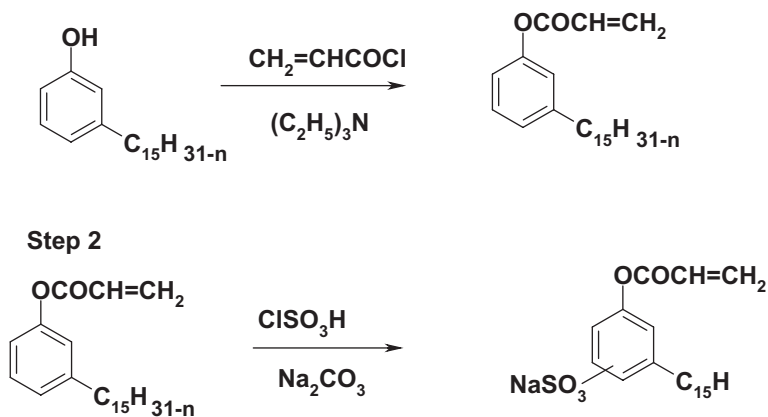
Anionic surfactants can also be obtained from non-ionic surfactants of cardanol prepared by ethoxylation of cardanol with ethylene oxide as represented in Scheme 4.7a, b [137]. The hydroxyl end group of oxyethylene unit was converted to anionic groups by reacting either with chlorosodium acetate or with ammonium sulfonic acid [97].

The reactive surfactants (surfmers) behave unlike conventional non-reactive surfactants and can act as part in the polymerization with the main monomer to produce new polymeric material for emulsion polymers applied in useful protective coatings and adhesives [51]. Polymerizable reactive anionic surfactants can also be obtained by introducing reactive groups into amphiphilic surfactants [7, 8]. In this respect, acrylate and sulfonate groups can be introduced to cardanol by reacting with acryloyl chloride in the presence of triethyl amine followed by sulfonation with chlorosulfonic acid as described in Scheme 4.8 [129]. It was also reported that acrylate group can be introduced to cardanol after converting the hydroxyl phenol to alcoholic group by etherification with chloroethanol in the presence of sodium hydroxide as reported in Scheme 4.9 [129]. The surface activity measurements of the prepared surfactants indicated that the micellization of the surfmers with an ethylene spacer between the phenyl ring and the acrylate group is more active at lower concentrations like polymeric surfactants [129].

Cardanol can be converted to anionic surfactant and to trithiocarbonate used as chain transfer in radical fragmentation chain transfer (RAFT) in emulsion polymerization of methyl methacrylate (MMA) [34]. The resulting cardanol-terminated

(a)

O[CH$_2$CH$_2$O]nH   + NaOH $\longrightarrow$ O[CH$_2$CH$_2$O]n-$_1$CH$_2$CH$_2$ONa

C$_{15}$H$_{31-n}$ C$_{15}$H$_{31-n}$

ClCH$_2$COONa $\downarrow$

O[CH$_2$CH$_2$O]n-$_1$CH$_2$COONa

C$_{15}$H$_{31-n}$

(b)

O[CH$_2$CH$_2$O]nH $\xrightarrow{\text{NH}_3\text{SO}_3\text{H}}$ O[CH$_2$CH$_2$O]nSO$_3$NH$_4$

C$_{15}$H$_{31-n}$ C$_{15}$H$_{31-n}$

Scheme 4.7 Preparation of cardanol anionic surfactants based on **a** ethoxylated carboxylate and **b** ethoxylated ammonium sulfate salts

OH $\xrightarrow[\text{(C}_2\text{H}_5)_3\text{N}]{\text{CH}_2=\text{CHCOCl}}$ OCOCH=CH$_2$

C$_{15}$H$_{31-n}$ C$_{15}$H$_{31-n}$

Step 2

OCOCH=CH$_2$ $\xrightarrow[\text{Na}_2\text{CO}_3]{\text{ClSO}_3\text{H}}$ OCOCH=CH$_2$

C$_{15}$H$_{31-n}$ NaSO$_3$ C$_{15}$H

Scheme 4.8 Synthesis of polymerizable cardanol anionic surfactant

poly(methyl methacrylate) (PMMA) was photo-polymerized to produce UV-cured resin within 20 min. The great advantages of using these materials over conventional curing systems are their high efficiency, energy saving, environmental friendliness, cost economy, etc. The cardanol-based RAFT chain transfer agent
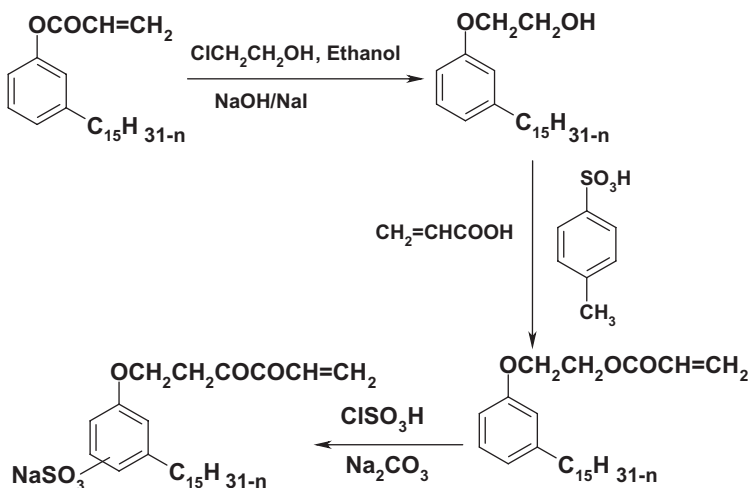
**Scheme 4.9** Synthesis of ethoxylated polymerizable cardanol anionic surfactant
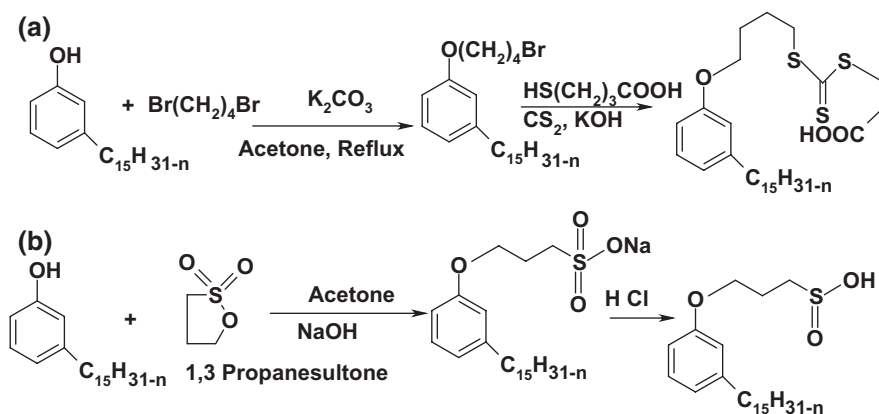
Scheme 4.10 **a** Chain transfer and **b** anionic surfactants

and a new cardanol-based anionic surfactant were prepared as represented in Scheme 4.10 [34].

Amphiphilic anionic surfactants can also prepared by reacting cardanol with 1,4-butanesultone, 1,3-propanesultone as sulfonation reagents using potassium tertiary butoxide as base catalyst. The scheme of preparation is represented in Scheme 4.11 [129].

