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Polyols from Cashew Nutshell Liquid (CNSL), corner-stone building blocks for cutting edge biobased additives and polymers

Emilie Rojtman[1,2]; Maxinne Denis[1]; Camille Sirvent[1]; Vincent Lapinte[2]; Sylvain Caillol[2*]; Benoit Briou[1*]

[1] Orpia Innovation, CNRS, Bâtiment Chimie Balard, 1919 Route de Mende, 34000 Montpellier, France; b.briou@orpiainnovation.com (B.B.), m.denis@orpiainnovation.com (M.D.)
[2] ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France; vincent.lapinte@umontpellier.fr (V.L.); sylvain.caillol@enscm.fr (S.C.)

Abstract:

Polyols are versatile molecules present in many polymers' material belonging to and often essential to our daily life. A major part of biobased polyol is coming from sugar or vegetable oil and is in direct competition with food industry. CNSL is a promising non-edible renewable resource, directly extracted from the shell off the cashew nut. The interesting chemical structure of CNSL and its derivatives (cardanol, cardol) lead to the synthesis of original polyols with hydrophobic and internal plasticizing properties. Useful for the development of additive, such as surfactant, or soft polymers, CNSL polyols are progressively building its own seat at the polymer industry.

Thus, this review focuses on CNSL as building block for various polyols. The many different chemical pathways leading to CNSL-based polyols are going to be reviewed and criticized. A certain focus will also be done about the use of these CNSL-based polyols as surfactants and polymer precursors and the contribution of their specific chemical structure (aromatic ring, long unsaturated alkyl chain) on the properties of the resulting polyesters or polyurethanes.

I) Introduction

Since their rise and democratization in the last century, polymer materials, commonly known as "plastic", have become ubiquitous and almost indispensable in our daily lives. Versatile, lightweight and resistant, practical, and economically affordable, polymers can be found in the automotive, construction, packaging, decoration or medical fields. The increase in the manufacturing and use of these synthetic materials coincided closely with the exploitation of petroleum. For more than 50 years, the chemical industry has been drawing its building blocks from petrochemicals (2). However, access to this fossil resource is becoming increasingly limited and restrictive. Easily accessible stocks are being depleted, increasing the costs of extracting petroleum materials from deeper in the ground or in geographical areas with harsh climatic phenomena (3). Access to this resource is becoming increasingly strategic from a geopolitical and economic point of view. In addition, health and environmental issues about pollution are more and more under scope (4). Recently, the Covid crisis and the international situation are pushing countries to take back control by increasing the innovation and developing the resources and knowledge present on their territory (5, 6). In addition, in the background, the climate crisis weighs and the growing interest in finding sustainable and eco-compatible alternatives for societies that are still growing in population and economy (7, 8).

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Researchers and industries are now increasingly turning to the development of the abundant and renewable biomass that it had been left aside in the last century, while coming up against the problems of production areas reserved for human and animal food and the preservation of forest areas. To respond to this giant puzzle, several bioresources are being considered, such as vegetable oils, wood, sugars, and agricultural waste. A new chemistry has also emerged since the 90s with the establishment of the definition and principles of a more sustainable chemistry, the Green Chemistry, by Anastas and Warner **(9)**.

Among the many polymer precursors, polyols are of particular interest since they can be found in a multitude of applications. If we put aside the use of polyols in the food industry as ingredient or food additive **(10, 11)** , they are also used in the synthesis of highly convenient polymers such as polyurethanes **(12, 13)** or polyesters **(14, 15)**. These types of polymers are among the most produced after polyolefins and represent a significant and growing challenge. Easily functionalized, these molecules are also used in the synthesis of precursors of esters in various fields of application such as non-ionic surfactants. In the additive sector, the demand for bio-based and non-toxic is high. Additives, not bound to polymers that eventually migrate, or surfactants, used directly in the presence of water, concentrates a health and ecological concern **(16-19)**. In view of the fields in which they are involved and the current environmental, economic, and climatic context, a particular interest is focused on the synthesis and application of bio-based polyols (Figure 1a).

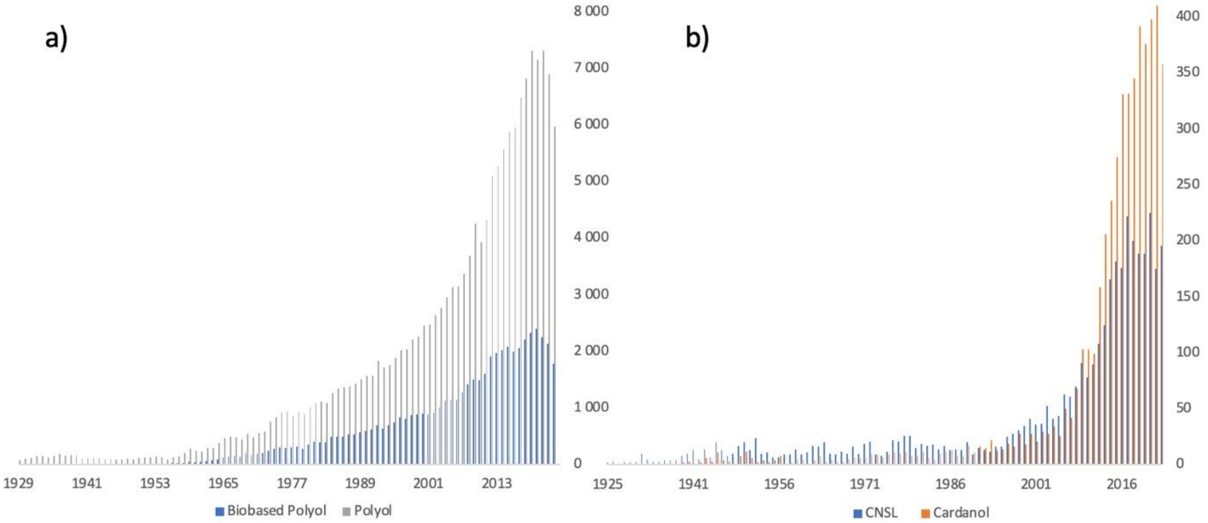

Figure 1: Graph showing the number of articles concerning polyols/biobased polyols (a) and CNSL/cardanol (b) from the 20s to the present day (source sci-finder)

Depending on their application, the sourcing of these bio-based polyols varies and seems to specialize. For the synthesis of non-ionic surfactants, sugars, and some of their derivatives **(20-22)**, vegetable oils **(23)** and even natural phenols such as cardanol **(23, 24)** are used. Finally, for monomers and polymers, they are generally linear derivatives from vegetable oils (25-27). However, the extraction and the production of such molecules (sugar, vegetable oil) induce direct conflict with the harvests reserved to produce biofuel, those reserved for direct animal and human food or for food additives such as erythritol **(28)** and sometimes glycerol **(29)**. This competition tends to accelerate the phenomena of deforestation**(30)** or environmental pollution with the use of dangerous fertilizers or pesticides, making the effort counterproductive in relation to the initial objectives sought.

The chemical structure of a polyol is of great importance regarding its use for a particular field of application. Whether it is sugar or vegetable oil derivatives, the extracted chemical molecules generally lack an aromatic ring which is then often provided by co-monomers, isocyanate for polyurethanes or carboxylic acid for polyesters. Generally, these aromatic rings provide structural rigidity and a gain in thermal stability to the resulting polymer structures. Natural phenols, such as vanillin or eugenol, can serve as platform of molecules for the synthesis of polyols carrying aromatic ring **(31-36)**. In addition, among these phenols, cashew nutshell oil (CNSL) derivatives have seen their interest grow very rapidly over the last 30 years for the synthesis of polymers or additives (Figure 1b). Resulting from the recovery of a waste product from the already existing agricultural production of cashew nuts, these natural lipid phenols are relevant candidates for the synthesis of tomorrow's bio-based polyols.

To our knowledge, CNSL derivatives for the synthesis of polyols are regularly present in specialized reviews about bio-based polyols **(37-39)** but the part devoted to it remains small in view of the many developments that these derivatives have demonstrated for some time. None of them dwells on the wide variety of polyol structures that can be obtained from CNSL derivatives, molecules that are nevertheless intensively sought-after, and, when they are mentioned, neglects the other components of CNSL to the detriment of cardanol. In this review, we propose to make a complete overview of the synthesis of polyol precursors based on CNSL derivatives, to map and criticize these various synthesis methods and then to demonstrate the interest of the use of such molecules and their impact on the properties of the materials obtained from it in the field of polymers and surfactants as never has been done before. Finally, in conclusion, the authors will present their point of view on the possible future developments and perspectives regarding the development of polyols from the CNSL.

II) Synthesis of diols from cashew nutshell liquid (CNSL)

1) Cashew Nutshell Liquid, a versatile biobased raw material

Cashew Nutshell Liquid is a natural dark-brown viscous liquid extracted from the shell of the cashew nut which protects the fruit of the cashew tree (*Anacardium Occidentale*) **(40, 41)**. This tree is native to Brazil and the coastal areas of Asia and Africa**.** Nowadays it is cultivated in many tropical and subtropical regions. Moreover, cashew nutshell is considered as a waste of food industry inedible. The annual world production of cashew nut is estimated at around 4M T/year **(42)**, and the shell represents 55-65 % of the mass of the cashew nut **(43)**.
Natural CNSL mainly contains three components: anacardic acid, cardol and cardanol. The chemical structures of these compounds are presented in Figure 2. CNSL can be extracted from the shell by different methods such as roasting, hot-oil bath, steam processing at 270 °C, quick roasting at 300 °C, and solvent extraction method **(44-46)**. Thereby, depending on the extracting method used, the composition and the percentage of the CNSL constituents differs, as presented in Figure 2. The extraction of CNSL at high temperatures leads to the decarboxylation of anacardic acid converted into cardanol (above 140 °C) and releases CO_2 **(47, 48)**. CNSL from those extraction methods is called “technical CNSL” mainly composed of cardol (10-20 %) and cardanol (70-80 %). In another hand, CNSL extracted at low temperature

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preserves anacardic acid leading to “natural CNSL”. Thus, natural CNSL is mainly composed of anacardic acid (60-70 %), cardol (10-20 %) and cardanol (<10 %). Methyl cardol is also present in both two CNSLs at a percentage inferior to 3 % as well as some traces of urushiol. The different compounds of CNSL can be isolated by precipitation or distillation. The first one separates anacardic acid from cardanol and cardol whereas the distillation is effective in separating cardanol and cardol **(49, 50)**.

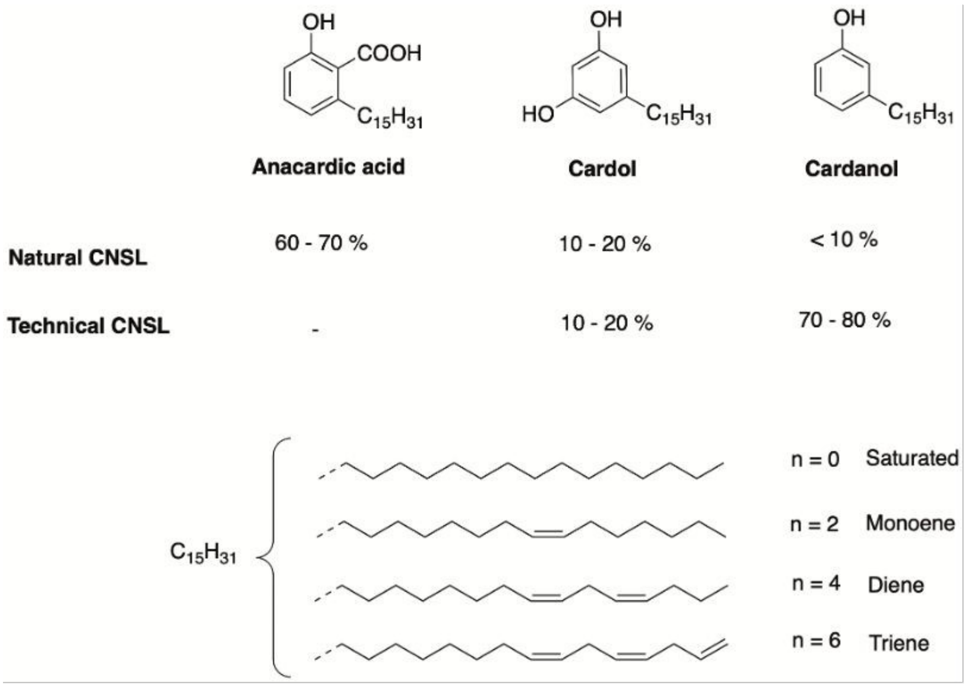

Figure 2: Chemical structures and compositions of the natural and technical CNSL’s compounds.

The aliphatic chain of each molecule of CNSL can be found in four different forms: saturated, monoene, diene or triene. These constituents also contain several reactive sites such as hydroxy functions, an aromatic ring, and unsaturated aliphatic chains, and a carboxylic acid function for the anacardic acid compound. CNSL behaves like vegetable oils thank to their unsaturated aliphatic chains. That is why they are present in oil form, whereas molecules with hydrogenated aliphatic chains are present in solid form.

Due to their various reactive functions, CNSL compounds are promising biobased phenol allowing functionalization through numerous reactions, as presented in Scheme 1 (40). Mannich **(51, 52)**, polycondensation **(53, 54)** and nitration reactions **(55, 56)** can occur on the aromatic ring. Then, the hydroxy functions could be functionalized through esterification **(57)**, etherification or nucleophilic substitution (58, 59). Moreover, epoxidation **(59, 60)**, hydrogenation **(61-63)**, carbonation **(64)**, thiol-ene **(65)** and Diels-Alder **(66)** reactions can also take place on the unsaturations of alkyl chain.

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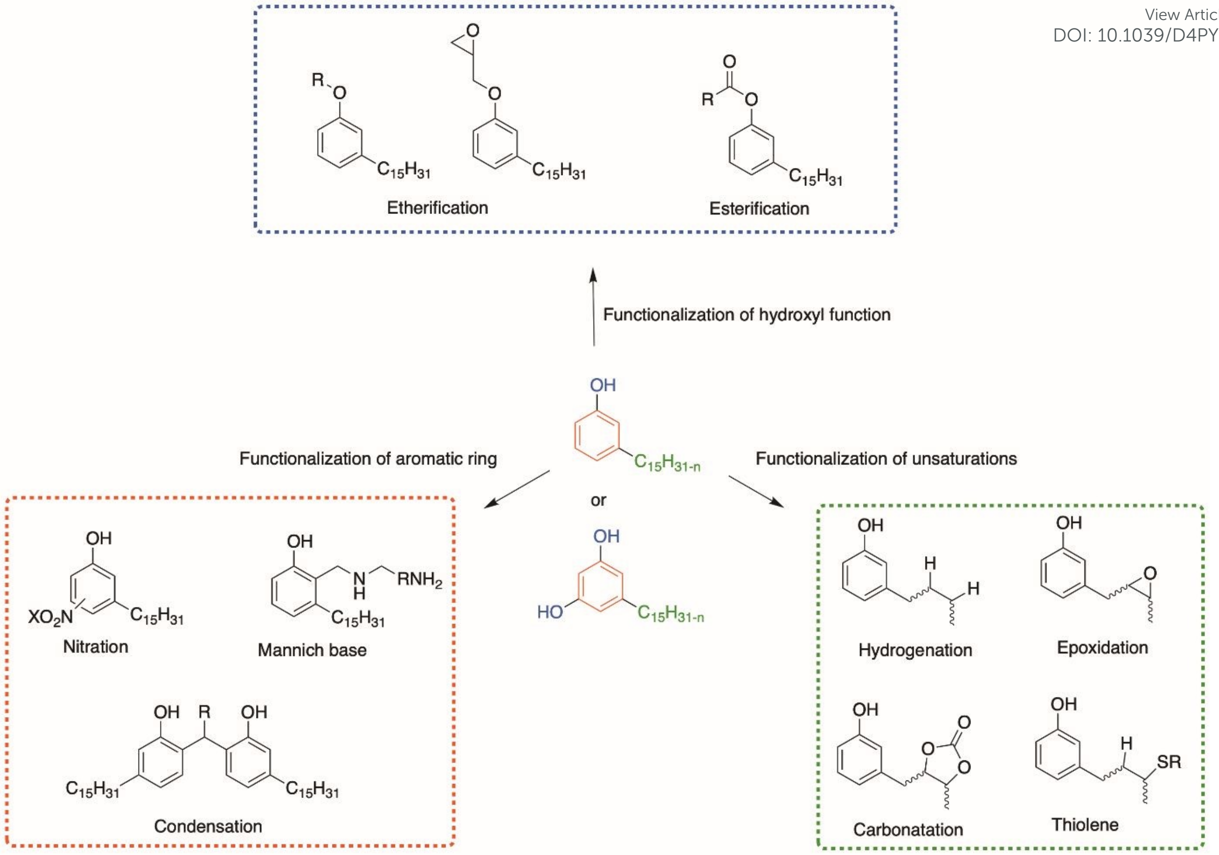

Scheme 1: Overview of different pathways to functionalize CNSL compounds.

This review focuses on the numerous pathways described in the literature to functionalize CNSL compounds into reactive polyols. The rigid aromatic ring and the flexible long alkyl chains differentiate CNSL molecules from other natural polyols such vanillin, eugenol, coumaric acid, or saccharides, tannins, glycerol, and vegetable oils (castor oil) (Figure 3), which exhibit either a rigid or a flexible structure. Thus, CNSL compounds can bring properties such plasticizing (60, 67) or lubricant effect (68, 69).

Due to all those reasons, CNSL compounds are very attractive as precursors of additives, surfactants or for the synthesis of novel bio-based polymers requiring the use of polyols such as polyurethanes, or polyesters.