Cardanol was also useful starting material for synthesizing anionic amphiphilic surfactants called cardanol azophenylsulfonic acid (CAPSA) (Fig. 4.3) [6].
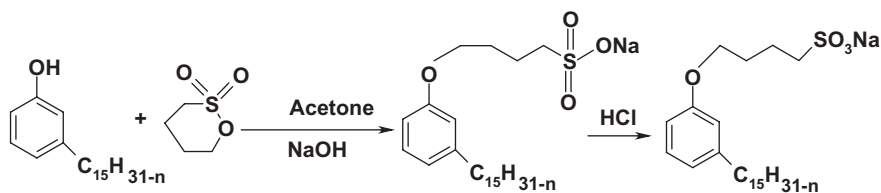
Scheme 4.11 Preparation of cardanol alkyl sulfate anionic surfactant

**Fig. 4.3** Cardanol azophenylsulfonic acid surfactant
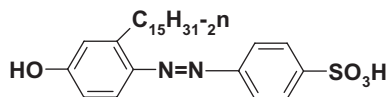
The anionic surfactants showed superior amphiphilic properties and are used as a template for preparation of polyaniline conducting polymers and their nanocomposites with clay as gathered in Table 4.2. It was also found that the morphology and size of the nanomaterials proved that the anionic surfactants based on cardanol have ability to self-assemble with rod-like micelles that are responsible for directing the formation of oriented nanoparticles.

The surface activity of anionic amphiphiles derived from cardanol can be modified by preparing Gemini surfactants that based on amphiphiles have more than two head and two tails linked by spacer groups. Several steps of chemical reaction and treatments were employed to prepare Gemini surfactants as illustrated in Scheme 4.12 [116]. In the first procedure, the etherification reaction was completed in the presence of 1,3-dibromopropane to generate cardanol separated with spacer groups. In the next step, the dicardanyl propyl ether was sulfonated using chlorosulfonic acid to form cardanol sulfonic acid Gemini surfactant. The last step used to neutralize the sulfonated cardanol dimmer using sodium hydroxide solution. The CMC for cardanol sulfonate Gemini surfactant was 6.20×10^{-2} mM, and surface tension at CMC was 36.92 mN m^{-1}.

Table 4.2 Surface activity and application of anionic surfactants based on cardanol

| Cardanol surfactants	Surface activity		Applications	References
	CMC (mM)	Surface tension at CMC (mN.m^{-1})		
PDPSA	0.372	31.2	Conducting polyaniline–clay nanocomposite	[40]
PDP	0.1	28.5	Conducting polyaniline nanomaterials	[48]
CAPSA	0.49	35.2	Material for supercapacitors	[49]
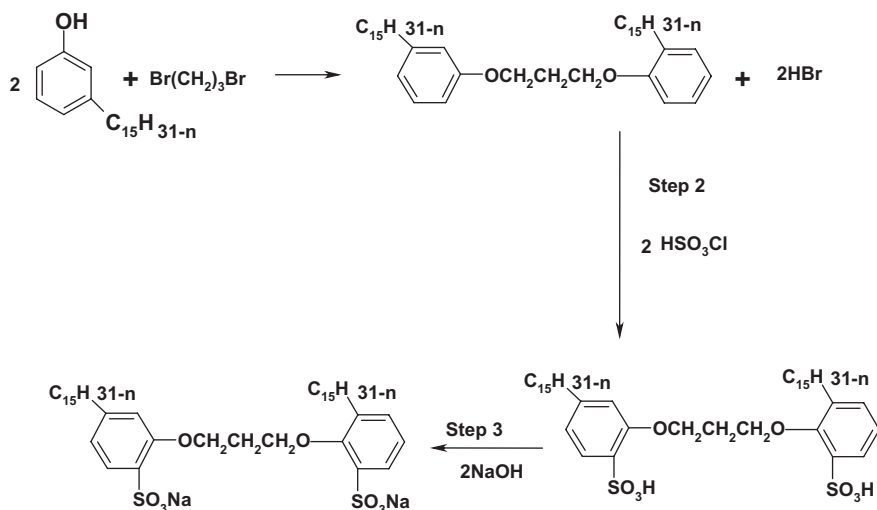
Scheme 4.12 Preparation of cardanol Gemini surfactants

4.2.3 Cationic Surfactants

Cationic amphiphiles can be produced from cardanol by attaching directly or indirectly to positively charged nitrogen atom. Moreover, synthesis of Gemini amphiphiles from cardanol as the new-generation amphiphilic molecules increases the efficiency and effectiveness as compared to their monomeric counterparts. In this respect, pyridinium and imidazolium Gemini amphiphiles are the most valuable and effective as recent class of cationic Gemini amphiphiles. It is necessary at the present time to develop of new amphiphilic molecule having better surface and interfacial properties to replace the conventional cationic surfactants. The cationic and Gemini amphiphiles have been used widely in production of biopolymers, nanomaterials, fabric softener, wetting agent, dispersant, emulsifier, foaming agent, bactericide, corrosion inhibitor, and the number of other applications continues to increase with time.

It was reported that the series of phenoxy ring containing long-chain imidazolium and pyridinium based on cardanol Gemini amphiphiles have been synthesized using different spacers (i.e., –S–(CH2)$_n$–S–, where n is 2, 3, 4 and 6) as represented in Scheme 4.13 [22]. The results of this work proved that the phenoxy group containing Gemini imidazolium and pyridinium amphiphiles has the potential to be used as gene delivery agent.

A cardanol can also be linked with quaternary ammonium salt to produce cationic surfactants. It was reported that [50] quaternary ammonium salt surfactant (3-cardanoxy-2-hydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride was prepared by linking cardanol with glycidyl trimethyl ammonium chloride (GTA)
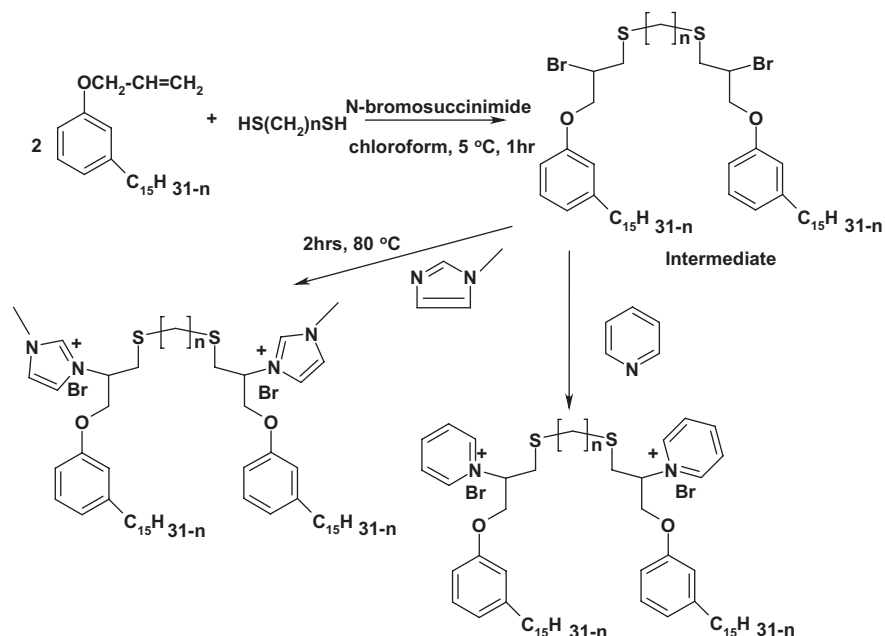
Scheme 4.13 Preparation of cardanol containing Gemini imidazolium and pyridinium amphiphiles

which can be prepared from reaction of epichlorohydrin and trimethylamine as starting materials. The produced amphiphiles showed greater surface activity characteristics through surface tension and conductivity measurements and reduced the water surface tension to 38.86 mN m^{-1}.

Cardanol was modified to produce Gemini surfactant based on phenoxy ring containing long-chain imidazolium and pyridinium amphiphiles which can be used as gene delivery agent. It is well established that the chemical structure of surfactants plays a major role to produce well-controlled size, shape and dispersed nanomaterials used in advanced polymer nanocomposites preparation. The bio-based surfactants based on cardanol have been used to exfoliate montmorillonite nanomaterials in epoxy. Sulfonated cardanol can be functionalized to form phenolic ethers, which are used as polymer additives or in nanofibers. Polyaniline–cardanol sulfonate was used to design a nanostructured electromagnetic iron–clay composite as sensor for the detection of ascorbic acid. Moreover, cardanol glucosides are used to prepare efficient nanotubes. Cardanol also attracted more attention in the production of silver, alumna, silica and magnetite nanomaterials having superior physicochemical characteristics and advanced applications.

4.3 Polymers and Resins

The chemical structure of cardanol represented in Scheme 4.1 shows great reactivity toward chemical reagents due to the presence of phenolic groups that are ortho and para directing groups for electrophilic aromatic substitution. Moreover, the presence of unsaturated alkyl groups increased the reactivity of cardanol to addition reactions to produce new valuable polymeric materials and resins having special characteristics as biopolymers. Figure 4.4 shows the chemical reactions based on phenolic nature of cardanol that is responsible for production of different chemicals, polymers and resins [44, 104, 145]. The aim of this section is hence to provide an overview of the field by highlighting and discussing the state-of-the-art, as well as selected perspectives of thermosetting materials derived not only from plant oils, but also from other renewable resources.

Cardanol can be polymerized directly either with using acids such as HCl, H_2SO_4, HNO_3 and H_3PO_4 at temperature of 150–190 °C [54] or with other catalysts such as $TiCl_4$, $SnC1_4$, $A1C1_3$ or $POC1_3$ [33] to obtain polymers that find several applications. Different metals, their oxides, hydroxides or carbonates, such as Cu, Al, Co, Ni, Pb, Mn, Sb, Zn and Fe, have been used to polymerize cardanol at temperatures ranging from 120 to 150 °C [52, 53].

Different reaction modifications can be carried out on phenolic hydroxyl, aromatic ring and unsaturation(s) in the alkenyl side chain to obtain advanced polymer as described in the forthcoming section.
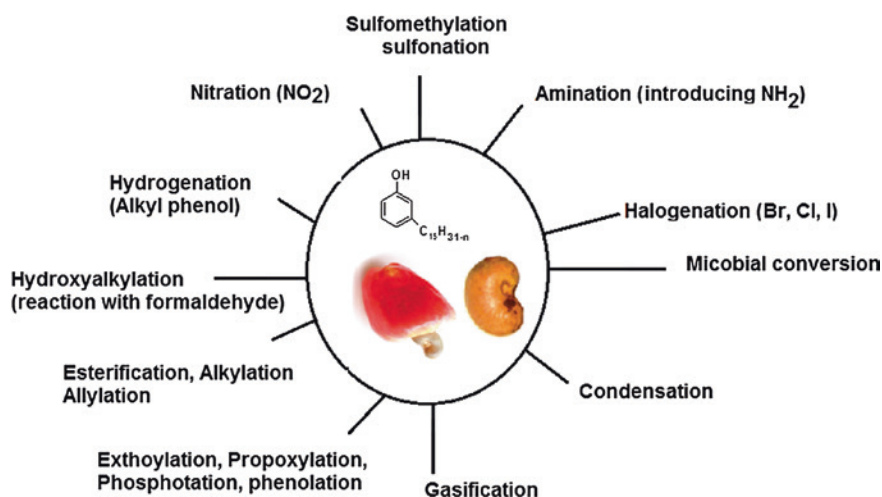

Fig. 4.4   Chemical reactions of cardanol

4.3.1 Thermosetting Cardanol Resins

There is of course increasing awareness of the need for green chemistry in chemical industries. Cardanol phenol attracted great attention to produce thermosetting materials having advanced properties and applications [104]. These materials were cured by light, heat or chemical initiators. The thermoset materials produced from cardanol such as phenolic, epoxy, polyester and polyurethane resins have merits over petroleum-based thermosetting materials as a novel and appropriate sustainable feedstock, a cost–performance basis with high eco-friendliness values [73, 119]. In previous works, rosin as natural product based on rosin was used to prepare advanced epoxy resins, curing agent, vinyl ester resins, polyester, alkyd and polyurethane [11, 14–16, 18].

Scheme 4.14 represents the use of cardanol as renewable resources in the design of thermosetting materials, such as epoxy, phenolic and vinyl ester resins. The properties of cardanol were increased by converting phenol cardanol to polyphenols using formaldehyde, paraformaldehyde and trioxane in the presence of sodium hydroxide or triethylamine as a catalyst to link phenol with methylene bridge or methyloyl groups [20, 56]. It was found that [57] when ammonia was used as the catalyst in the cardanol–formaldehyde reaction the products were solid, but they were viscous liquids when sodium hydroxide, sulfuric acid or oxalic acid was used. Moreover, the condensation reactions between cardanol and hexamine, which is used as a source of formaldehyde and ammonia, are generally carried out at higher temperatures [2].
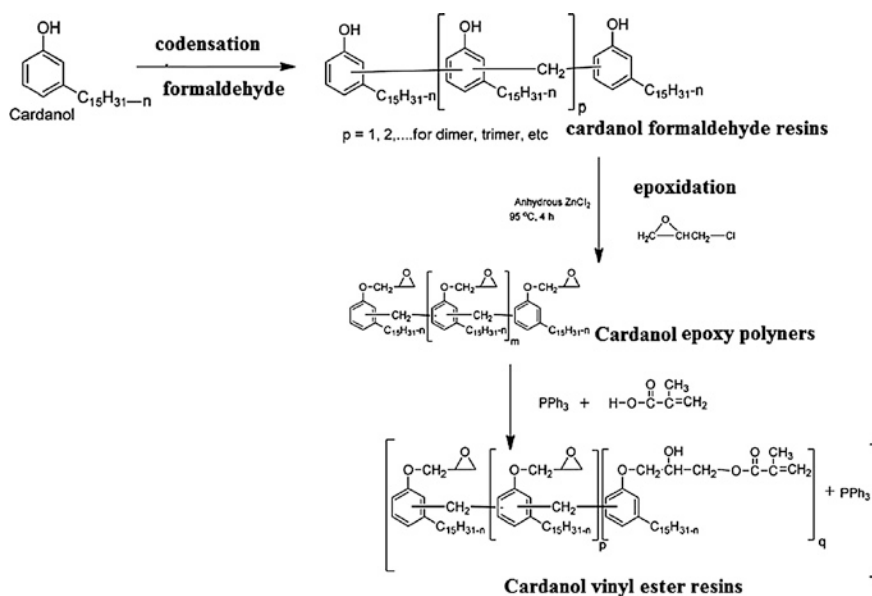
Scheme 4.14 Preparation of different cardanol epoxy and vinyl ester resins

It was reported that cardanol and its polymers have interesting structural features for chemical modification and polymerization into specialty polymers. Cardanol–formaldehyde resins have superior properties when compared to conventional phenolic resins, such as flexibility (due to the internal plasticization effect of the long chain), that improved their processability. The presence of long alkyl groups increased the weathering resistance of cardanol polymers because it acts as water-repellent group [146]. In addition, cardanol polymers have useful characteristics such as heat and electrical resistance, antimicrobial properties and insect resistance. However, in some cases natural fibers have been added, such as ramie, flax, and hemp fibers were added to cardanol–formaldehyde resins to resist the steric hindrance and reduced intermolecular interactions imparted by the C15 side chain for fabric structural applications (Maffezzoli et al. 2004). It was also reported that epoxy resin based on diglycidyl ether of bisphenol A was added with the cardanol–formaldehyde resins in order to reduce the amount of water released during the process and to reduce the porosity of cardanol–formaldehyde resins (Maffezzoli et al. 2004).