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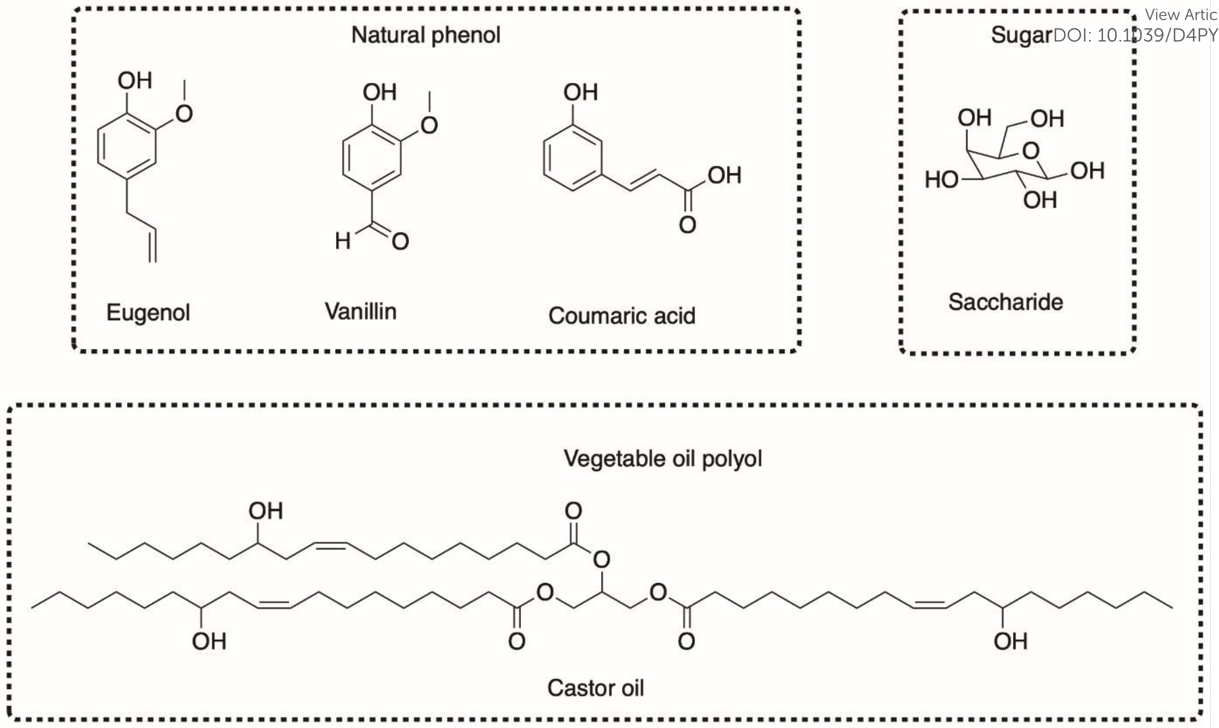

Figure 3: Structure of different bio-based polyols

2) Chemical pathways from CNSL to polyols

a. Modification of the phenolic hydroxy moiety

Compounds derived from CNSL can already be used as "alcohol", or "diol" for cardol, containing two hydroxy functions. These molecules were described for the synthesis of esters (60, 70), polyesters (71), or as blocking agents, for cardanol, that react with isocyanate functions to free the isocyanate moieties later during the synthesis of polyurethanes (72). However, this phenolic hydroxy function has a relatively low reactivity compared to a primary alcohol function. In addition, the resulting phenol esters are more sensitive to hydrolysis which can be an advantage for the design of biodegradable products but can also be a disadvantage if the desired properties are the durability and resistance of the resulted material.

This phenolic hydroxy can then be used to introduce by various methods, primary or secondary alcohol functions.

- Etherification of cardanol

Another way to provide an alcohol function is by reacting 3-chloropropane-1,2-diol (73) (Scheme 2). Cardanol, 3-monochloropropanediol (3-MCPD) and sodium hydroxide were mixed in stoichiometric conditions. A viscous liquid was obtained in 87 % yield. Nevertheless, this reaction used a toxic component, 3 MCPD, which is a chemical food contaminant and suspected of being carcinogenic to humans.

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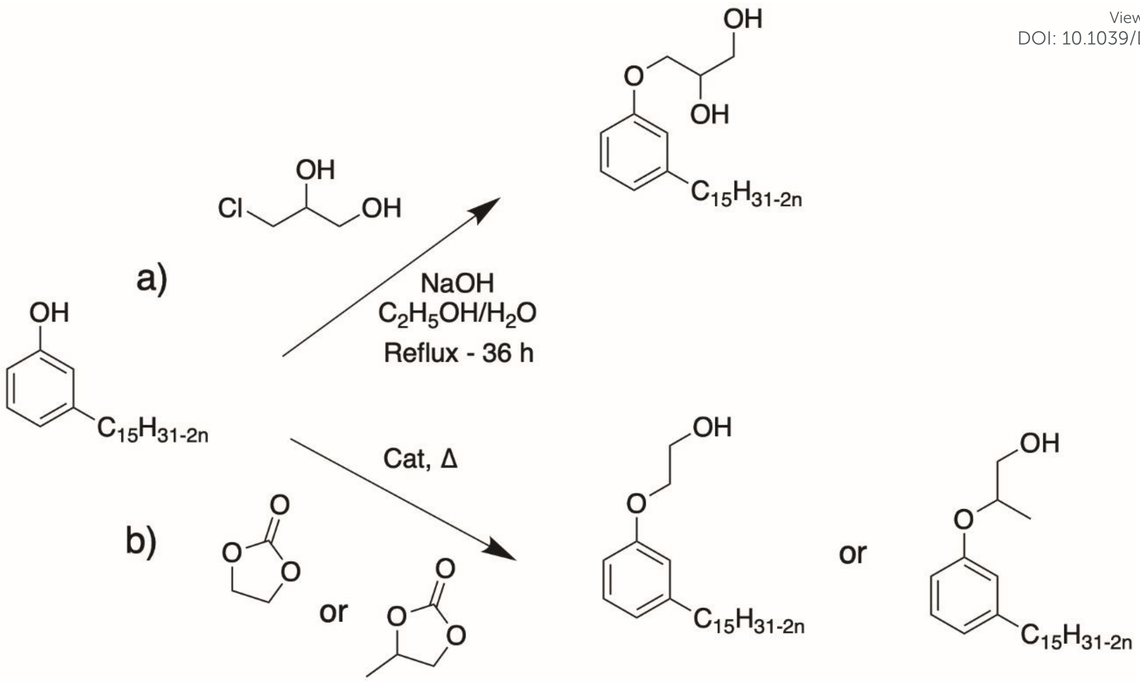

Scheme 2: Synthetic pathway of etherification of cardanol to form a) a diol **(73)** *and b) an alcohol* **(74)**.

- Hydroxyalkylation by ring-opening of cyclocarbonate

A first way to provide an alcohol function on a derivative of CNSL is to open a cyclocarbonate and more particularly the ethylene cyclocarbonate. Dia *et al.* of Cardolite corp. have filed a patent in 1998 on the hydroxyalkylation of cardanol with ethylene carbonate and propylene carbonate using various catalysts such as triethylamine, imidazole derivatives or alkali metal hydroxides and carbonates Scheme 2. These reactions take place between 140 and 180 ° C and reach a minimum of 90% conversion up to 98%, containing only mono-ethoxylated derivatives **(74)**. This method has the advantage of producing only CO_2 co-product previously captured and used for the synthesis of the cyclocarbonate itself (75, 76). This methods is also described with other natural phenols such as eugenol for the synthesis of ethoxylated compound with the use of 1,5-diazabicyclo(4.3.0)non-5-ene (DBN) as a catalyst **(77)**.

- Epoxidation of cardanol

Surresh *et al.* have reported a synthetic route using epichlorohydrin and an hydrolysis (78, 79) Scheme 3. Cardanol and $ZnCl_2$ were mixed under alkaline conditions at 95 °C. A stoichiometric amount of sodium hydroxide was added. The product named Epicard was obtained in 85 % yield. Then, the epoxy ring was opened under acidic conditions.

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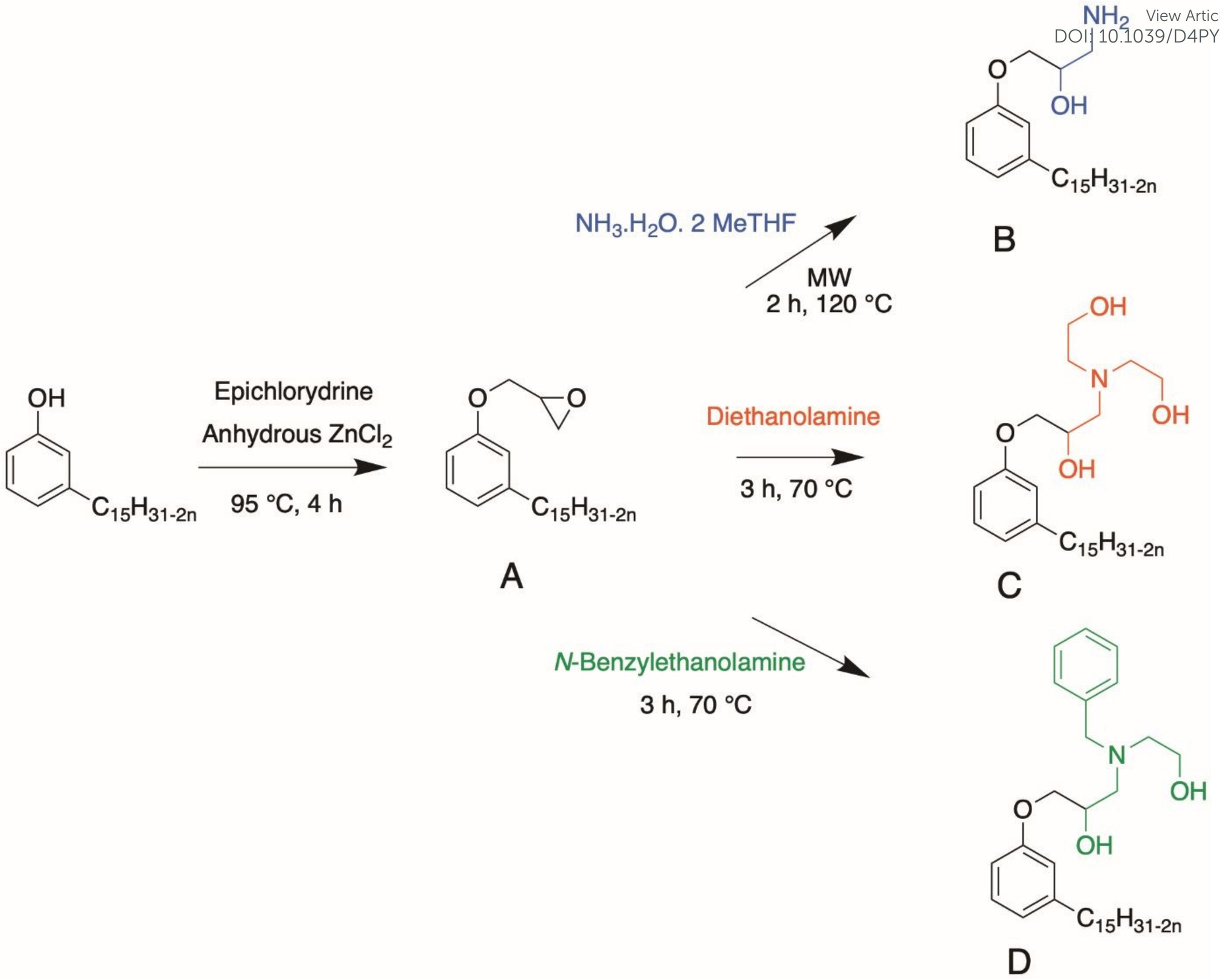

Scheme 3: Synthesis pathways of cardanol epoxidized, and then epoxy ring opening to obtain cardanol-based polyols **(78-82)**.

In the literature, several syntheses have been described to open an epoxy ring and then leading to the formation of at least one hydroxy function. Indeed, the following paragraph deals with the epoxy ring opening by amination (80-82), or with a thiol compound (83) and also in acid conditions with hydrolysis reaction (1).

- Amination of epoxy rings.

Mora *et al.* studied the ring opening of epoxy into hydroxy group leading to the formation of a highly reactive β-hydroxyamine (80) (Scheme 3). Epoxidized cardanol and ammonium hydroxide in 2-MeTHF reacted under microwave irradiations during 2 h at 120 °C. A brown, high viscous compound was obtained in a 99 % yield. This synthesis was interesting due to the use of non-toxic amination route and the bio-based origin of the solvent. Huo *et al.* have reported another way to open epoxy ring into hydroxy group using amine diols (81, 82) (Scheme 3. In this article, cardanol glycidyl ether and amine, diethanolamine (DEA) or N-benzylethanolamine (N-BEN), were mixed with an equimolar mixture. The final product can be mixed with silicone and isocyanate to produce polyurethanes with high thermal stability.

- Epoxy ring opening with a thiol compound.

Another way to open the epoxy ring into the hydroxy group of cardanol and generate cardanol-based polyol is by using a thiol alcohol (83) (Scheme 4). Cardanol glycidyl ether was mixed with a thiol compound, 2-mercaptoethanol, and 2,2-dimethoxy-2-phenylacetophenone under UV irradiations for 24 h. Then a catalytic quantity of lithium hydroxide and ethanol were

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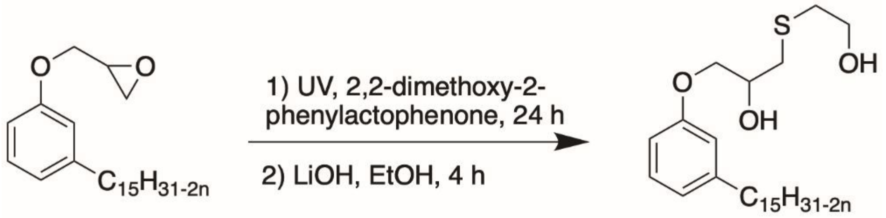
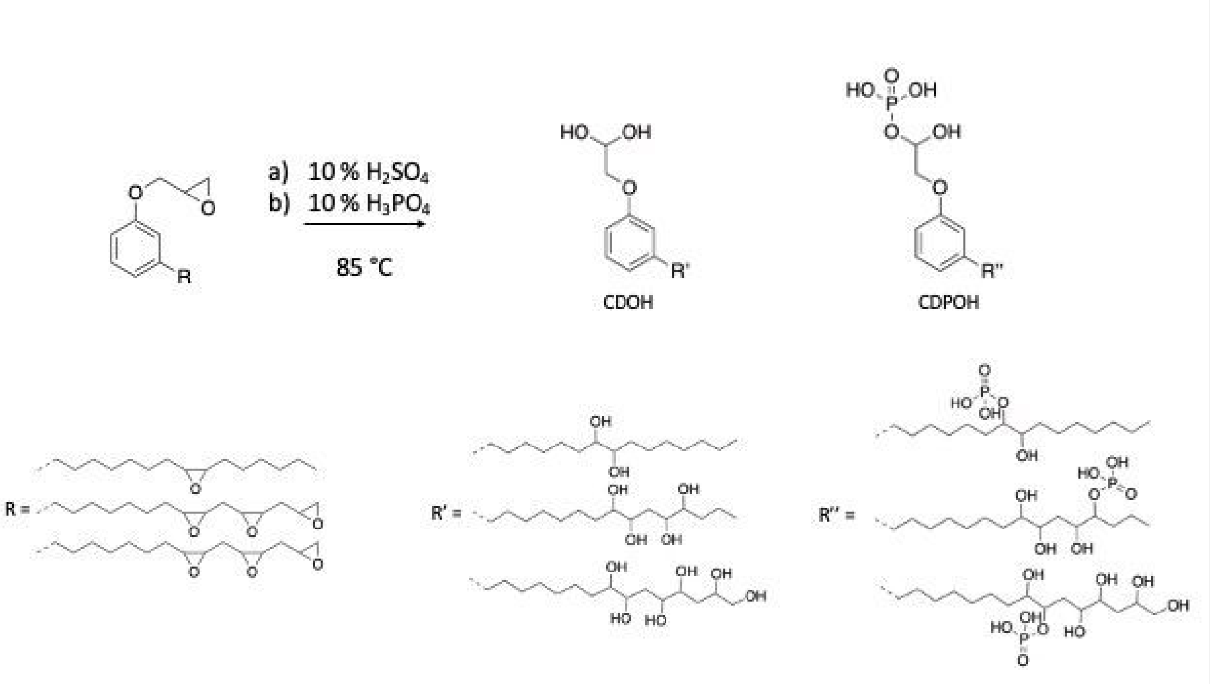
added to the mixture which was stirred for 4h at room temperature. The hydroxy number of products was 357 mg KOH/g. Then, the cardanol based polyols can be mixed with the 1,6-diisocyanatehexane (HDI) trimer to yield polyurethane with good mechanical properties.



Scheme 4: Epoxy ring opening of cardanol derivative by a thiol by Wang et al.[(83)]

- Hydrolysis reaction

Epoxy ring can also be opened under acid conditions as described by Somisetti *et al.*[(1)] using sulfuric acid or phosphoric acid. During this reaction, epoxidized cardanol in isopropyl alcohol was agitated in presence of a solution of 10 % sulfuric acid or 10 % phosphoric acid (Scheme 5).



Scheme 5: Hydrolysis reaction to open epoxy ring by Somisetti et al. [(1)]

Thereby, several methods have been described to modify the phenolic hydroxy moiety of CNSL compounds, and more especially cardanol, leading to the formation of reactive hydroxylated compounds, as presented in Scheme 6. Otherwise, in the literature, numerous researches have also highlighted the functionalization of unsaturated alkyl chain to obtain hydroxy reactive functions.

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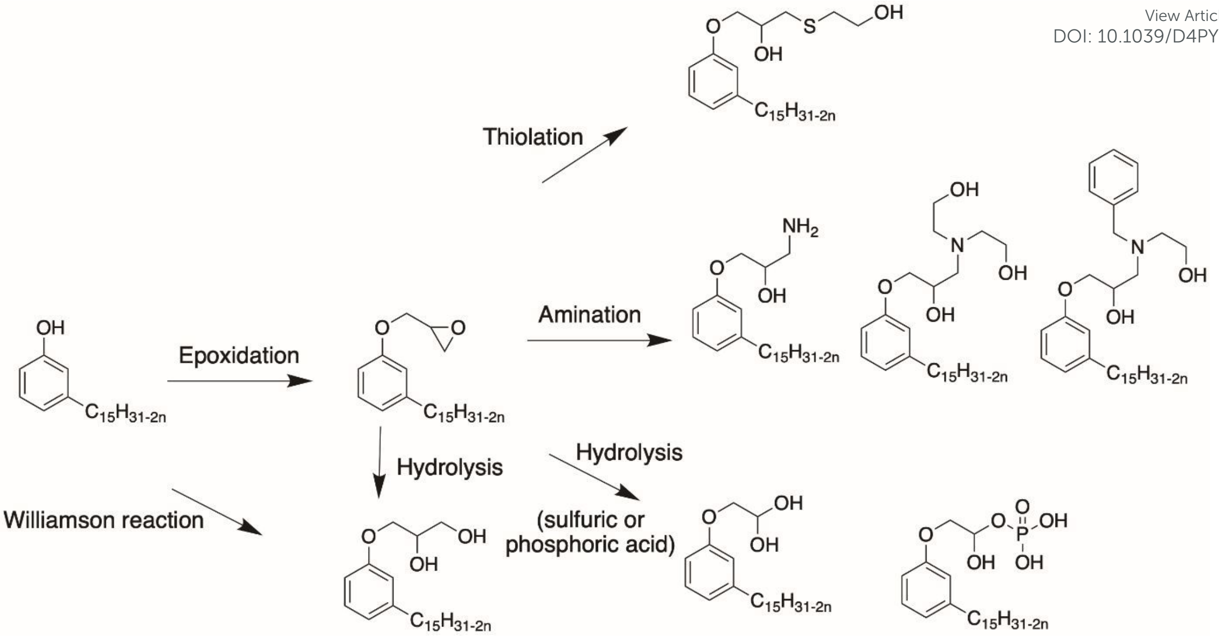
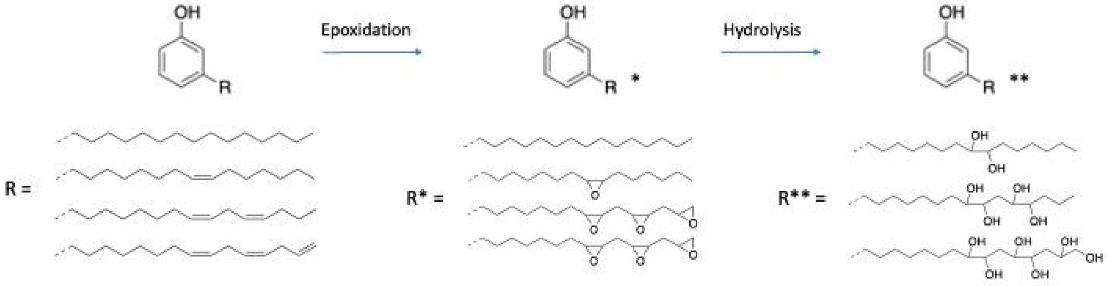


Scheme 6: Synthetic scheme of the formation of reactive hydroxylated CNSL compounds, by modifying the phenolic hydroxy moiety.

b. Modification of the unsaturated alkyl chain double bonds

However, the unsaturations of the fatty alkyl chains can also be functionalized to provide higher functionality in hydroxy functions. The most common way to transform double bonds into hydroxy functions consists in the epoxidation in the presence of peroxide compounds (Scheme 7) followed by the ring opening of epoxy ring. The use of peroxy acids such as *meta*-chloroperbenzoic acid (*m*CPBA), which has a versatile oxidizing power and relative ease of handling, constitutes one of the most useful synthetic procedures for the epoxidation of alkenes on a laboratory scale **(84)**. Another peroxide, the hydrogen peroxy (H_2O_2) has also been widely used for the epoxidation of double bonds. Depending on the environment and the position of double bonds in the alkyl chain, H_2O_2 is more or less effective than *m*-CPBA **(85)**. Indeed, Jaillet *et al.* have demonstrated that terminal double bonds are not epoxidized by *m*CPBA by contrast to H_2O_2 which yields a conversion of 25 %. The authors have also highlighted that complete epoxidation of the internal and terminal double bonds of cardanol is not possible. Nevertheless, the presence of peroxide in the concentrated resulting product could cause an explosion explaining why a purification of the resulting product to remove all the traces of peroxide is required. Moreover, this method is not industrially viable. Thiol-ene coupling and oxidative cleavage are also common pathways to form polyol from double bonds.



Scheme 7: Epoxidation of cardanol alkyd chain double bonds following by hydrolysis.

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- Ring opening of epoxy

The ring opening of epoxy function led to the formation of hydroxy groups. Many articles highlighted the different pathways allowing to open an epoxy ring.

- Polyols by hydrolysis of epoxy rings

A first way to open an epoxy group is the hydrolysis which can occur in acid or basic conditions (saponification) (Scheme 7). Suresh reported the saponification of epoxidized cardanol with a solution of 10 % sodium acetate at 80 °C for 4 hours even if the quantity of sodium acetate solution was not mentioned (86). The yield was not specified but a hydroxy value of 397 mg KOH.g^{-1} was calculated. This polyol was introduced in the formulation of rigid polyurethane foams with 4,4’-diisocyanate crosslinker and a blowing agent. The resulting foams have displayed a good compressive strength, and uniform cells structure in the case of foams prepared using modified cardanol.

Somisetti *et al.* have studied the epoxy rings opening by hydrolysis in acid conditions **(1)**. Epoxidized cardanol reacted with 10 % sulfuric acid (H_2SO_4) or 10 % phosphoric acid (H_3PO_4) in isopropyl alcohol at 60-70 °C. Then, the hydroxylated and phosphated cardanol-based polyols (CDOH and CDPOH) presented in Scheme 8 with a hydroxy value of 420 and 330 mg KOH.g^{-1}, respectively, were introduced in the formulation of PU films. The thermo-mechanical analysis has showed similar results for both PU films. The presence of the phosphate group in CDPOH-PU increases the adhesion to the metal substrate and thereby enhances its surface protection over its counterpart polyurethane, the CDOH-PU. Moreover, all the films exhibited excellent anti-corrosion and anti-microbial properties.

- Polyols by amination of epoxy rings

Another way to open the epoxy ring on the alkyl chains of CNSL molecules is by reacting amine bearing pendant hydroxyls. Some articles described the formation of β-hydroxyamines. Huo *et al.* have reported the synthesis of a novel cardanol-based polyol (81). Epoxidized cardanol (PCGE) and diethanolamine (DEA) (molar ratio 1:1.2) produced a final product with epoxy value less than 0.01 mol/100 g (Scheme 9). This polyol, with a hydroxy value of 553 mg KOH.g^{-1}, was employed for the formulation of PU foams with MDI and a blowing agent. The mechanical and thermal properties exhibited better results with cardanol-based PU foam than reference poly(ethylene glycol) PU foam. This could be due to the combination of the hard aromatic structure and long flexible alkyl chain of cardanol. Moreover, due to the numerous reactive sites present on the alkyl chain of cardanol, the viscosity of cardanol-based PU increased faster, the crosslinking density was higher, leading to an average cell size smaller.

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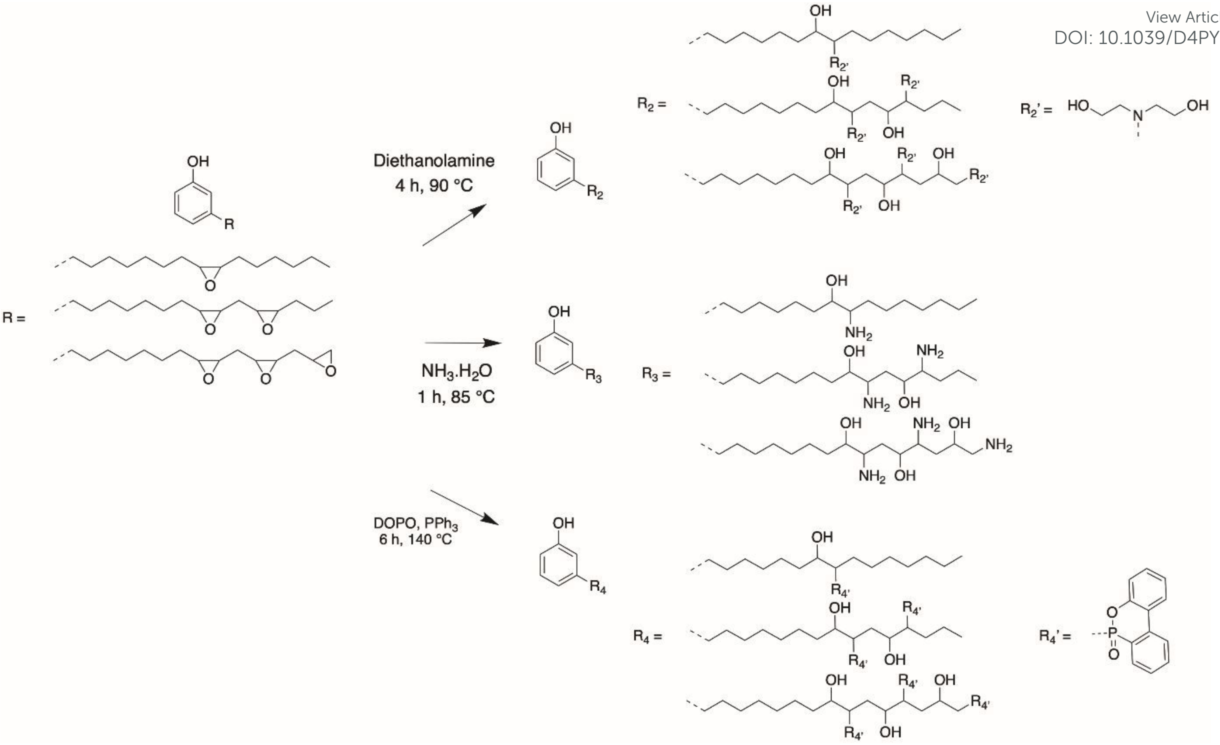


Scheme 8: Amination of epoxy ring by Huo.[(81)] *and Mora et al.*[(80)] *and phosphorylation by Bo et al.* [(87)]

Mora *et al.* have also studied the impact of amine for the epoxy ring opening into alkyl chain of cardanol [(80)]. Epoxidized cardanol reacted under microwave irradiations with an excess of ammonium hydroxide (Scheme 8). A 99 % yield of a white solid was reached unfortunately without any hydroxy value. Nevertheless, this synthesis is very interesting due to its full bio-based origin and the use of non-toxic amination route. Then, the hydroxy amine cardanol-based was mixed with epoxy prepolymers to obtain epoxy thermosets with good mechanical properties and high thermal stabilities.

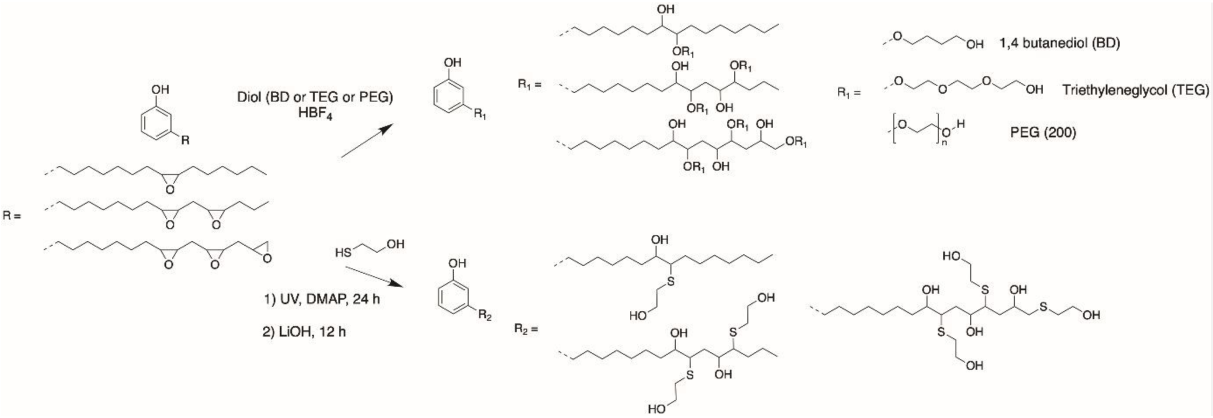
- Polyols by phosphorylation of epoxy rings

Bo *et al.* have reported the synthesis of a phosphorus cardanol-based polyol **[(87)]** from epoxidized cardanol and a phosphorus compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) catalyzed by triphenylphosphine (Scheme 8). This phosphorus cardanol-based polyol, with a hydroxy value of 287 mg $KOH.g^{-1}$, has demonstrated excellent thermal and flame-retardant properties. Indeed, this compound may release PO° free radicals and o-phenylphenoxyl free radical, acting as scavengers of H° and OH° flame radicals. Moreover, the phosphaphenanthrene group may generate a char residue acting as a barrier for the polymer matrix. This method has the advantage of synthetizing a bio-based polyol with flame retardant properties, able to act in both condensed and gas phase for optimum efficiency.

- (Polymeric) polyols by etherification of epoxy rings

The epoxy ring on the alkyl chains of CNSL molecules can also be opened by reacting diol compounds with acid catalyst leading to the formation of ether groups and reactive internal hydroxy functions. This etherification reaction has been described by Kim *et al.*[(88)] Epoxidized cardanol and diol reagents such as 1,4-butanediol (BD) or triethylene glycol (TEG) or poly(ethylene glycol) (PEG M_w: 200 $g.mol^{-1}$), were added at a molar ratio of 1:5. The reaction was carried out in acid catalyst conditions with 1_{wt}% of fluoroboric acid at 80 °C for 2 h

(Scheme 9). Three bio-polyols bearing both secondly and primary alcohol moieties were successfully synthetized, but the yield of the reactions were not mentioned by the authors whereas the hydroxy values were 369, 341, 328 mg $KOH.g^{-1}$ for BD, TEG and PEG cardanol-based polyol, respectively. Then, the cardanol-based polyols were employed as bio-based polyols for polyurethane films with excellent mechanical and thermal properties thanks to the unique structure of cardanol. Thereby, cardanol-based polyols are excellent candidates to replace petroleum-based polyols.



Scheme 9: Formation of polyol cardanol by etherification of epoxy ring by Kim et al. **(88)** *and Addition of functionalized thiol on epoxy ring by Wang et al.* **(83)**

- Polyols by addition of thiol on epoxy rings

Wang *et al.* have reported another way to open the epoxy ring in alkyl chain of cardanol to produce cardanol-based polyol (83). Epoxidized cardanol and a thiol compound, 2-mercaptoethanol, reacted for 24 h under UV irradiation using 2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator with a catalytic amount of lithium hydroxide. The conversion reached up to more than 90 % with a hydroxy value of 440 mg $KOH.g^{-1}$ (Scheme 9). The cardanol-based polyols were used as precursors of thermosetting polyurethane films with 1,6-diisocyanatohexane (HDI) trimer with excellent mechanical properties.

Hydroxy functionalized thiols can open the epoxy ring leading to the formation of a tertiary and a primary alcohol. However, thiol-ene coupling between unsaturation and hydroxy functionalized thiols is a key step to synthesize primary hydroxy groups on fatty acid chains to synthesize cardanol-based polyols.

- Thiol-ene coupling

Thiol-ene coupling is a green, practical, and atom-efficient reaction. Several articles focus on the thiol-ene coupling on CNSL compounds.

- Direct addition of alcohol moieties by thiol-ene reaction

Fu *et al.* have reported the synthesis of a cardanol-based polyol with 2-mercaptoethanol and 2-hydroxy-2-methylpropiophenone, a UV radical initiator **(89)**. The reaction was carried out under UV irradiation (365 nm) for 15, 22 and 50 h (Scheme 10). The results have demonstrated that the longer the reaction time, the greater the conversion, leading to an increase in hydroxy functionality. The hydroxy values were 313, 336 and 386 mg $KOH.g^{-1}$, respectively. Brown liquid cardanol-based polyols were achieved with a yield between 78 and 81 %. Thermosetting polyurethane films were shaped with HDI and these polyols providing good thermal and hydrophobic properties which suggested that they could be useful as a hydrophobic material.

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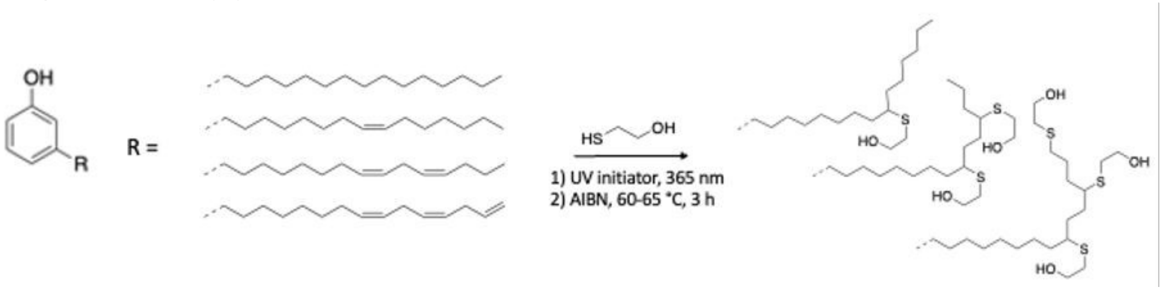
The thiol-ene coupling can also occur with a thermal radical initiator such as azobisisobutyronitrile (AIBN). Shrestha *et al.* have slowly introduced an excess of 2-mercaptoethanol to cardanol at 60-65 °C for 3 h (90) (Scheme 10). A transparent, light brown-red color cardanol-based polyol was synthesized with a hydroxy number of 310 mg $KOH.g^{-1}$ and used with MDI to elaborate rigid PU foams with very good physical-mechanical properties. So, they could find versatile applications such as thermal insulations of freezers, buildings, storage tanks and pipes.