Recently, a novel benzoxazine prepolymer derived from cardanol was used to prepare phenolic resins in the presence of formaldehyde and an amine as represented in Scheme 4.15. A faster polymerization of cardanol-based benzoxazine monomer can be carried out at ambient temperature in the presence of cationic catalysts such as PCl$_5$. The benzoxazine-based family of phenolics showed interesting characteristics as advanced composites such as good thermal properties and flame retardancy originated from phenolics, together with the mechanical performances and molecular design flexibility [31].
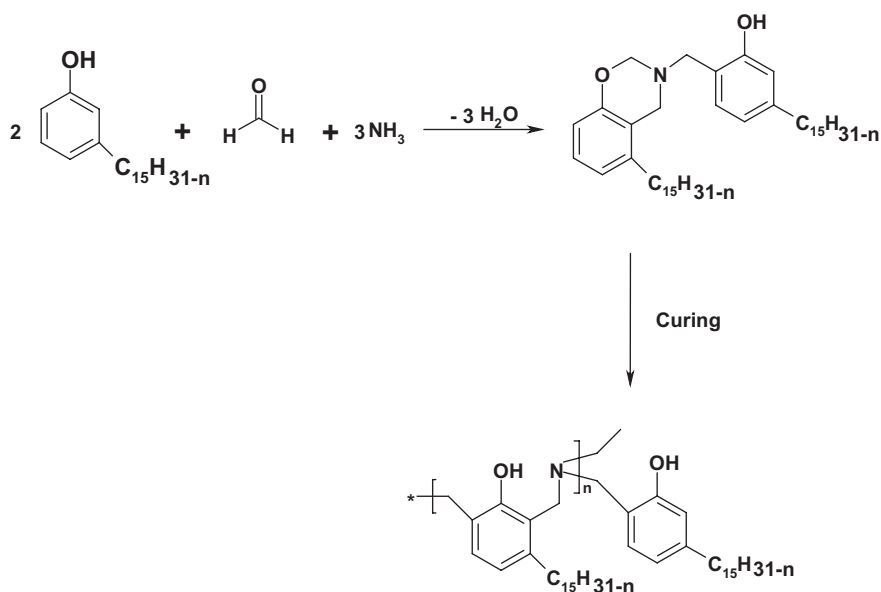
Scheme 4.15 Preparation of cardanol phenolic resins

Epoxy thermosets are the most common polymers that were produced more than 3 million tones and have different applications in coating, adhesives and composites. Epoxy resins are most commonly produced from derivatives of petroleum. More recently, bio-based feedstocks were used with great attention to produce epoxy from plastic waste and natural products as cheap sources [11–14, 16–18]. The phenolic hydroxyl group of cardanol or unsaturated double bonds on the C15 alkyl side chain can be reacted either with epichlorohydrin (ECH) or with epoxidized, respectively, to produce epoxy resins. Moreover, production of polyphenol from cardanol used to prepare epoxy resins as represented in Scheme 4.14. Cardanol was used in partial or total substitution of phenol in thermoset resins such as novolac resins [32, 59], vinyl esters [125, 126] and also in epoxy resins modification [139]. The literature reports a number of workers [35, 36, 63] who have reported the synthesis of various types of epoxy compounds based on CNSL and its derivatives. Hydroxyl group of cardanol was reacted with ECH to produce epoxy using $ZnCl_2$ as catalyst in basic condition at temperature 95 °C [144]. This product is commercially available at Cardolite Corporation. The Cardolite (commercial epoxy based on cardanol) resins have been modified with bisphenol A to obtain adhesives having greater impact strength and shear resistance [44]. The curing agents of epoxy resins were also prepared from cardanol such as polyamines (Lubi and Thachil 2000) and self-cured epoxy based on cardanol [117] to apply in surface coatings. The double bonds of alkyl group attached to cardanol phenyl group can be epoxidized by reacting with chloroperbenzoic acid, perbenzoic acid and performic acid to produce polyepoxy cardanol [48, 71, 95, 128]. The epoxidation of these double bonds could also be performed with enzymes such as Candida antarctica lipase, with acetic acid and hydrogen peroxide, in toluene (yield 95 %) [76]. The chemical structure of epoxidized cardanol is represented in Fig. 4.5.

Modified epoxy resins based on cardanol (Fig. 4.6) were synthesized in two steps by phenolation of aliphatic chain ($C_{15}H_{31}$), followed by reaction of phenol hydroxyl groups with epichlorohydrin [60]. The modified epoxy based on cardanol showed good performances after curing with polyamines when compared to diglycidyl ether based on bisphenol A [60].

Vinyl ester resins can be prepared as illustrated in Scheme 4.14. The functionalization of cardanol with acrylic/methacrylic monomer can be obtained to produce an eco-friendly vinyl ester resin [1, 45, 77, 93]. The esterification of epoxy resin of cardanol–formaldehyde resins with methacrylic or acrylic acid can be obtained at temperature ranging from 80 to 100 °C in the presence of triphenylphosphine as a catalyst [5, 123–126]. The produced cardanol vinyl ester resin can be cured with styrene as monomer and benzoyl peroxide as initiator at 120 °C at faster rate than the classical poly(vinyl ester) resin with high thermal stability up to 285 °C [125, 126].

Polyurethane (PU) polymers play an important role for their diverse applications in coatings, adhesives, sealants, elastomers and plastics because they exhibit many desirable characteristics. Cardanol derivatives have been explored in polyurethanes for different applications [24, 25, 27, 47, 74, 90]. It is well established that PUs were produced from reactions between polyols and polyisocynates. In

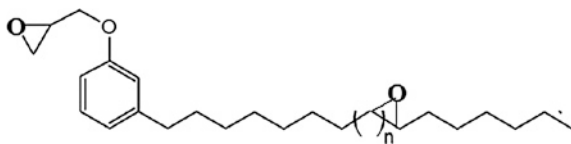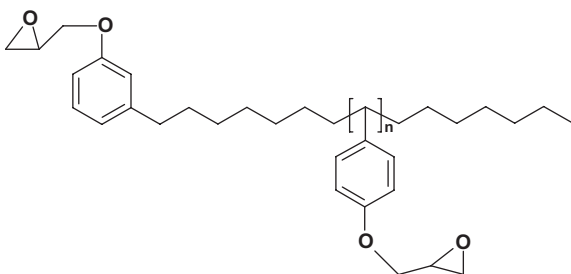**Fig. 4.5** Epoxidized cardanol



Fig. 4.6 Cardanol diglycidyl ether

this respect, different polyols can be produced from cardanol phenols as represented in Scheme 4.16.