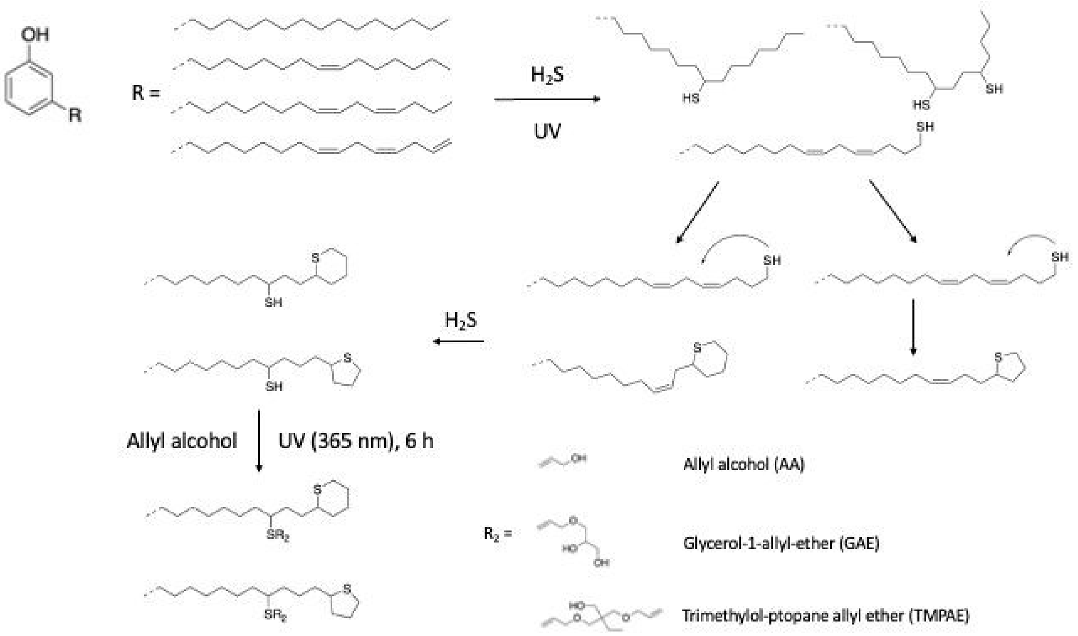


Scheme 10: Thiol-ene coupling on unsaturations of cardanol alkyl chains by 1) photochemical initiator Fu et al. **(89)***, or 2) thermal initiator Shrestha et al.* **(90)**

These renewable polyfunctional compounds can be very interesting for the synthesis of bio-based polymers which make them suitable alternative materials to replace petroleum-based materials.

- Intramolecular thiol-ene reaction via H_2S

The intramolecular thiol-ene reaction is another way to convert unsaturations of alkyl chain of CNSL compounds into thiol groups. The resulting thiols grafted onto alkyl chain can react with polyols exhibiting an alkene function to perform a thiol-ene reaction. Shrestha *et al.* have described a photochemical thiol-ene reaction with cardanol and an excess amount of hydrogen sulfite (H_2S) in the presence of UV light (91). Due to high mobility, intramolecular addition of the terminal thiol group to the neighboring double bonds is possible, forming cyclic thioethers containing 5- and 6-membered rings (Scheme 11).



Scheme 11: Intramolecular thiol-ene reaction by Shrestha et al. **(91)**

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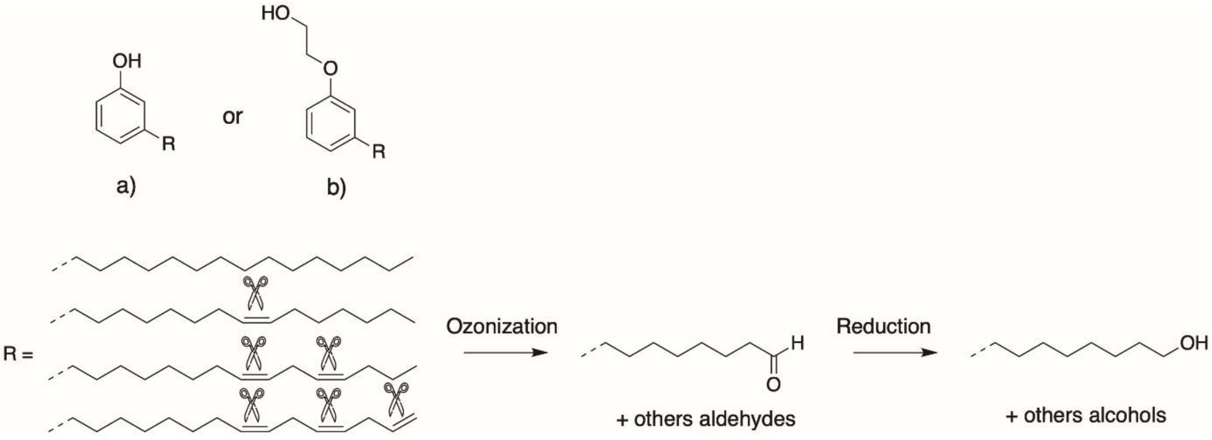
Different allylic alcohols such as allyl alcohol (AA), glycerol-1-allyl-ether (GAE), trimethylol-propane allyl ether (TMPAE) perform a second photochemical thiol-ene reaction in the presence of a photoinitiator (2-hydroxy-2-methylpropiophenone) at room temperature for 6 h under UV light (365 nm) (Scheme 11). The corresponding polyols were produced with hydroxy number of 300, 389 and 413 mg KOH.g^{-1}, respectively. The authors successfully synthetized bio-based polyols for rigid polyurethane foams with excellent physical and mechanical properties. Nevertheless, this synthesis required several steps unlike the thiol-ene couplings previously described.

- Oxidative cleavage

An alternative way towards cardanol-based polyols consists in oxidative cleavage through ozonization and reduction of the alkyl chain. Tyman *et al.* (92, 93) have reported the synthesis of cardanol-based polyol through oxidative cleavage and reduction of the aldehyde in a two steps synthesis (Scheme 12a). Firstly, cardanol was saturated with ozone at – 78 °C to complete the ozonization and zinc/acetic acid were added leading to aldehyde. In the second step, sodium borohydride ($NaBH_4$) reduced the cardanol aldehyde with a 74 % yield. The reaction was successful even if the experimental conditions do not allow industrial viability. Moreover, the oxidative cleavage provides only one hydroxy group per alkyl chain whereas the functionality was higher with the previously methods. The ozonolysis of cardanol subsequently led to a patent filed by Varma and Sivaram from General Electric Company (94).



Scheme 12: Oxidative cleavage of unsaturation alkyl chain of cardanol by Tyman et al. and Dinon et al. (92, 93, 95)

Oxidative cleavage can also be conducted on cardanol previously modified by ethoxylation. Indeed, Dinon *et al.* of Cardolite corp. (95) filled a patent in 2019 about the oxidative cleavage of ethoxylated cardanol with potassium peroxymonosulfate, ozonized air and Sudan Red III as a color indicator at 0 °C (Scheme 12b). The reduction reaction was occurred with a reducing agent such as triphenylphosphine; sodium, potassium, or calcium iodide in presence of acetic acid; dimethyl sulphite; trimethylphosphate; thiourea or zinc/acetic acid mixture. The oxidative cleavage is an interesting industrial way to easily synthesize cardanol-based polyol.

Numerous bio-based polyols have been reported in the literature and were described in this review. Moreover, the functionalization of unsaturations of alkyl chain of CNSL compounds lead to the formation of bio-based polyols with relatively high hydroxy number which increased the crosslink density of the cardanol-based polymers and therefore increased the mechanical properties including elastic modulus, tensile strength, and hardness.

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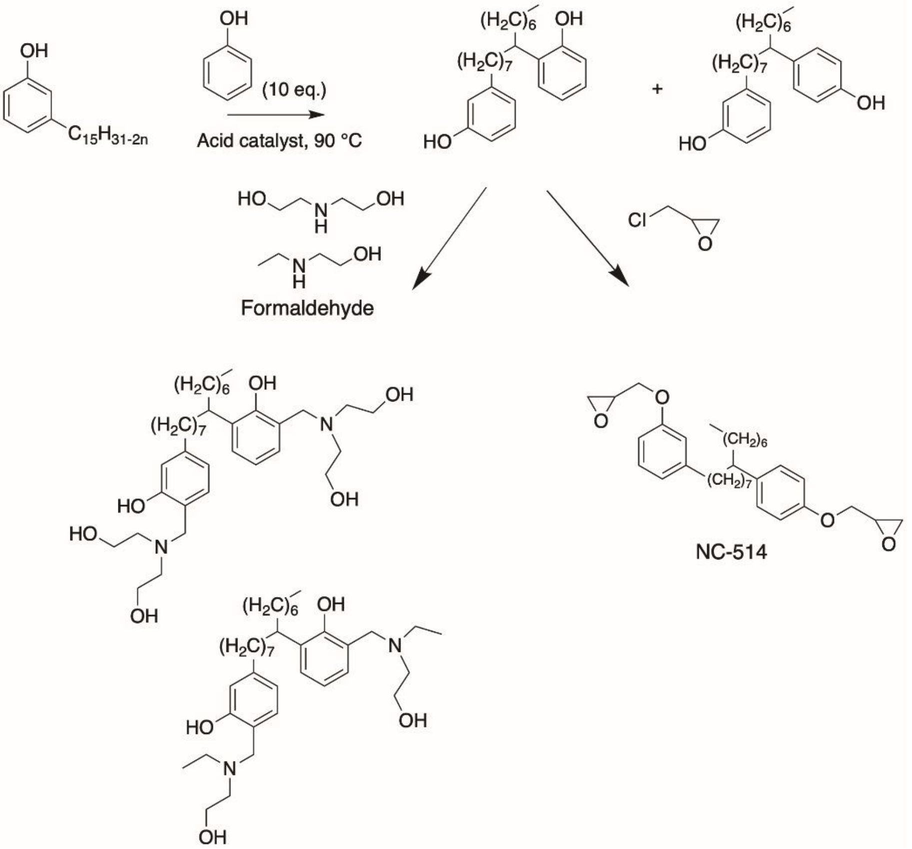
Moreover, it is possible to functionalize both hydroxy group of the phenol and the unsaturations of alkyl chain of CNSL compounds to generate monomers with even more functionality.

c. Formation of bisphenols based on cardanol

In the literature, several authors have reported the modification of the alkyl chain unsaturations of cardanol with a phenol to give a cardanol bisphenol. Ramasri *et al.*(96) have reported the synthesis on a cardanol bearing a mono-unsaturated alkyl chain using excess of phenol and catalyzed by $HClO_4$ (Scheme 13). More recently, Jing *et al.*(97) have described a triphenol using the same strategy with two unsaturations on the alkyl chain, catalyzed by sulfuric acid. This type of strategy can also be used to add phenol functions to the unsaturations of vegetable oils (98).



Scheme 13: Synthesis of bisphenol cardanol through alkyl chain unsaturations by Ramasri et al.(96) *and then, the formation of a polyol by Ramasri et al.* (99) *and NC-514 molecule.*

Ramasri *et al.*(99) have described the synthesis of Mannich base cardanol bisphenol. The cardanol bisphenol was dissolved in ethanol in presence of an amine such as 2-ethylamino-ethanol solution or diethanolamine followed by the addition of formaldehyde solution (Scheme 13. Those Mannich base cardanol bisphenols were then neutralized with acetic acid before being added in paint formulations and used for electrodeposition. As expected, the Mannich base from diethanolamine, which exhibited the highest functionality, showed higher values for adhesion and scratch hardness related to the Mannich base from 2-ethylaminoethanol. Moreover, Cardolite corp. synthetized a cardanol bisphenol in two steps and commercialized under the name NC-514 (Scheme 13). The first step was the phenylation of aliphatic chain, followed by reaction of phenol hydroxy groups with epichlorohydrin.

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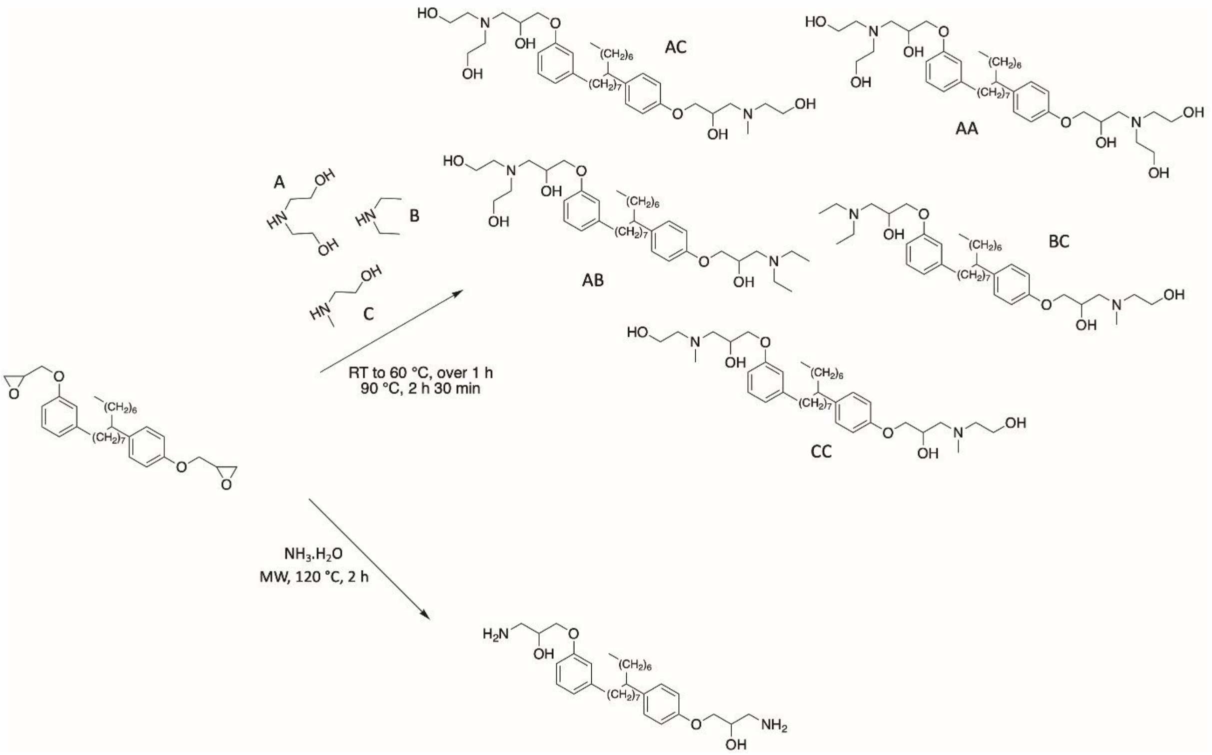
Based on this commercial epoxidized cardanol bisphenol, numerous articles described the synthesis of other polyols. Kathalewar *et al.* have reported cardanol based polyols with variable functionalities by reacting NC-514 with several secondary amines (diethanolamine, diethylamine, 2-methylaminoethanol) (100) (Scheme 14). Despite the unmentioned yield of the reaction by the authors, the hydroxy value of the polyols was estimated between 241 and 449 mg KOH.g^{-1}. Consequently, the authors synthetized a wide range of polyols with variable number of hydroxy functionalities. These polyols reacted with polyisocyanates to produce polyurethane coatings with excellent chemical and thermal resistance and anticorrosive performance. As expected, the higher the functionality of polyol, the higher the crosslinking density and therefore increased physical properties such as hardness, impact, tensile performance.



Scheme 14: Synthesis of various polyols based on commercial NC-514 by Kathalewar et al. **(100)***. and Mora et al* **(80)***.*

Mora *et al.* have successfully aminated NC-514 using ammonium hydroxide solution under microwave irradiations (80) (Scheme 14). A brown and high viscous compound was reached in 99 % yield. The functionalized NC-514 cardanol exhibited two different reactive functions: hydroxy and amine groups. These β-hydroxyamines were able to react with epoxy groups to form epoxy-amine thermosets with good thermomechanical properties and high thermal stability.

Balgude *et al.* reported the synthesis of polyols based on NC-514 which reacted with different biobased acids such as tartaric acid, citric acid and adipic acid **(101, 102)**. Firstly, epoxy cardanol NC-514 was stirred with one of the acids in presence of a phase transfer catalyst (tetrabutylammonium bromide). Triphenylphosphine (PPh_3) catalyzed the opening of the epoxy ring involving a nucleophilic attack (Scheme 15). The yield of the reactions was not mentioned by the authors but and the hydroxy values of the polyols exhibited values between 96 and 275 mg KOH.g^{-1}. The polyols were mixed with different commercial isocyanates, HDI and isophorone diisocyanate (IPDI) to give bi-components water based polyurethane coatings.

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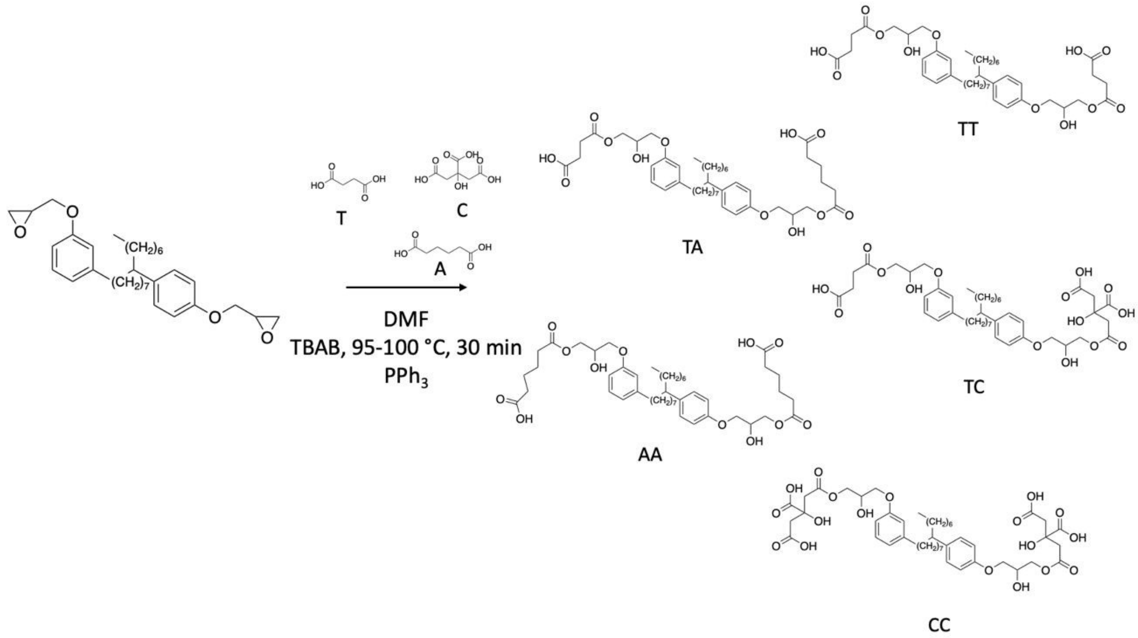
The high crosslinking density, with the polyols having the highest hydroxy functions, of the cured films showed a great impact on chemical resistance, thermal stability, and anticorrosive performances of the polyurethane coatings.



Scheme 15: NC-514 modified with biobased acid to form novel cardanol based polyols [(101, 102)].

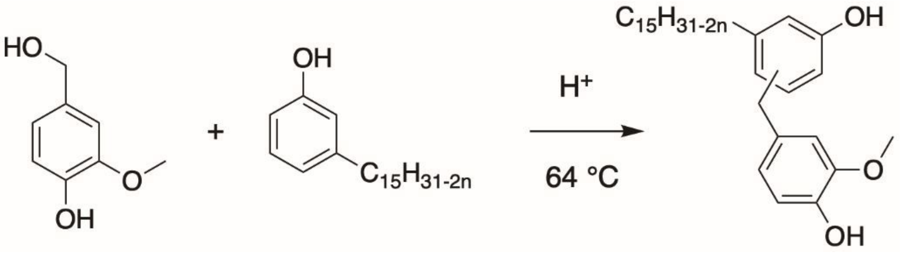
Nevertheless, a study reported by Jaillet *et al.* in 2014 (103) highlighted a far higher molar mass of NC-514 than the theoretical molar mass which indicated that the commercial cardanol NC-514 corresponded to a mix of polymers of epoxidized cardanol.

d. Modification of the aromatic ring

The last functionalizable reactive site of CNSL compounds is the aromatic ring. Three main methods were reported in the literature: the condensation, the azo coupling and the Mannich reaction leading to different CNSL-based polyols.

- Condensation

The condensation of two biobased phenols was reported by basset *et al.* leading to the formation of a cardanol-based diol (104). Vanillyl alcohol and cardanol were coupled together according to an electrophilic aromatic condensation in a 70 % yield (Scheme 16). Despite the high amount of renewable atom carbon of the vanillyl alcohol cardanol, the reaction time is very long. Moreover, the hydroxy value was not investigated because the aim of this article is the methacrylation of the alcohol groups before polymerizing hydroxy.



Scheme 16: Condensation of vanillyl alcohol and cardanol to form cardanol-based polyol by Basset et al.(104).

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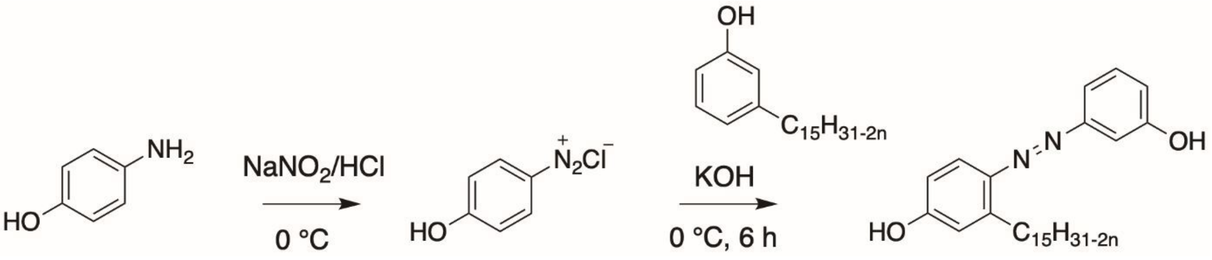
- Azo coupling

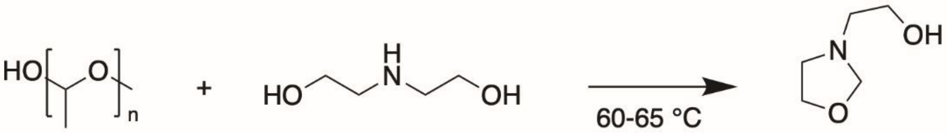
The azo coupling on CNSL compounds bearing hydroxy functions can be performed leading to a colored conjugated system. Bhunia *et al.* have reported the two steps synthesis of an azo cardanol-based polyol with an aromatic dye containing both hydroxy and amine functions (105-107). The red dye formed reached a yield of 80 % (Scheme 17). Nevertheless, the hydroxy value was not mentioned by the authors. A polyurethane was synthesized by reacting the azo cardanol-based diol with a diisocyanate (MDI) leading to material with high thermal stability and UV resistance due to the conjugated system. The same compound was synthetized by Nayak *et al.* (108) mixed with ester polyols and diisocyanates compounds to produce interpenetrating network (IPN) polyurethane with high thermal stability.



Scheme 17: Azo cardanol-based polyol synthesis by Bhunia et al. (105-107)

- Mannich reaction

The most reported reaction to synthesize polyol from an aromatic ring is the Mannich reaction which consists in a condensation of an aldehyde, a primary or secondary amine and a carbonyl compound. Usually, the first step is the building of the cyclic ring, oxazolidine (109-111) (Scheme 18). The synthesis of oxazolidine was carried out by reacting diethanolamine with paraformaldehyde (109, 112, 113).



Scheme 18: Chemical pathway to oxazolidine.

Asif *et al.* have synthetized a cardanol-based Mannich polyol with cardanol added dropwise over oxazolidine intermediate (112) (Scheme 19 structure 3). This renewable cardanol-based polyol with a hydroxy number of 187 mg KOH.g^{-1} was further used in the formulation of PU nanocomposite coatings. Those materials have showed good physico-chemical properties and excellent anti-corrosion and chemical resistance. The hydrophobic character was also investigated, and the results have demonstrated an increased up of the value with the amount of cardanol-based polyol introduced into the formulation.

Ionescu *et al.* (113) have reported the synthesis of Mannich polyols from cardanol with oxazolidine. Depending on the molar ratio cardanol/oxazolidine, three structures of Mannich polyol can be synthetized in practically quantitative yields (Scheme 19, structures 1, 2 and 3). The cardanol-based polyols exhibited hydroxy number of 350 and 436 mg KOH.g^{-1} for the structures 1 and 2 whereas this value was not mentioned by the authors for the structure 3. The Mannich polyols from cardanol have much lower viscosity and a higher renewable content than petroleum-based Mannich polyols. Moreover, they are very reactive, that is why they

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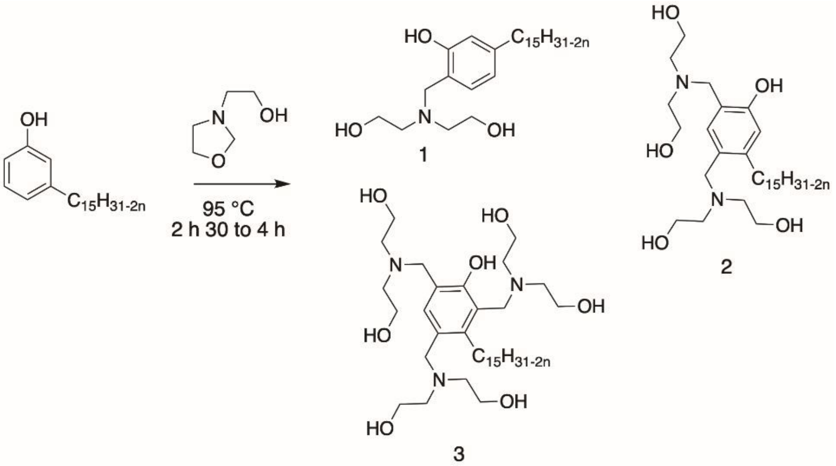
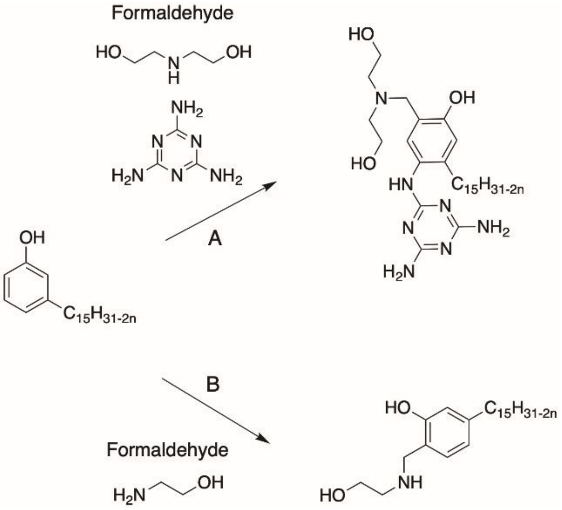
were especially suitable from spray rigid polyurethane foams, but they can also be used in molded rigid PU foams and as crosslinkers in many other PU applications such as coatings. Moreover, the obtained rigid PU foams exhibited good physico-mechanical and fire-retardant properties. Ionesco *et al.* and Asif *et al.* reported the same cardanol Mannich polyol (Structure 3), but with different hydroxyl values. The method used by the authors was not the same. Indeed, Ionesco *et al.* determined the hydroxyl value by using p-toluenesulfonyl isocyanate method (ASTM 1899-1997) whereas Asif *et al.* have used ASTM D 6342-12 methods.



Scheme 19: Synthesis of Mannich based polyol by Ionescu et al. **(113)** *and Asif et al.* **(112)**

The Mannich reaction can also be performed without the formation of the cyclic oxazolidine in the first step. Zhang *et al.* have described this solvent-free synthesis with cardanol and paraformaldehyde but also with melamine to bring flame retardant properties (114) (Scheme 20). Nevertheless, the yield of the reaction and the hydroxy value of the polyol were not mentioned by the authors. Several rigid polyurethane foams were produced from this cardanol-based polyol with excellent mechanical properties, high thermal stability, and flame-retardant properties.



*Scheme 20: Synthesis of Mannich based polyol by Zhang et al.***(114)** *(A) and Oh et al.* **(115)** *(B)*

Another cardanol based Mannich reaction synthetized by Oh *et al.***(115)**, have been described in a Korean patent where cardanol, formaldehyde and ethanolamine were combined to give a diol aromatic with a hydroxy value of 315 mg KOH.g^{-1} (Scheme 20)**.** Several important information such as the description of the synthesis, the temperature and the time

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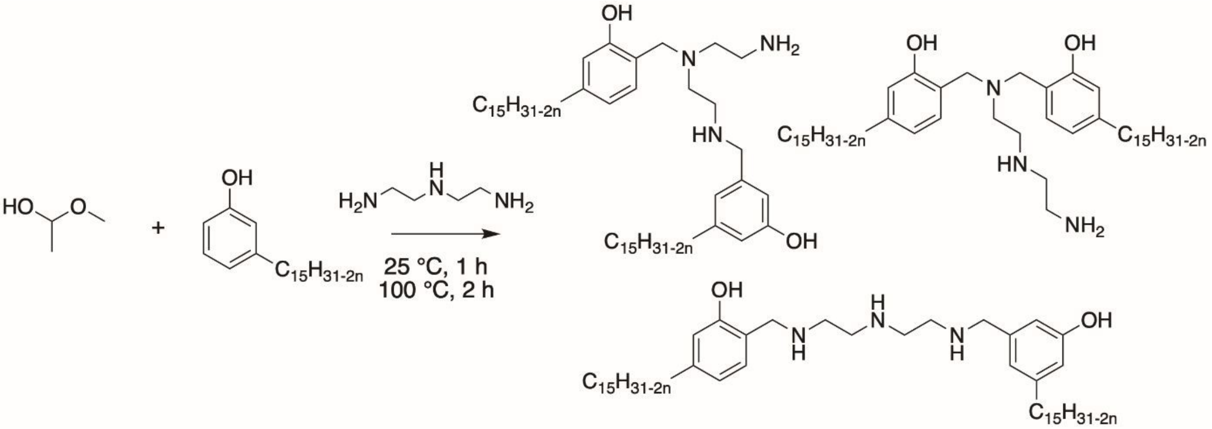
of the reaction were not mentioned in the patent. Furthermore, the properties of the resulting PU were not described.

The Mannich based reaction can also be used for dimer cardanol based polyol. Indeed, this pathway can increase the hydroxy number and increase the crosslinking density which could enhance physico-mechanical properties of the polymers.

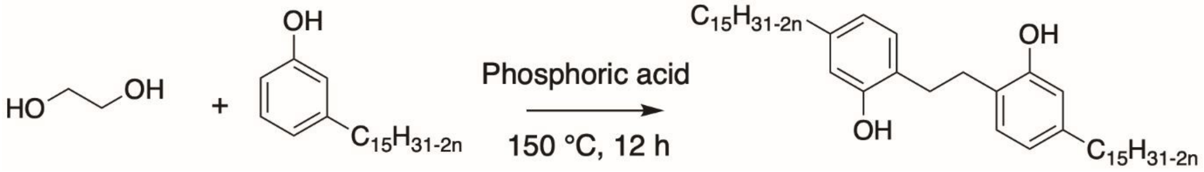
- Dimerization of CNSL through aromatic rings

Dimers of CNSL compound can result from the dimerization of cardanol in presence of polyamines. Tyman *et al.* have reported the synthesis of several dimer cardanol diols by Mannich reactions with diethylenetriamine **(116)** (Scheme 21). Aqueous formaldehyde (35–40%) was added dropwise over the mixture of cardanol and dimethylamine. This triamine exhibited two primary amines and one secondary amine, providing a complex isomeric mixture (the ratio of each final cardanol dimer was not mentioned by the authors) as showed in Scheme 21.



Scheme 21: Dimerization of cardanol by Tyman et al.(116)*.*

Tan *et al.* have synthetized another dimer by reacting cardanol with glycol and catalyzed by phosphoric acid (2 wt%)(117) (Scheme 22). The yield of the reaction and the hydroxy value of the product were not discussed by the authors. A relevant aspect of this synthesis is the absence of formaldehyde, a toxic compound, as with the Mannich reaction. This reaction could be interesting with other diols, if possible, bio-based, to obtain a fully bio-based cardanol dimer.



Scheme 22: Dimerization of cardanol by Tan et al (117)*.*

A synthetic route towards thiobiscardanol was studied by Tyman *et al.* (118) using sulfur dichloride (Scheme 23)**.** The yield of the reaction was not reported by the authors but the use of a catalyst such as iron powder allowed to enhance the conversion of the reaction. The same authors own a patent, demonstrating the commercial interest of the dimer (119). Nevertheless, some solvents are more toxic than others (benzene) and their use tends to be banned.

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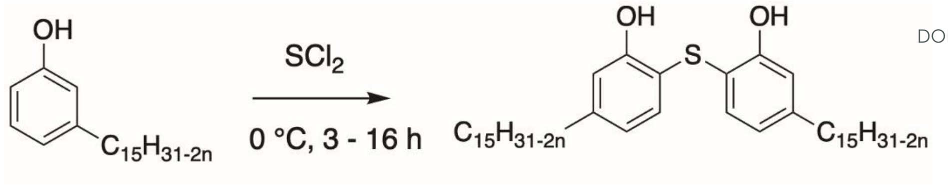
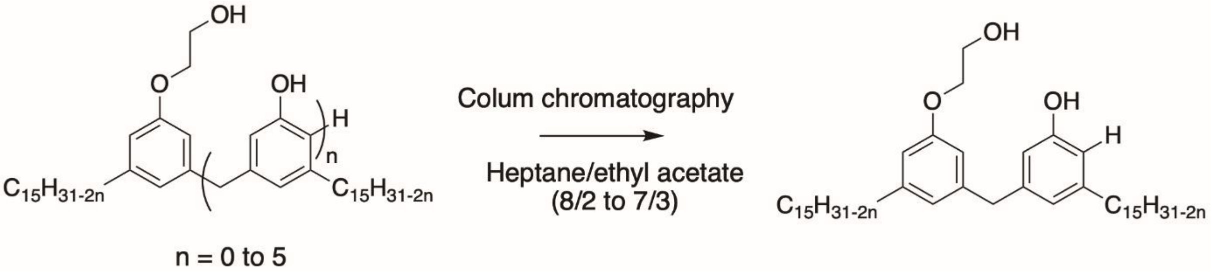


Scheme 23: Synthesis of thiobicardanol by Tyman et al.(118).

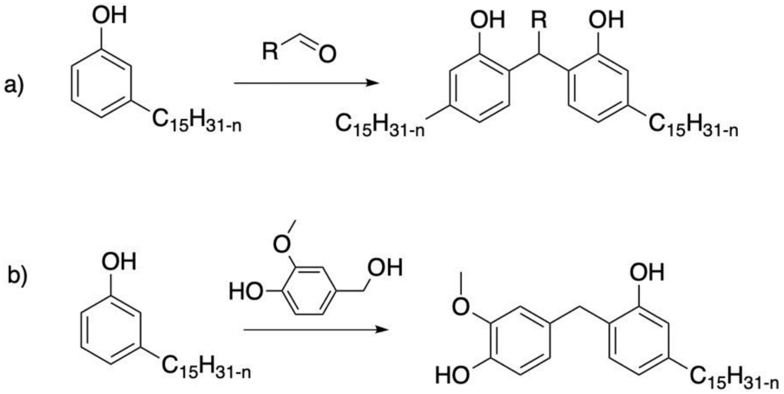
The separation and purification of a commercial Cardolite cardanol-based oligomers by over column chromatography has allowed Hassouma *et al.* to reported a cardanol-based dimer (120) (Scheme 24). This method is not efficient enough to be applied in industry with 20 wt% of dimers related to the total mass of the Cardolite resin introduced.