The PU produced from cardanol polyol derivatives has better thermal, mechanical and chemical characteristics [24, 25, 90, 91, 112, 113, 130]. Low-viscosity polyols with a range of hydroxyl values have been prepared [127]. Scheme 4.16 shows the production of trihydroxy cardanol from reaction of cardanol with ECH and diethanol amine. For synthesizing polyols, the authors have prepared first monoglycidyl ether of cardanol, followed by ring opening to prepare the diol or reaction with diethanol amine to give a triol (Scheme 4.16). The cardanol-based polyols have better hydrolytic stability compared to the triglyceride oil-based polyols. The cardanol-based PU exhibited excellent thermal stability. The second route to produce cardanol-based triol was based on the reaction of the glycerol monochlorohydrin with cardanol [127].

Mannich [61, 96] polyols cardanol can be produced from its reaction with formaldehyde and aliphatic amines (ethylene diamine, diethylene triamine and triethylenetetramine) (Scheme 4.17). These cardanol-based Mannich polyols produced rigid polyurethane foams that have excellent good physico-mechanical and fireproofing properties and applied for coating of different substrates [3].

Melamine cardanol-derived Mannich base polyol (MCMP) can also be prepared (Scheme 4.18) via a two-step process. First, cardanol was allowed to react with paraformaldehyde melamine and diethanolamine to yield mixed Mannich bases which were subsequently propoxylated to give the MCMP [147]. Polyisocyanate reacted with MCMP to produce rigid PU. It was demonstrated that the melamine incorporated into the MCMP molecular structure increased the thermal stability and the flame retardancy of the PU.

Cardanol (Fig. 4.1) contains alkyl groups that have different degrees of unsaturation, namely monoene, diene and triene. However, phenol reacted with cardanol via Friedel–Crafts alkylation (Scheme 4.19) to produce resole-type prepolymer after reaction with formaldehyde under basic conditions [55].
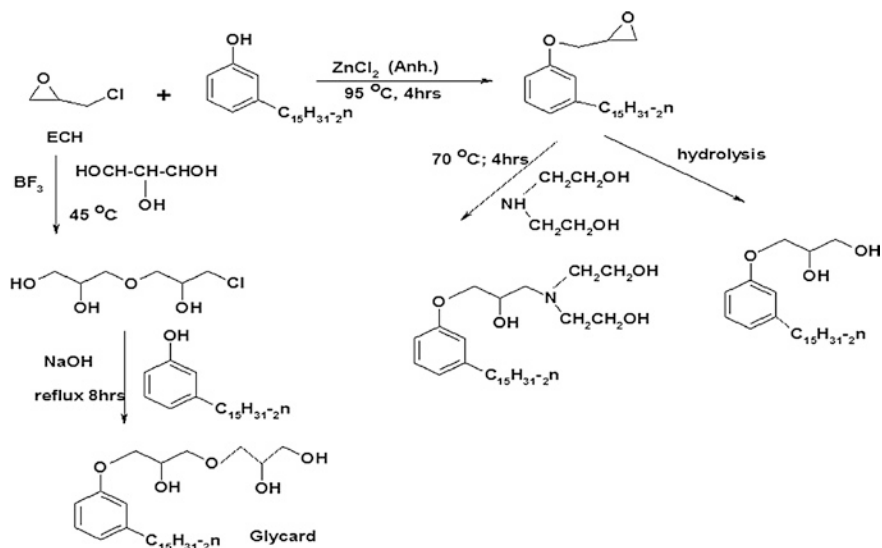
Scheme 4.16 Preparation of different cardanol polyols
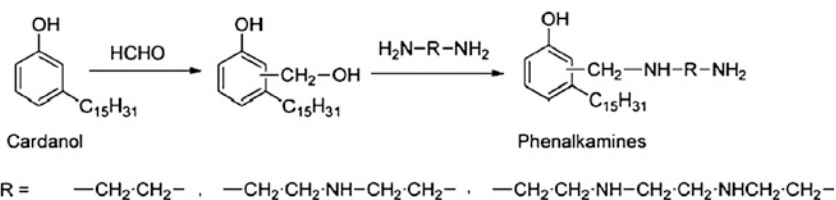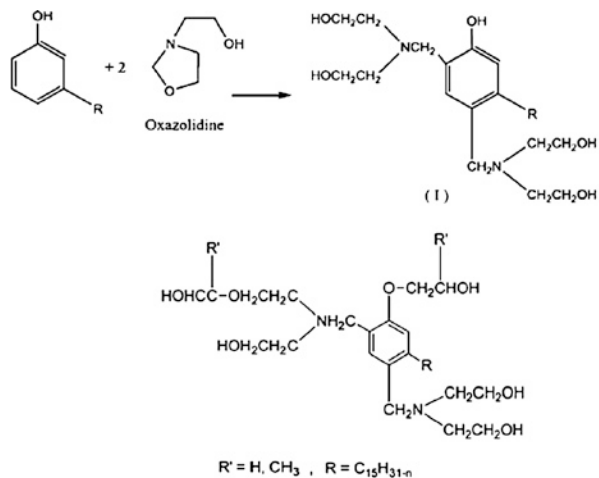
**Scheme 4.17** Preparation of cardanol-based Mannich polyols
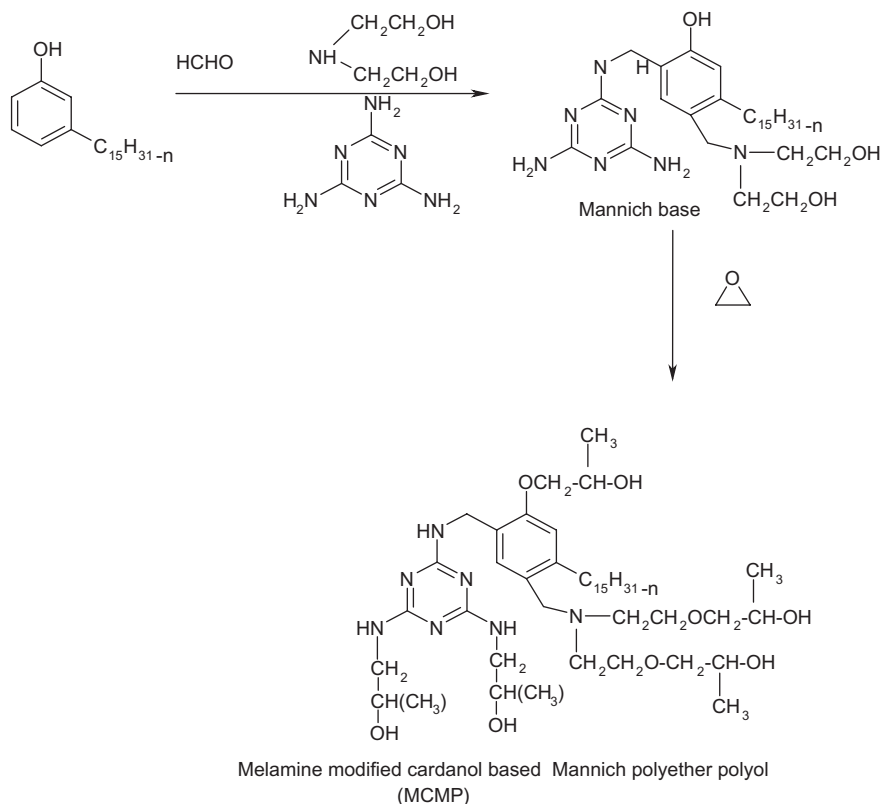
Scheme 4.18 Preparation of melamine cardanol-derived Mannich base polyol

These prepolymers were used to synthesize phenolic foams [65]. The phenolic foams based on cardanol increased the flexural strength as compared to pure phenolic foams because the incorporation of cardanol does improve the toughness of phenolic foams.