Scheme 24: Separation of Cardolite resin for cardanol-based dimer (120).

The chemistry of phenolic resins is appropriate for pure dimers, either by playing with the number of equivalents or by going through a purification step on a column to isolate only the dimers. Briou et al. describe, for example, the synthesis of a dimer by condensation of cardanol with nonanal in acid catalysis under dilute conditions (121) (Scheme 25a). The monitoring of the reaction by NMR spectroscopy also highlights the addition of the aldehyde on the least substituted ortho position of the aromatic ring. In the first step of the mechanism, a methyl moiety is obtained. Then, the condensation of the methylol group occurs on another ortho position of a free cardanol. Very recently, Yokoyama et al.(122) described the synthesis of other cardanol dimers from aliphatic or aromatic aldehydes and even acetone.

In the same way, a molecule containing a methylol group can be condensed in acidic condition, without addition of aldehyde first. This is the case for vanillyl alcohol, another natural phenol which can condense with guaiacol (104) and cardanol (123) (Scheme 25b).



Scheme 25: Synthesis of cardanol dimers from a) controlled condensation with aldehydes (121, 122), b) condensation with vanillyl alcohol (123).

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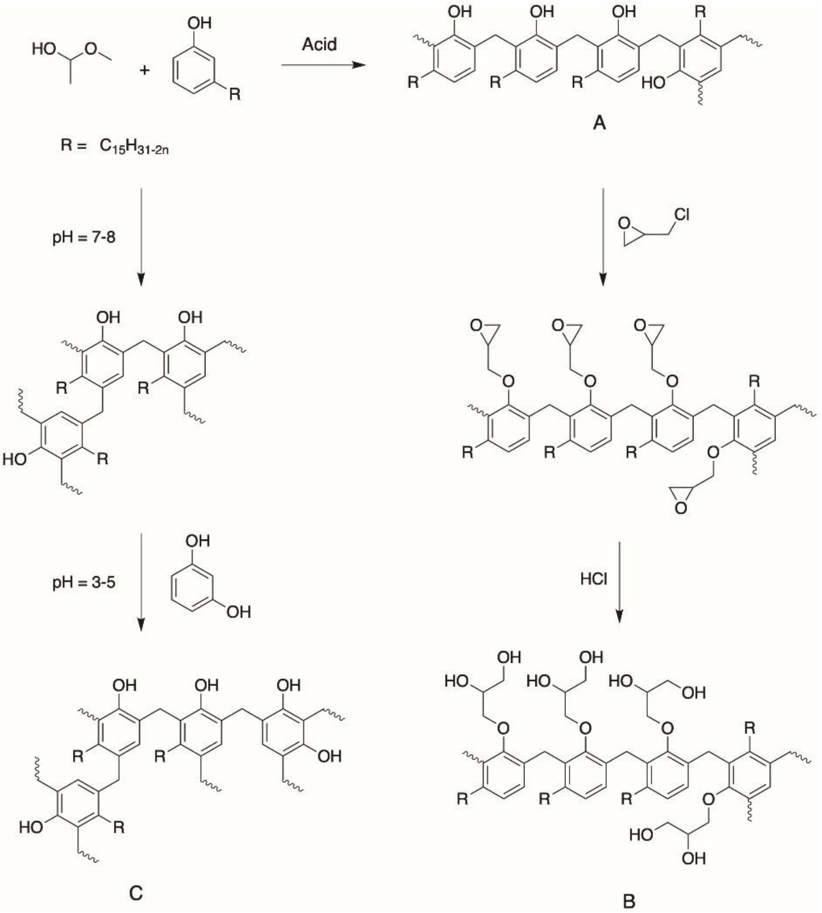
e. Polyols from CNSL-based polymers

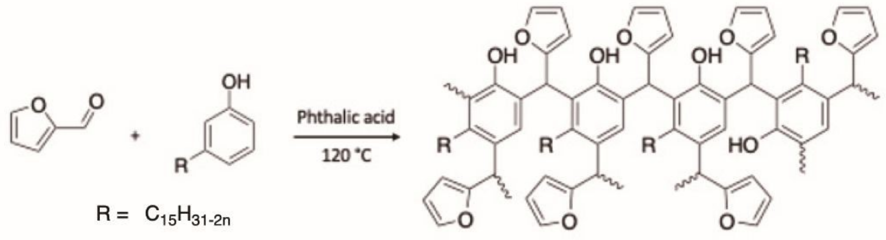
One of the most reported pathways in the literature is the cardanol based phenolic resins. Usually, phenolic resins result from phenol and formaldehyde at high temperatures producing two types of phenolic resins: novolacs, prepared under acid catalysis, and resoles, obtained under basic catalysis. Several articles described the synthesis of polyols from CNSL-based novolac resins with formaldehyde derivatives (Scheme 26). Mythili *et al.* (124) have mixed cardanol, formaldehyde using acid catalyst (glutaric acid) at 120 °C for 3 h. After that, the reaction was heated up to 150 °C for additional 5 h, leading to cardanol formaldehyde resin with a hydroxy value of 157 KOH.g^{-1}. Then, this resin was mixed with a diisocyanate (MDI) to form rigid polyurethane which improved mechanical and thermal properties as well as chemical resistance.



Scheme 26: polyols from cardanol-based novolac resins synthetized by A) Mythili et al. (124), B) Sathiyalekshmi et al. (125, 126) and C) Mahajan et al. (35).

Sathiyalekshmi *et al.* have reported the synthesis of another cardanol formaldehyde resin by mixing cardanol, formaldehyde in acid conditions with adipic acid at 120 °C for 5 h and then, 150 °C for 20 min (125, 126). The cardanol resin was epoxidized with epichlorohydrin and treated with 15 % alcoholic sodium hydroxide. The epoxidized cardanol formaldehyde resin was further subjected to hydrolysis to convert the epoxy group into hydroxyalkyl group with hydrochloric acid at 120 °C for 1 – 2 h (Scheme 26). The authors did not mention the hydroxy value of the final cardanol resin. However, the epoxy ring opening reaction led to increase this value compared to the cardanol formaldehyde resins studied above. Finally, rigid polyurethanes ensued with good aging performances, high thermal stability, and excellent mechanical properties. Mahajan *et al.* have prepared cardanol formaldehyde microcapsules to bring self-healing properties to polyurethane coatings **(35)**. Those microcapsules were synthetized through in situ polymerization technique using an oil-in-water emulsion. Cardanol and ammonium chloride were added over an aqueous solution containing poly(vinyl alcohol) and sodium lauryl sulphate. The pH of the mixture was maintained between 7 and 8 thanks to a sodium hydroxide solution (5 wt%). Linseed oil was added dropwise to form a stable emulsion. Then, formaldehyde was added, and the temperature of the reaction was raised to 85 °C for 3 h. After that, the pH of the reaction was decreased to 3 - 5 with a hydrochloric acid solution and resorcinol was added as a crosslinker (Scheme 26). The PU coatings on mild steel surface showed increase self-healing and corrosion performances with increase the cardanol formaldehyde microcapsules. Thus, they were sustainable approach for protection metals substrates.

For a greener CNSL-based novolac resins, formaldehyde, a petro-sourced aldehyde, can be substituted by another bio-based aldehyde. Indeed, Joy *et al.* have reported the synthesis of a polyol with cardanol and furfural under an acid catalyst solution (phthalic acid) **(127)**. Then, the solution was heated to 120 °C but the time of the reaction was not mentioned by the authors (Scheme 27). The obtained polyol multinuclear cardanol furfural resin exhibited a hydroxy value of 174 KOH.g^{-1}. Thanks to the substitution of formaldehyde, a petrosourced aldehyde, by furfural, a bio-based aldehyde, the amount of renewable atom carbons of the polyol increased. Nevertheless, furfural is a toxic compound, classified as carcinogenic, mutagenic, toxic for reproduction (CMR).



*Scheme 27: Polyol based cardanol furfural resin by Joy et al.***(127)**.

For polyol based cardanol phenolic resin, other bio-based and non-toxic aldehyde compound could be considered (128-130). Moreover, compared to the previously mentioned pathways, the formation of polyols from CNSL-based polymers lead to reactive compounds with a low hydroxy value. Moreover, a decrease of solubility and an increase of viscosity are some disadvantages that can appear with the high molar masses of polyols derived from CNSL-based polymers.

f. Conclusion

In this part, many pathways have been described to synthetize polyols based CNSL compounds as summarized in Scheme 28. The reactive functions of CNSL compounds such as hydroxy group of the phenol, unsaturation of the alkyl chains and aromatic ring can be easily to functionalize. Moreover, most of the articles reported the use of cardanol but the synthesis described could be applied for the other CNSL compounds (cardol or anacardic acid).

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Depending on the structure of the desired final polymer and the intended application, the hydroxy value is very important. Indeed, the higher the hydroxy value, the greater the crosslinking density, leading to high physical-mechanical properties which are more or less suitable for some applications. In this part, numerous polyols with a wide range of hydroxyl value (from 96 to 553 mg KOH/g) making them versatile for many applications, have been described. Most of the cardanol polyols were used for numerous polyurethane materials from rigid PU foams to PU coatings, passing by flexible foams. Nevertheless, CNSL compounds can also be versatile polyols for the synthesis of other polymers such as polyesters. This was very few reported in the literature.

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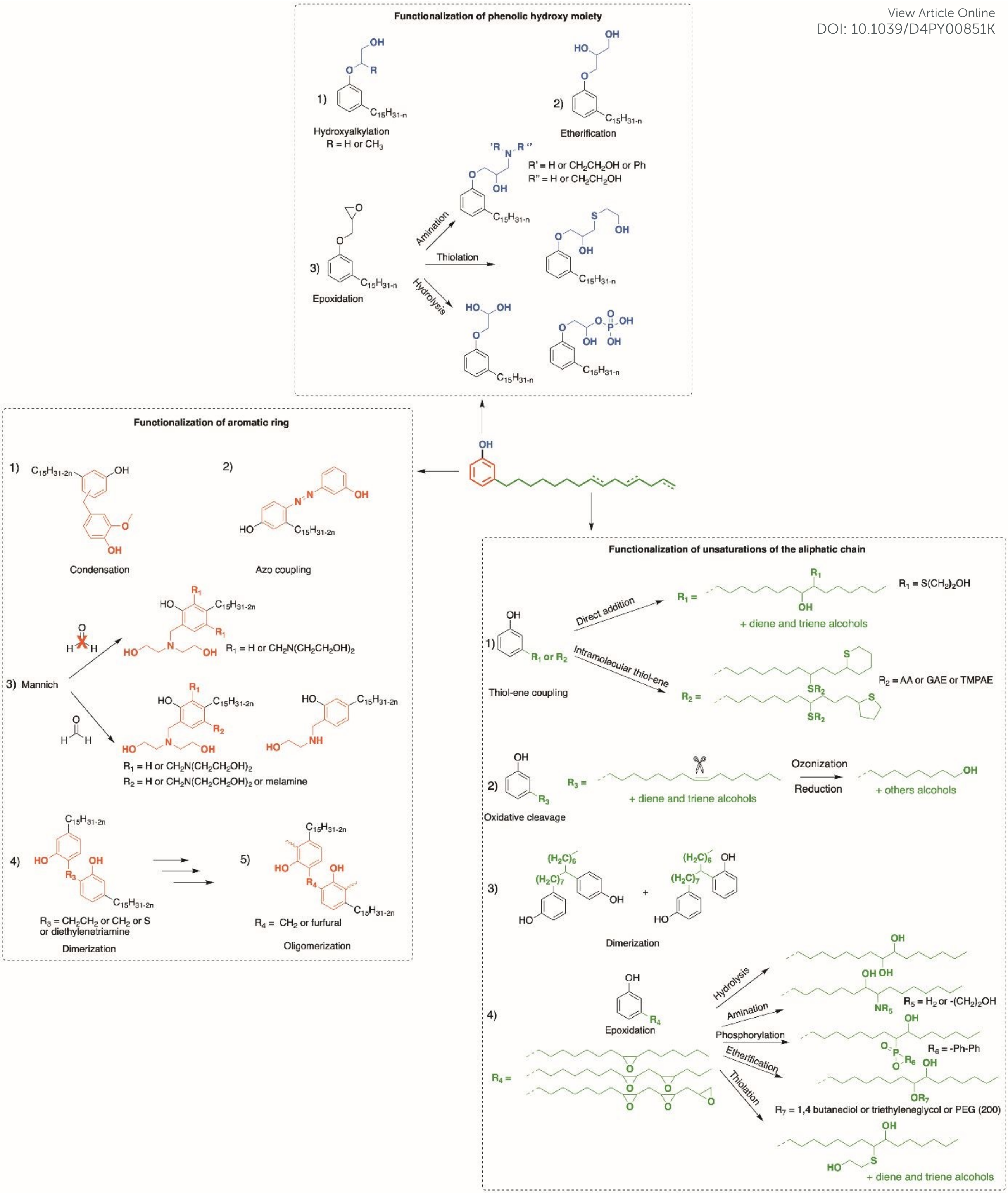

Scheme 28: Several pathways to synthetize polyols based CNSL compounds.

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III) Use of CNSL-based polyols in a wide range of applications

In the previous part, we were able to highlight the plurality of synthesis methods to obtain polyols from CNSL derivatives, mainly cardanol. Depending on their chemical structure, polyols can be used in a wide variety of applications, ranging from foam to paint and coatings. Thanks to their special structure, CNSL derivatives are regularly used in the synthesis of polymer materials. The presence of the phenolic ring in its molecules confers a gain in thermal stability and the long dangling alkyl chain influences the glass transition temperature of the resulting material, thus improving their flexibility. This dangling chain also brings a hydrophobic behavior to CNSL derivatives, making the use of these molecules relevant in the synthesis of surfactants or coatings. All these characteristics of CNSL derivatives allow a direct application of polyols from these biobased synthons through the synthesis of polyurethane, polyester, and surfactant (Figure 4).

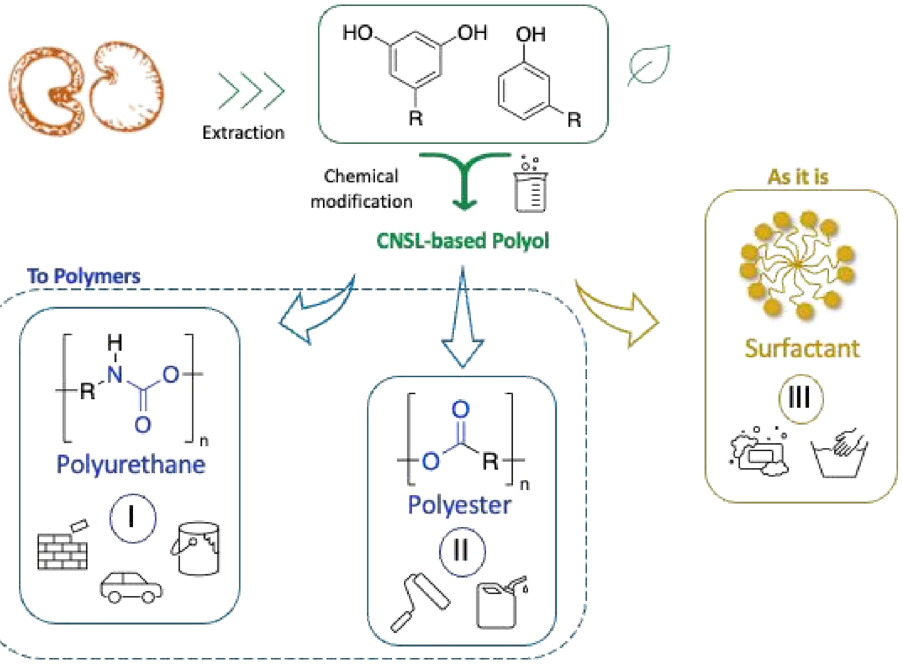

Figure 4: Figure summarizing the applications of CNSL-derived polyols in the chemical industry.

1) Applications and properties of polyurethanes from CNSL-based polyols

Polyurethanes (PUs) are widely used in many applications: foams, coatings, adhesives, elastomers (131). Looking at PU consumption by product type in 2024 (132), we can see that foams account for the large majority of the market, followed by coatings, elastomers and adhesives and sealants. The global market in volume for PUs was 21 Mt in 2022 (133), i.e. around 5 % of global plastic production. The particularity of the PUs comes from their versatility and the presence of soft and hard segments that can be modulated to suit the target application. However, conventional PUs have two major drawbacks. First, they involve the use of isocyanate, which are highly toxic for human, and moisture sensitive (134). They release toxic volatile molecules under harsh conditions. Polymeric isocyanates can be a solution to reduce their toxicity as they have high vapor pressure (135). Then, PUs are mainly derived from petroleum-based feedstocks (136).

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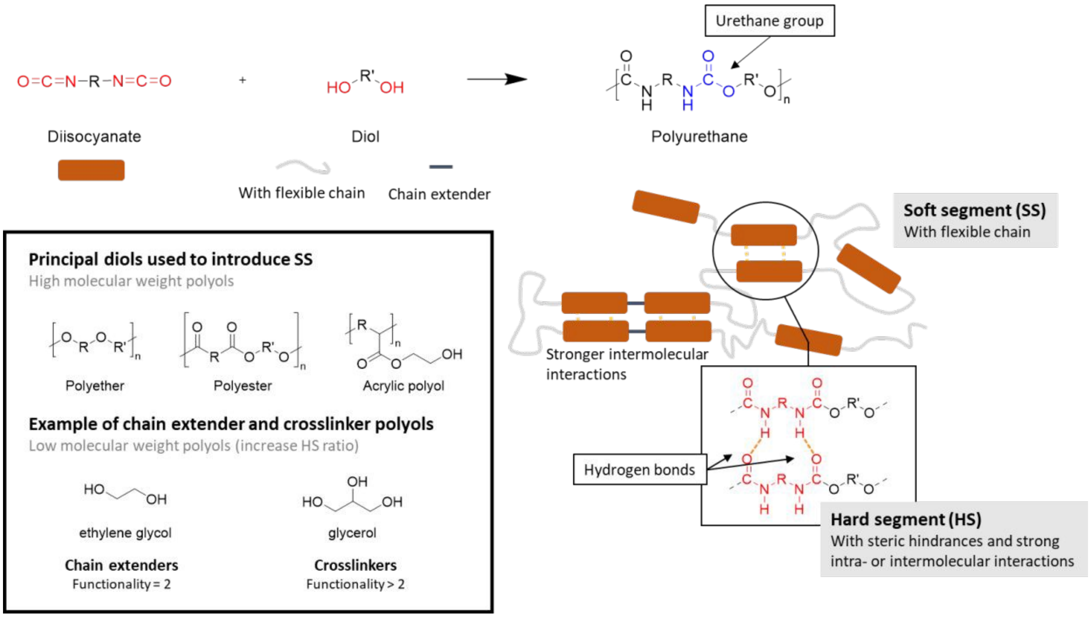
a. Synthesis of PU and utilization of biobased aromatic compounds as polyols

PUs are characterized by the presence of urethane bonds. They are synthesized from the reaction between an isocyanate and a polyol that contain respectively two or more isocyanate groups and hydroxyl groups. PU are multiblock copolymers that consist of alternating soft segments (SS) and hard segments (HS). The choice of appropriate monomers allows the SS/HS ratio to be modulated, giving polyurethane properties that can be varied. Polyols with high molecular weight are mainly used to introduce SS thanks to the presence of flexible chain that have sub-ambient glass transition temperature (T_g) where molecules that introduce HS have higher T_g (137). A wide variety of polyols are commercially available for this purpose. The most common are polyesters, polyether and acrylic polyols (135). An overview of polyurethane synthesis features was proposed Scheme 29.



Scheme 29: overview of polyurethane synthesis features (137) [5,6]

Isocyanates are mostly responsible for the HS as they add rigidity to the material due to steric hindrances or strong intra- and intermolecular interactions, such as hydrogen bonds **(137)**. The range of commercially available isocyanates is more limited than for polyols. Aromatic diisocyanates such as toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) are widely used in PU synthesis due to their reactivity and their impact on the properties of the material (138).

Low-molar-mass diols can also contribute to the HS and act as chain-extenders (functionality *f* = 2) or cross-linkers (*f* = 3 or more) (137). In particular, the addition of a cross-linker with several hydroxyl groups increases the proximity between the urethane groups, thereby strengthening the interactions between the chains. Aliphatic low-molar-mass diols are usually chosen for the synthesis of PUs, such as ethylene glycol and 1,4-butanediol (BDO). However, it has been shown that cyclic or aromatic low-molar-mass diols can improve packing and decrease the mobility. The resulting structures are mechanically strong, thermally stable and fire resistant compared with those obtained with aliphatic diols **(135)**.

In a sustainable development context, efforts are made to use biobased monomers for the synthesis of PU. Biobased isocyanates have been reported in the literature but their use on a larger scale is still limited because of the high costs of their synthesis as they didn't naturally exist (136). The industry has therefore turned more towards the production of biobased polyols. These molecules are often used as crosslinkers due to their multifunctional behavior. The majority of the polyols on the market are aliphatic polyols derived from triglycerides, which are naturally abundant and economically competitive with petrochemical-based polyols. The synthesis of aromatic biobased polyols is still very limited on an industrial scale (139).

The use of abundant resources such as lignin, tannins and CNSL derivatives open up interesting perspectives for the synthesis of biobased aromatic polyols. Lignin is one of the most abundant organic materials, with more than 50 million tons estimated each year (140). Furthermore, its use in PU synthesis has two main drawbacks due to its complex structure: the difficulty to obtain molecules with homogenous reproducible characteristics and their poor compatibility with other raw materials (141). The global production of cardanol has been estimated at 800 kt/year in 2022 (142). Although its unsaturation composition may differ depending on the geographical origin of the CNSL, it is a small molecule that can be easily modified to obtain a homogeneous raw material. The presence of the alkyl C15 chain has also been studied to improve compatibility. However, cardanol is monofunctional and needs to be functionalized before using it as a polyol in PU synthesis (40). In particular, cardanol can be easily modified to obtain hydrogenated cardanol. Sakulsaknimitr *et al.* (143) synthesized PUs starting from a cardanol-based polyol and hydrogenated cardanol-based polyol. The presence or absence of double bonds does not appear to influence the thermal properties of the material. No studies have been carried out on the influence of double bonds in cardanol-based polyol on the mechanical properties of resulting PUs. Depending on the chemical modification of cardanol, it has been reported that both elastomers (144) and semi-crystalline (107) polyurethanes can be obtained. By adjusting the hydroxyl equivalent weight (HEW) and the functionality of the polyols produced, it is also possible to modulate the rigidity and cross-linking density of the material. Mythili *et al.* (145) found that PUs using cardanol-based phenolic polyols can lead to a higher thermal stability and better mechanical strength. Different cardanol/formaldehyde ratios were used: the more cardanol in the resin, the better the properties of the PU. However, no characterization of the molecular weight of these polymers was carried out, so it is not possible to draw any real conclusions. They attributed that to the presence of a high cross-linking in the material. As a biphenolic compound, cardol is potentially suitable as a starting material for the production of PU. Moreover, there are no articles on this subject, probably because of its low availability.

b. Cardanol-based polyols in polyurethane foams (PUFs)

PUFs are polyurethanes that consist of a solid phase and a gas phase. The formulation of this type of material is relatively complex, mainly composed of polyol, isocyanate, blowing agent and surfactant. PUFs can be rigid or flexible depending on the cell structure of the foam which is highly determined by their formulation. The formation of the foam is possible thanks to the presence of a blowing agent, usually water, which produces CO_2 by reacting with isocyanate. Surfactant plays important role in foam stabilization. Polyols are mainly used to introduce SS in PUF where isocyanates bring rigidity. They are several characteristics of polyols

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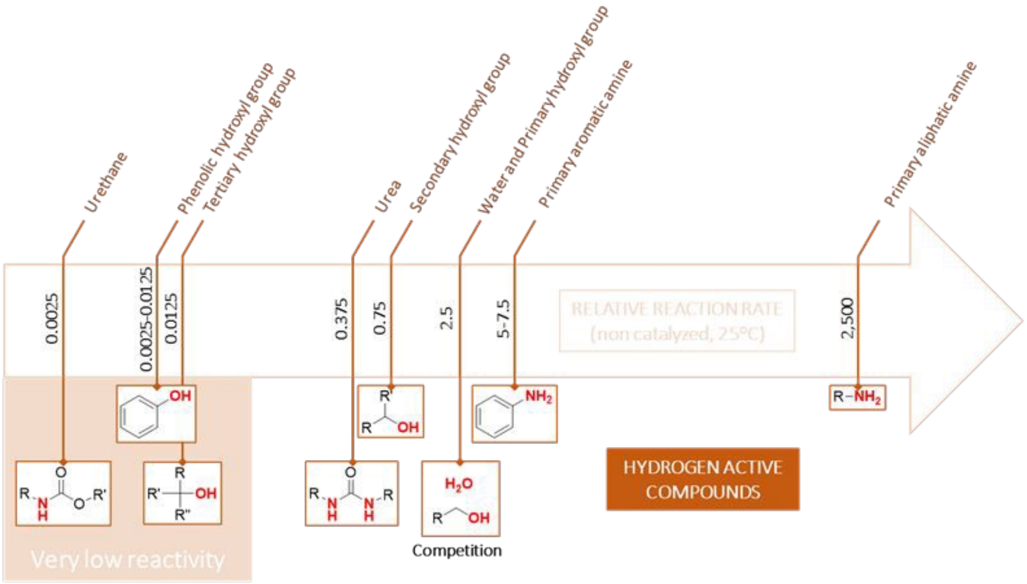
that influence the flexibility of the resulting material. The main characteristics are reported in the Table 1.

Table 1: properties of polyols used as precursors of PUF (146, 147)

PUF type	**Rigid**	**Flexible**
Hydroxyl value (mg KOH/g)	200-800	15-100
Acid value (mg KOH/g)	0.05-0.1	0.05-0.1
Functionality	2-8	2-3
Molecular weight (g/mol)	300-1000	3000-6500
Viscosity (Pa.s)	2-50	0.2-20

To obtain a foam with a homogeneous structure and good mechanical properties, polyols containing primary hydroxyl groups are generally used. In fact, there is a competition between the formation of urethane bond with primary alcohol and CO_2 as they have similar reactivity (Scheme 30) With secondary hydroxyl group, as their reactivity is lower that of the water, the formation of urethane bonds will be slowed down and more urea will be produced.

Furthermore, the use of polyols with tertiary hydroxyl or phenolic groups is not envisaged due to their very low reactivity. For this purpose, phenolic group of cardanol was modified by alkoxylation to produce primary or secondary alcohols.(82, 86, 90, 91, 111, 113, 114). However, Suresh *et al.* (86) made two polyols by peracid oxidation of cardanol double bonds and one of them was epoxidized with epichlorohydrin at phenolic group and then hydrolyzed in alcohol. Results showed that characteristic times were not so different. Mechanical properties appear to be altered with the modification of the phenolic group: foam density increases by 7 kg/m^3 and compressive strength by 15 kPa. These increases can be explained by the greater reactivity linked to the modification of the phenolic group, but also by the higher functionality of the polyol, which increases the crosslinking density. Polyol containing phenolic group display two glass transition temperatures due to the heterogeneous hydroxyl nature.



Scheme 30: Relative reactivity of different alcohols, amines or other N-H containing groups against isocyanates (147)

A polyol with low acid value is required because the acid properties can reduce the activity of the tertiary amines, which are used as catalyst especially for isocyanate-water reaction (147).

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Then, using modified cardanol by thiol-ene reactions can increase the rise time of the foam due to unreacted thiol remaining in the monomer structure as shown Shrestha *et al* *(91)*. This acid behavior can also affect the cellular structure of the foam because it disturbs the balance between gelling reaction and gas formation: closed-cell content is 10% lower for the PUF using polyol with 13.47 mg KOH/g acid value and the cell size is higher. The glass transition temperature (T_g), unlike the mechanical properties, also seems to be affected, with a decrease of almost 20 °C compared to the foam obtained with practically the same characteristics and an acid value of 0.79 mg KOH/g. This property was not discussed in this article and no other publication seems to deal with this subject in the field of PUFs.

On the contrary, Mannich modified cardanol (111, 113, 114) are very commonly used in foam formulation because they are extremely reactive in the foaming process due to the presence of tertiary nitrogen, which helps catalyze the isocyanate-water reaction. Huo *et al.* (82) reported other auto-catalytic polyols by introducing a tertiary amine through epoxide ring-opening with amines and hydrosilated unsaturated alkyl chain bonds using hexamethyltrisiloxane (HMTS), which exhibited similar properties. In addition, it appears that HMTS was introduced to increase the catalytic effect of the polyol and decrease its viscosity (148). However, no comparison between the polyol viscosities containing or not organosilicon and properties for PUF production was realized in their studies. Nevertheless, when the acid value of the polyols formed via a thiol-ene reaction was suitable, the characteristic duration of a PU foam and the mechanical properties are comparable to those obtained with tertiary nitrogen containing polyols.

The presence of aromatic ring in cardanol structure was also considered to be of interest in PUFs as it can provide a flame-retardant effect, particularly as it allows the char layer to expand (146). Zhang *et al.* *(114)* showed that without any flame retardant (FR), polyol from cardanol could have 22.5 % Limiting Oxygen Index (LOI). This value can also be correlated to the potential melamine moiety and is higher than that of other non-flame retardant PUFs, which is around 19%. It can be really useful in PUFs formulation as the addition of FR can alter its properties, such as thermal conductivity and cell structure (149).

Cardanol-based polyols described in the literature (82, 86, 90, 91, 111, 114) for PUF synthesis are mostly low molecular weight molecules, below 1000 g/mol, leading to rigid PUFs. Polyether or polyester from cardanol have not been used in the synthesis of polyurethane. Shrestha *et al.* (91) reported cardanol-based novolacs with 2 to 4 units of cardanol that are one of the polyols with the higher molecular weight tested. They mentioned that polyols with more than 2 units are relatively viscous. For this reason, they limited themselves to two polyols with 2 units for PU synthesis. However, the difference of viscosity with the monomer having 3 units is not significative. Modification of the phenolic group with propylene oxide increase their viscosity, a difference of about 50 Pa.s with approximatively the same HEW and acid value. The mechanical properties should be affected by an increase of the viscosity because the density and the compression strength at 10% strain have increase respectively of about 20 kg/m^3 and 100 kPa. In addition, this difference in viscosity can be explained by the cardanol/formaldehyde ratio in the preparation of the resin used as a polyol. In fact, a greater quantity of formaldehyde can cause alkylation of the aromatic ring of cardanol and increase its molecular weight. This data could have been interesting to explain this phenomenon.

In conclusion, cardanol-based Mannich polyols seem to be the most widely used for the PUFs because highly reactive and weakly viscous. Comparable results such as thermal and

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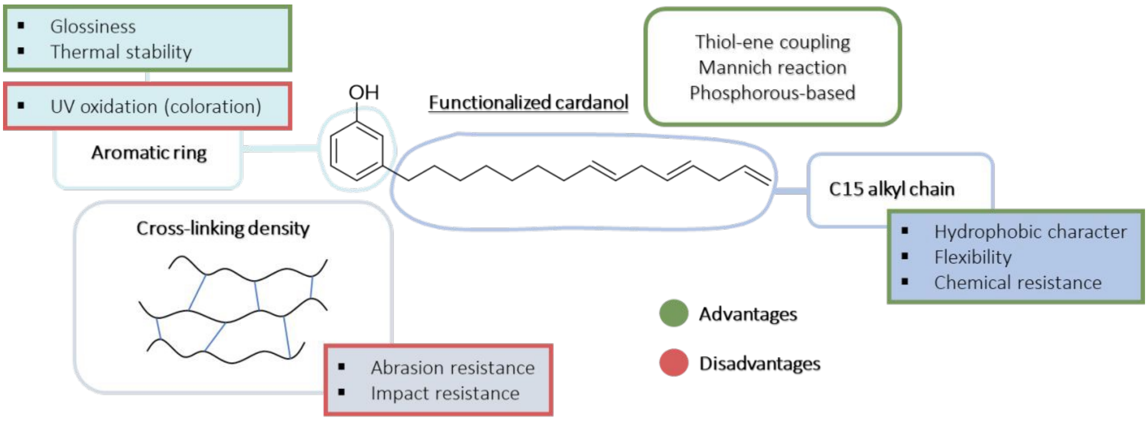
mechanical properties were obtained with other cardanol-based monomers. As a result, no real trend regarding the preferred structure exists but the use of polyols containing a tertiary nitrogen may avoid the use of an external catalyst. If the polyol viscosity is low, adding cardanol units can increase its viscosity to improve PUF properties. Monomer purity also seems to be an important factor, as the presence of residual reagents such as thiols can interfere with foam formation. However, the results reported in many publications are difficult to compare because of the formulation. Some important data, such as average cell diameter, closed-cell content, characteristic times, thermal conductivity, glass transition temperature, compressive strength and fire resistance of the foams are not recorded. In addition, the results are sometimes not sufficiently discussed to better understand the impact of polyol parameters on thermal and mechanical properties of the PUF. All the publications deal with the formulation of rigid foam, in part due to the use of low molecular weight polyols. It would therefore be interesting to study the synthesis of flexible PUFs using, for example, a polyester or polyether synthesized from cardanol.

c. Cardanol-based polyols in coatings

Polyurethane coatings are attracting a great deal of interest due to their ability to offer improved abrasion resistance, greater hardness, enhanced chemical resistance and superior mechanical properties compared with polyester and polyesteramide coatings (150).



Scheme 31: Summary of the coating properties enhanced by cardanol-based polyol according to the present literature.

Polyols are used as a base binder for the preparation of polyurethane coatings. Different polyols from natural and renewable resources have already been studied[1]. Among the main CNSL compounds, only cardanol seems to have been considered as a biobased polyol from CNSL. A wide variety of polyol based cardanol structures are used in the PU coating manufacturing due to these multiple reactive sites (1, 83, 87, 100, 101, 151-153). Scheme 31 summarizes the advantages and disadvantages of employing cardanol-based polyols in the synthesis of coatings, in line with current literature.

The first advantage of using CNSL compounds for coating applications is their long aliphatic chain. Indeed, the C15 chain gives the film a rather hydrophobic character, enhancing its flexibility, chemical resistance and mechanical properties such as tensile strength and elongation, even with high cross-link density (100). Actually, high cross-link density can be interesting for films having a certain hardness, chemical and water resistance (152). This cross-link density can be modulated by increasing the number of hydroxyl functions in the polyol structure coming from modified cardanol. However, too much cross-link density can lead to a loss of abrasion resistance because of the hardness of the surface. Impact resistance can also be reduced but this negative effect can be balanced by the presence of the long aliphatic chain. The aromatic ring in cardanol structure also confers interesting properties to the film, such as glossiness and thermal stability (151). Moreover, depending on its final application, this can be a disadvantage, as the color of the film can be altered by prolonged exposure to UV light.