Synthesis of new polyphenols with attractive properties from natural phenolic compounds such as cardanol by oxidative polymerization using enzymes has been reviewed by Uyama et al. [140, 141]. Enzymic homo- and copolymerization of alkylphenols derived from cashew nutshell gave homopolymers that are soluble in organic solvents, but the copolymers were cross-linked, with negligible solubility [4]. The enzymic polymerization was found to be dependent on the solvent mixture used. Polymerization in a dioxane–water solvent mixture resulted in spherical particles in the case of homopolymerization, while structures without distinctive morphologies were obtained in the case of copolymerization.

A unique polyol (Scheme 4.20) has been designed and synthesized by condensation of cardanol with epoxy resin using ethyltriphenylphosphonium bromide
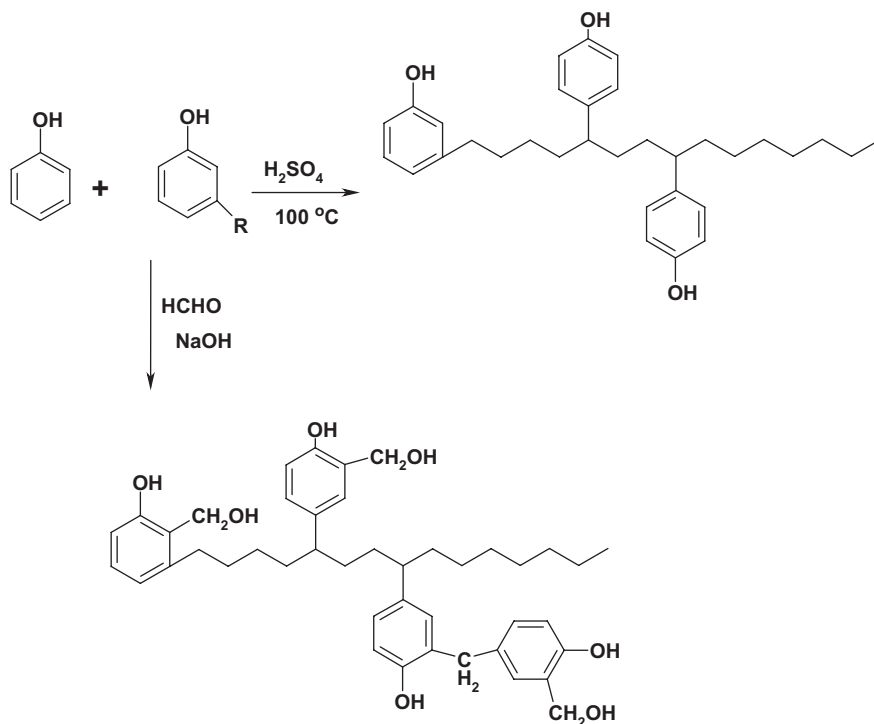
Scheme 4.19 Cardanol polyphenol polyols

(ETPPB) as catalyst and subsequently been used as polyol component (soft segment) in synthesis of polyurethane dispersion. The clear coating compositions prepared from these PUs, with and without drier (catalyst) additive, have been applied on metal substrate and cured under ambient conditions [94].

Rekha and Asha [105, 106] reported the synthesis of UV-curable telechelic urethane–methacrylate cross-linkers based on cardanol. They demonstrated that the presence of both the hydrogen bonding units and bulky hydrophobic terminal units was required for the formation of three-dimensional honeycomb patterns or vesicles from a solvent mixture of tetrahydrofuran (THF) and water or THF alone [37]. Cardanol and the saturated analogue, viz. 3-pentadecylphenol, were incorporated as pendant units to the side chain urethane–methacrylate through hydrogen bondable urethane linkage (Scheme 4.21), and the authors observed various morphologies such as tubes, spheres and honeycomb patterns in dropcast films [37].
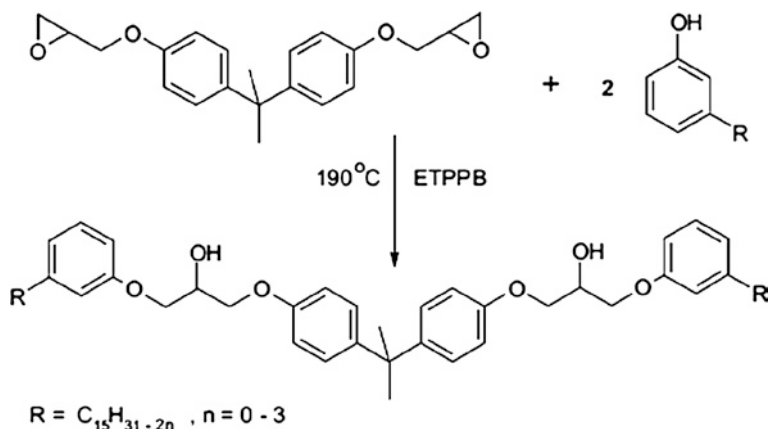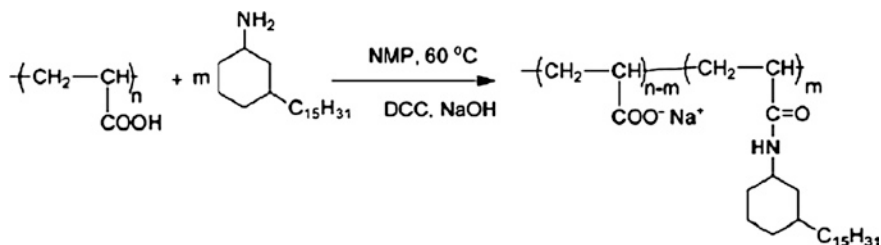
Scheme 4.20 Preparation of cardanol polyols soft segments
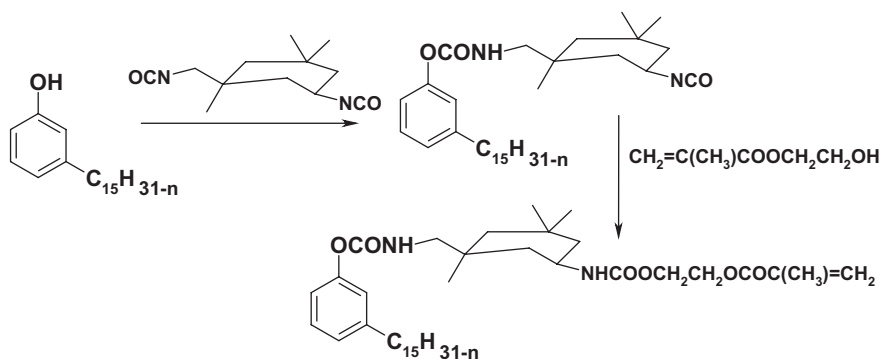
Scheme 4.21 Preparation of cardanol polyurethane methacrylate

4.3.2 Production of Biopolymers

There is of course increasing awareness of the need for green chemistry in chemical industries. For example, high-content cardanol, by-product derived from the cashew industry, has recently been used to produce bio-composites [31]. The bio-composites can be produced either by introducing of biodegradable groups to conventional polymers or by producing composites based on naturally occurred polymers based on renewable materials. Natural polymers are produced from feedstocks derived from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources. To provide added value to biodegradable polymers, some advanced technologies have been applied. They include active packaging technology and natural fiber reinforcements. Nanoclay has been used with biodegradable polymers, especially with starch and aliphatic polyesters

Scheme 4.22 Preparation of hydrogenated cardanol poly(acrylic acid)

to prepare nano-biocomposites. It is well reported that the conventional polymers based on petroleum resources are resistant to degradation [26, 89]. The addition of biodegradable polymeric materials has encouraged the development of such materials from readily available, renewable inexpensive natural sources [41–43, 75, 78, 114]. These renewable resources hold beneficial characteristics for being non-toxic, biodegradable and environmentally friendly.

There are different methods based on random and block copolymerization or grafting used to improve both the biodegradation rate and the mechanical properties of the final products of the biodegradable polymers. Shedge et al. [115] incorporated 3-pentadecylcyclohexylamine (3-PDCA) derived from hydrogenated cardanol onto poly(acrylic acid) to prepare a series of hydrophobically modified poly(acrylic acid) (Scheme 4.22).

Kadam et al. [70] reported the preparation method of 1-isocyanato-3-pentadecyl-cyclohexane (1-IPDC) from 3-pentadecylcyclohexylamine (3-PDCA) (Scheme 4.21). It was end-capped with poly(ethylene oxide) (PEO) of different molecular weights to improve the self-assembling properties of these associating polymers.

Hourdet et al. [58] reported synthesis of hydrophobically modified polyacryla-mides, used in petroleum applications, containing random distribution of hydro-phobes and studied their thermodynamic properties. These copolymers were obtained by free radical solution copolymerization of trimethylsilylacrylamide with a hydrophobic comonomer, namely 3-pentadecylcyclohexylacrylamide [3-PDCAM] (Scheme 4.23).

Flexible thermoset polymer can be produced from cardanyl acrylate or 3-pen-tadecenyl phenyl acrylate, obtained by the base-catalyzed reaction of cardanol and acryloyl chloride (Scheme 4.24) [69, 92, 118].

Preparation of liquid crystal based on renewable cardanol moieties was studied by modification of cardanol with methacrylate groups followed by radical polymerization as described in Scheme 4.25 [85]. The poly(methyl meth-acrylate) derivatives containing the cardanol moieties were prepared using 2-hydroxy-3-cardanylpropyl methacrylate (HCPM) and methacrylate (MMA) as monomers. These polymer films exhibited good optical transparency in the vis-ible light region. The LC cells made from the polymer having 100 mol% of
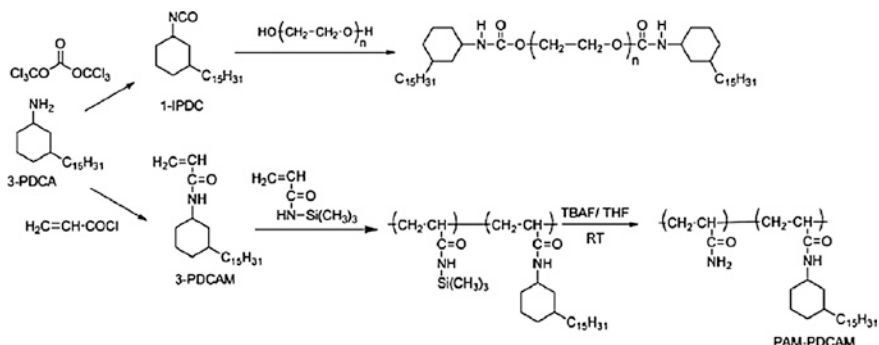
Scheme 4.23 Preparation of hydrophobically modified polycardanol–co-polyacrylamides
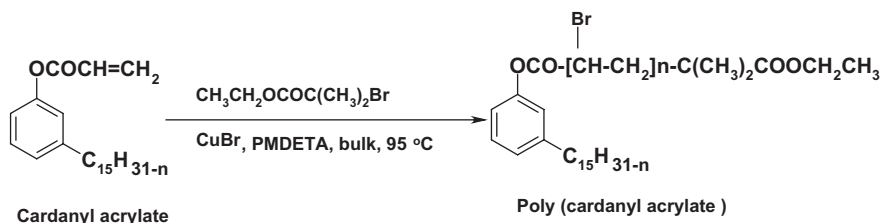

Scheme 4.24 Preparation of flexible polymer of 3-pentadecenyl phenyl acrylate

2-hydroxy-3-cardanylpropyl methacrylate (HCP100) as the alignment layer showed vertical LC alignment. The thermal stability of the LC cell made from UV-irradiated modified cardanol film was enhanced due to the formation of the cross-linked structure of the unsaturated hydrocarbon in the cardanol group.

Cardanol has been utilized as a starting material for the synthesis of bifunctional monomers that can be used to produce biopolymers using step growth method (Fig. 4.7) [19, 23, 46, 62, 72, 82–84, 86–88, 99, 107–110, 143].

These bifunctional monomers were utilized for the synthesis of a variety of high-performance polymers such as aromatic polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s, polyesters, polyhydrazides, polyoxadiazoles having higher thermal and mechanical properties. The results confirmed that the presence of the C15 alkyl chain along the polymer backbone disrupted the packing of polymer chains, as well as provided the additional "handle" for interaction with solvents, thereby enhancing the solubility of these polymers when compared to control polymers, i.e., polymers without the C15 alkyl chain. The polymers containing pendent pentadecyl chains indicated the depression in glass transition temperature (T_g) which could be attributed to the presence of pentadecyl chains, which decreases the intermolecular interactions and increases the segmental motion in the polymer backbone. A large window between glass transition temperatures and initial decomposition temperatures of
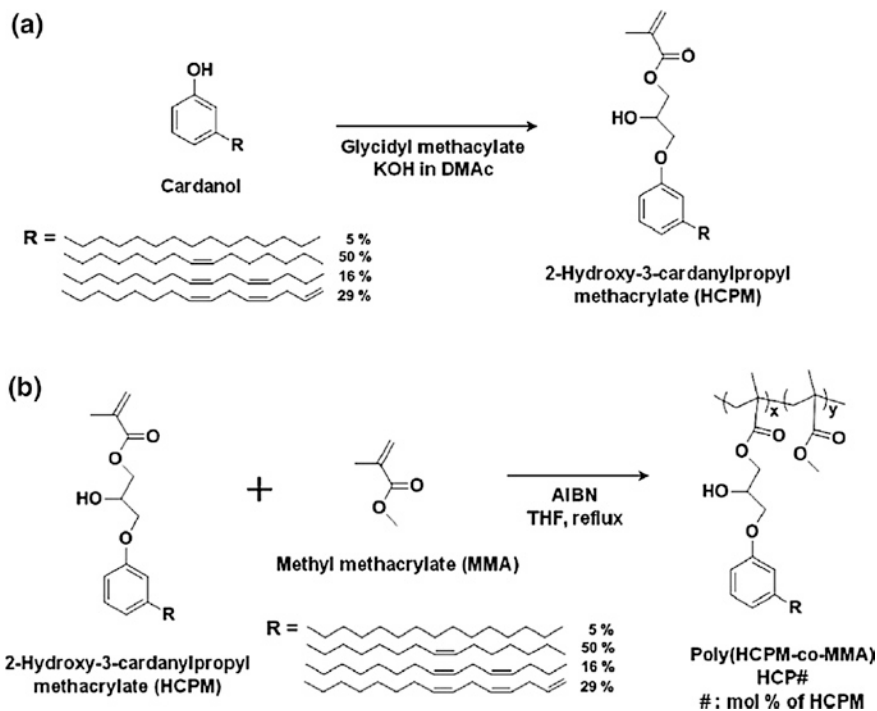
Scheme 4.25 Preparation of poly(methyl methacrylate) derivatives containing the cardanol moieties

the polymers containing pendent pentadecyl chains was observed, which gives an opportunity for these polymers to be melt-processed or compression-molded.

The application of amphiphilic materials based on cardanol used for preparation of nanomaterials and exfoliation of clay has an important role in the preparation of nanocomposites with superior characteristics. The clay minerals were completely exfoliated after organic modification with cardanol, incorporating reactive groups: $-N(CH_3)_2$, \NH$_2$ or two NH_2 functional groups as illustrated in Scheme 4.26 [100]. The exfoliated organic modified clay was used to prepare epoxy nanocomposites.

It was also reported that cardanol derivatives can be used as capping agent for iron oxide nanomaterials to act as oil spill collectors [142]. It was found that cardanol–furfuraldehyde/maghemite composites, represented in Scheme 4.27, used to produce magnetic green resins able to collect petroleum spilled on the water due to their lower density allowing their easy flotation and magnetic behaviors.

The cardanol and furfural resins were polymerized through acid catalysis (Scheme 4.27) to produce resins that act as capping agent for magnetic materials and have ability to easily disperse in crude oil.

Fig. 4.7 Bifunctional bio-cardanol monomers

Scheme 4.26 Preparation of cardanol alkyl amines
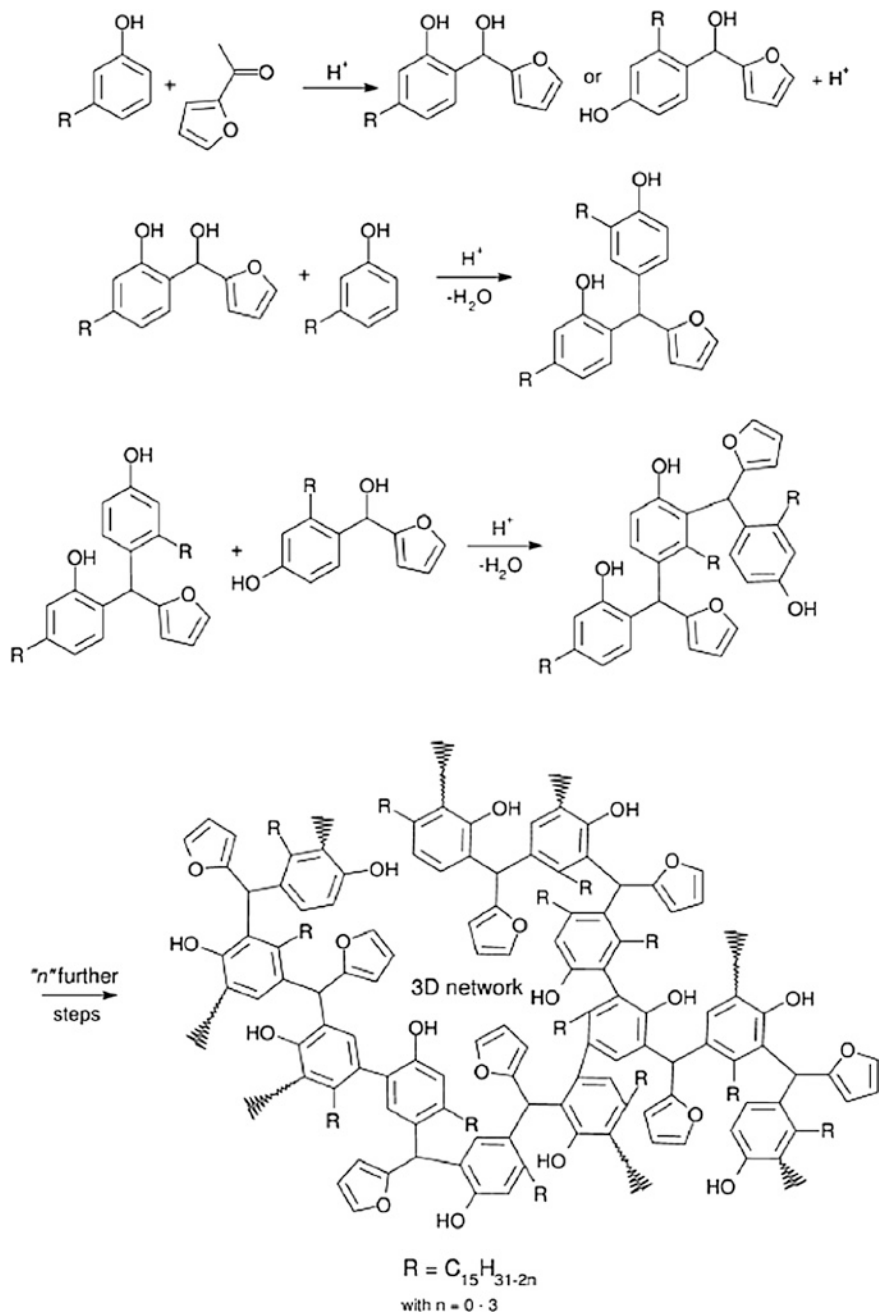
Scheme 4.27 Preparation of cardanol–furfuraldehyde composites

4.4 Conclusions and Outlook

The cardanol attracted great attention to produce advanced chemicals based on different routes of chemical modification of the alkyl side chain in the *meta* position, aromatic moieties and phenol groups, which allow the formation of products with a potential industrial value. The cheap price and abundantly available (world availability: 450,000 metric tons per year) versatile industrial raw material of great promise for the replacement of petrochemicals. Considerable attention has been devoted to transformations of the cardanol to different types of surfactants. Cardanol surfactants have outstanding antimicrobial properties which can assist mankind fight parasites and harmful microorganisms in the agricultural and medicinal fields. It can be a valuable alternative to many of the troublesome chemical agents in use today. The development of surfactants to reactive surfactants based on assist to develop new materials with superior properties and added values such as conducting nanomaterials and high-performance polymers to address the issue of processability by taking advantage of the flexible pentadecyl chain. The polymeric materials based on cardanol such as epoxy resins, phenalkamines, friction materials, brake lining agents have already found place in the market (M/s Cardolite).

In spite of the massive literature accumulated on the applications of cardanol, many areas remain which have yet to utilize this attractive raw material. The use of cardanol in the field of engineering polymers has not been widely reported. It could be a promising candidate for making bio-based composites. Moreover, cardanol is a valuable raw material for generating a variety of soft nanomaterials such as nanotubes, nanofibers, gels and surfactants. Novel bio-based surfactants, glycolipids and polymers can be derived from cardanol, and their subsequent self-assembly into functional soft materials. It is expected from these studies that new soft materials can be produced from using cardanol surfactants. Therefore, the prepared surfactants contribute to the environment encouraging nobler uses to some of the available renewable resources. A number of water-based resins can be synthesized with cardanol surfactants to apply in the coating industry due to a number of advantages they possess, including eco-friendly technology, room temperature synthesis, chemical inertness, high oxidation and abrasion resistance, excellent thermal stability, very low health hazard. The commercialization of all these technologies, however, will require further research and development for cost-effective solutions.

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