The modification of the cardanol structure can result in different properties. Wazarkar and Sabnis (151) demonstrated that polyols based cardanol modified by thiol-ene coupling can have better mechanical, chemical, thermal and anticorrosive(1) properties than different PU coatings based on commercial acrylic. Furthermore, the curing temperature of the film with the cardanol-based polyol seemed to be 10 °C higher than that with commercial acrylics. This may be caused by the low reactivity of the phenolic group. However, the curing can be carried out at lower temperatures, but the reaction time can be affected. Asif *et al*.(112) cured their Cardanol Mannich polyol containing phenolic group film at room temperature for 48 hours. Wang et al. (83) investigated another cardanol-based polyol by thiol-ene/thiol-epoxy. It was shown that converting phenolic hydroxyl into aliphatic hydroxyl improved the thermal stability of the resulting PU, a difference of more than 40 °C was achieved.

Polyols containing phosphorous also appear to increase the mechanical performance of the film and its anticorrosive properties (1, 153). This contribution to the structure of cardanol can also confer flame-retardant properties (87, 153). It has been reported in the literature that hyperbranched PUs could easily catch fire (131). It would therefore be interesting to include flame retardant tests to the study of PU coatings as they have found numerous applications in high performance coatings such for automotive appliance and wood industries (150).

Athawale and Shetty (154) studied the influence of NCO/OH ratio on the coating properties of a cardanol-based PU coating. The diol used reacted with TDI and IPDI. Independently of the isocyanate used, more than 1.6 NCO/OH ratio leaded to inflexible, less glossy and slow drying coating. Otherwise, using one or another isocyanate impacted other parameters such as the hardness of the film and its chemical resistance. In fact, the choice of the isocyanate also plays a role in the final properties of the PU coating. If the mechanical properties and the hardness of the film are only slightly modified, its thermal stability can be significantly changed. Using cyclic isocyanate instead of aliphatic isocyanate can increase the degradation temperature of the film by up to 50 °C. There is also an increase in T_g but this is less relevant, rising by a maximum of 6 °C (112). Consequently, it is difficult to deduce a trend in the thermal stability of the coating with regard to articles using a cardanol-based polyol for the process as there is no one isocyanate that is preferentially chosen.

d. Conclusion

Cardanol-based polyols have been studied in the synthesis of PU as aromatic biobased compounds. The presence of the aromatic ring gives mechanical strength to the PU structure, improves its thermal stability and fire-resistant properties. These cardanol-based monomers have been widely used to produce rigid PU foams. Various structures were obtained, although the current state of the art does not allow us to observe any trends in the use of a particular monomer. They generally contain more than two hydroxyl groups, which help to increase crosslinking density and then improve the mechanical properties. The phenolic group is usually functionalized to improve the reactivity of the monomer. In addition, the complexity of the foam formulation and the lack of basic characterization of PU foams in some cases make it difficult to interpret the results. Standard characterizations should be at least the measurement of material density, cell size and density, tensile and compression tests and thermal analysis by TGA and DSC. Regarding the flammability of PU foams, fire resistance tests could be added such as LOI measurement. In coating applications, cardanol-based PU offers advantages such as chemical resistance, thermal stability or surface properties. Even there, the number of articles is not sufficient to give a trend on the type of monomers preferred and the lack of homogeneity of the characterizations makes comparison difficult. Here, the presence of the aromatic ring can be problematic if yellowing due to oxidation needs to be avoided. One idea would be to use cardanol-based monomers in which the aromatic ring has been hydrogenated.

2) Applications and properties of polyesters from CNSL-based polyols

In a context of sustainability and the effort to prevent the accumulation of plastic waste, the synthesis of aliphatic polyesters appears to be a promising solution owing to their ability to easily degrade under the external conditions. The most studied degradation pathways for this type of polymer are enzymatic hydrolysis (155, 156) and microbial degradation (157), known as composting. The biodegradation properties of polyesters result from the capacity of ester bonds to undergo hydrolytic cleavage (158). Furthermore, aliphatic polyesters represent only a small part of the world market compared with aromatic polyesters. In 2022, aliphatic polyesters with poly(lactic acid) (PLA)(159) represented 0.35 Mt when aromatic polyesters with poly(ethylene terephthalate) (PET) (160) represented 25 Mt. In fact, aromatic polyesters are widely used because of their excellent thermal and mechanical properties. If they are usually resistant against microbial attack in mild conditions, many works have been done to improve their biodegradable ability such as developing aliphatic-aromatic co-polyesters. Then, the use of renewable resources to produce aromatic polyesters that can compete with PET in terms of properties is challenging. The addition of cardanol-based compounds would appear to be of interest in the development of this type of material. Moreover, Han *et al.*(161) mentioned that improving the chain mobility could contribute to biodegradability. Therefore, adding C15 alkyl chain could potentially aids this objective. In this part, the use of cardanol-based polyols in different polyester applications and their impact on the material properties were discussed.

a. Synthesis of polyester and utilization of biobased aromatic compounds as polyol

Polyesters are characterized by the presence of ester bonds, generally obtained by reacting a diol with a dicarboxylic acid. Polyesters are obtained by step-grown polymerization, and more specifically by polycondensation since water molecules are produced during the esterification reaction. In step-grown polymerization, the monomers first react together to form dimers, which then react together to form tetramers, and so on until long-chain polymers are obtained as shown in Scheme 32. High molecular weights are usually difficult to obtain with this type of polymerization, given the Carothers equation. In fact, high conversion rate is

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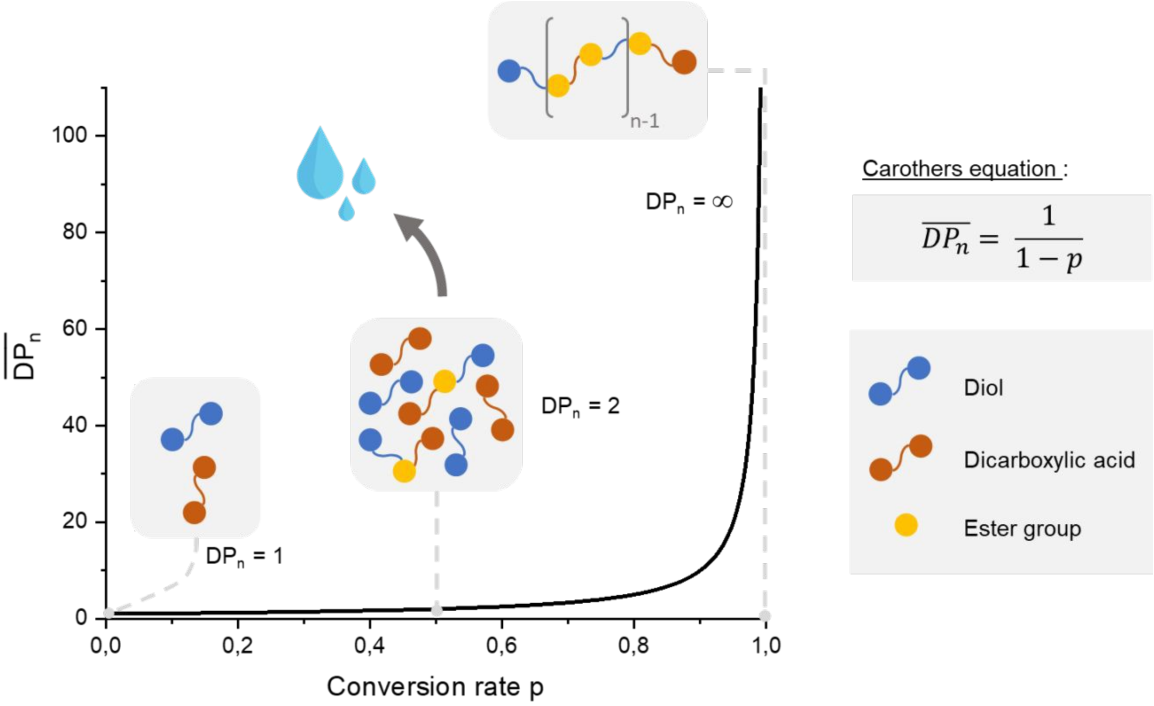
required to promote mass growth, implying perfect stoichiometry and the use of monomers with a high degree of purity.



Scheme 32: Explanation of step-grown polymerization with Carothers equation – case of linear polyesters using equimolar quantities.

Polyesters can be divided into aliphatic polyesters and aromatic polyesters. Aliphatic polyesters represent one of the most important class of biodegradable polymers and have received attention from both industry and academia, in particular for biomedical applications **(162)**. Biodegradability is attributed to the ability of ester bonds to be hydrolyzed. However, the thermal and mechanical properties of these polyesters are not always suitable for all applications, especially their low melting point. Thus, the incorporation of aromatic rings into the polymer helps to improve these properties. As shown before, PET is the most used aromatic polyester as it is widely in the textile and packaging industries and is not considered as a biodegradable polyester (163). On the one hand, a significant amount of research is being carried out into the physical and chemical recycling of PET (164). Liu *et al.*(165) performed glycolysis of PET waste with a cardanol-based diol which has interesting properties for the synthesis of UV-curable coating. On the other hand, efforts are being made to find biobased alternatives to PET (162). In this last case, it is the dicarboxylic acid that is tending to be replaced, but it is also possible to add rigidity to the structure using a biobased aromatic diol. Lignin derivatives such as vanillin are increasingly being studied as a source of bio-based aromatics. Like CNSL-compounds such cardanol, it needs to be functionalized to obtain a diol. Moreover, the production of vanillin from lignin is still low compared with the production of petroleum-based vanillin where cardanol can easily obtained from natural feedstocks (166).

Among CNSL compounds, cardanol is the most widely CNSL-compounds used in polyester. Only one paper **(71)** described the synthesis of polyester from cardol and none from anacardic acid. More specifically, polyesters were synthesized by polycondensation in solution using two distinct acyl chlorides, adipoyl chloride and terephthaloyl chloride, and cardol as the diol reactant. They did not succeed in obtaining high molecular weight. However, the lack of data does not allow to really conclude. As mentioned above, the reactivity of the phenolic hydroxyl

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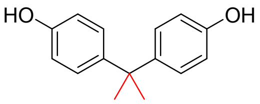
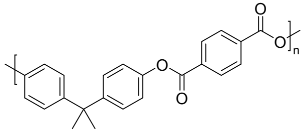
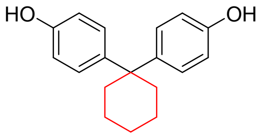
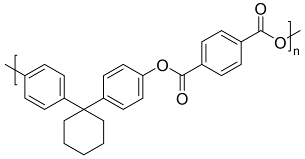
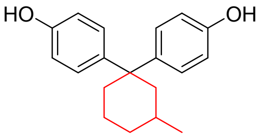
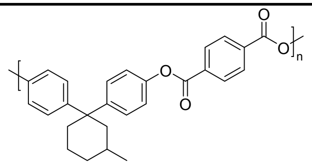
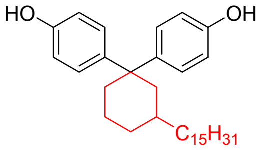
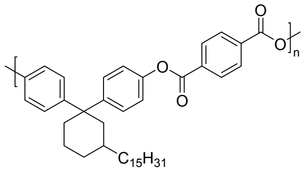
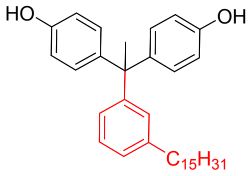
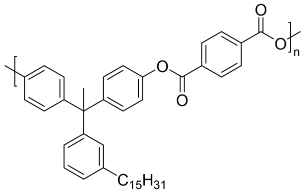
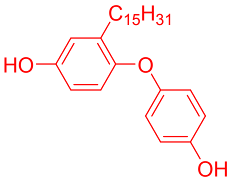
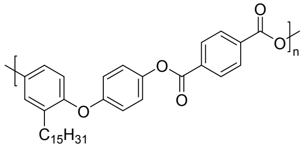
group is relatively low, which is why it is often functionalized. It would therefore have been interesting to carry out additional analyses, such as NMR and SEC analysis, to monitor polymerization reaction progress. In this way, it would have been possible to compare the reactivity of the cardol phenolic hydroxyl groups towards polycondensation. Using resorcinol and adipoyl chloride to synthesize polyester, Goto and Abe (167) succeeded in obtaining a Mn higher than 70,000 g mol^{-1}. Given the structural similarities between resorcinol and cardol, this seems promising for the synthesis of polyesters using cardol as a diol. Moreover, Makame et al. found their cardol-based polyesters to be poorly soluble in chlorinated hydrocarbons whereas Goto and Abe showed resorcinol-based polyesters are soluble in them. This result is surprising as it has been reported in several articles (168-171) that the presence of the C15 alkyl chain improves the solubility of aromatic polyesters in commonly used organic solvents. Indeed, Wadgaonkar et al. worked (169-171) on the modification of bisphenol A (BPA) with cardanol derivatives, especially 3-pentadecyl, in particular hydrogenated cardanol: 3-pentadecylphenol and 3-pentacyclohexanone. They studied their impact on the solubility and thermal properties of the synthetized polyesters. The solubility tests and thermal analyses of the polyesters obtained from modified-BPA and terephthaloyl chloride are given in Table 2. They showed that adding a cardanol segment into the molecule allowed synthesized polyesters to be solubilized in the usual organic solvents such as chloroform and tetrahydrofuran. Furthermore, the addition of this segment results in a significant drop of the glass transition temperature T_g due to the internal plasticizer effect of the long aliphatic chain of the cardanol derivatives. A lower thermal stability can also be observed with the introduction of the C15 chain, regarding the initial decomposition temperature T_{onset}. These trends were also confirmed when they produced copolyesters with BPA and cardanol derivatives modified BPA as diols. More specifically, they demonstrated that the solubility in common organic solvent can be significantly improved with only 15 mol% of cardanol derivatives modified BPA

Table 2: Properties of the polyesters obtained from terephthaloyl chloride and modified-bisphenol A

Starting material for BPA-modification	Diol monomer	Resulting polyester	Solubility^a	M_n^{b} (kg/mol)	T_{onset}^{c} (°C)	T_g^{d} (°C)	Reference
BPA			–	–	487	210-234	**(169)**50,52
Cyclohexanone			–	–	475	–	**(169)**
3-methylcyclohexanone			–	–	460	263	**(169)**
3-pentadecylcyclohexanone (cardanol derivatives)			Dichloromethane, Chloroform, Trichloroethylene, Tetrahydrofuran	58.4	438	94	**(169)**
3-pentadecylphenol (cardanol derivatives)			Dichloromethane, Chloroform, Tetrahydrofuran, Pyridine, *m*-Cresol	48.5	370	82	**(170)**

3-pentadecylphenol (cardanol derivatives)			Dichloromethane, Chloroform, Tetrahydrofuran, *m*-Cresol, Pyridine	48.3	–	47	**(171)**

[a] solubility of the polyester at room temperature in various organic solvents at 3 wt% concentration

[b] measured by GPC in chloroform, polystyrene was used as a calibration standard

[c] initial decomposition temperature measured by TGA

[d] glass Transition temperature measured by DSC

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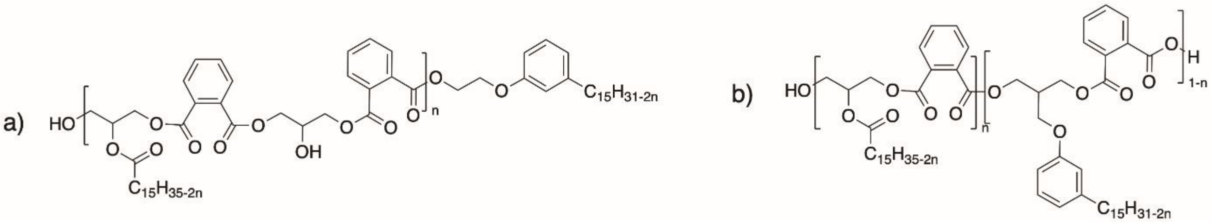
b. Cardanol-based polyol in alkyd resins

Alkyd resins are a specific class of polyesters modified by unsaturated fatty acids, which are widely used as binders in paints or varnishes formulations (172). They are synthetized by polycondensation between polyols and polyacids (173, 174). In those polymers, polyacids used to exhibit a functionality of 1 or 2 whereas polyols may have a wide range functionality from 1 to 4. The greater the functionality of the monomers, the higher the increase in mass and therefore the growth of the chains was rapid. CNSL compounds, are compatible with alkyd resins thanks to their hydrophobic alkyl side chain but those compounds are still very little used in these polymers. A recent article has reported the impact of mono- and difunctional hydroxyl cardanol monomer in the synthesis of novel alkyd resins (175) (Scheme 33). Denis *et al.* have demonstrated that the cardanol monomers increased the renewable carbon content (up to 12 %) as well as the thermal stability of the alkyd resins. The hardness also increased with the amount of aromatic ring provided from cardanol. Nevertheless, the color of alkyd resins got darker and darker with the increasing amounts of cardanol used for the synthesis, which is a limitation for the formulations of paints except for primers.



Scheme 33: Structures of alkyd resins with a) monofunctional hydroxyl cardanol and b) difunctional hydroxyl cardanol by Denis et al. (175)

c. Cardanol-based polyester as plasticizer for PLA

An example of the use of cardanol-based polyester as plasticizer for the formulation of PLA films was reported by Vallin *et al.* in 2023 (176). Polyesters, from dimethyl succinate (DMS) or dimethyl adipate (DMA), were synthesized using an enzyme catalytic polycondensation by trans-esterification route or a metal-catalyzed polycondensation. A comparison of these two methods showed that the use of a metal catalyst enables higher M_n to be achieved, but results in a very pronounced coloring of the samples. However, the number average molar mass is still low for a polymer, around 4,000 g mol^{-1}. This may be due to the type of agitation chosen, as magnetic agitation does not allow proper mixing when viscosity rise, especially in bulk polycondensation, or because of the too low reaction temperature. Then, the dark color of the metal-catalyzed sample could be improved with an adapted purification process. In fact, they did not mention any purification processes such as precipitation. In terms of thermal properties, their cardanol-based polyesters have a T_g around -40 °C and a decomposition temperature around 380 °C with DMS as the diacid and respectively -60 and 400 °C using DMA. Different PLA films were formulated by solvent casting with 2-10 % w/w of cardanol-based polyesters inside. The glass transition of the different samples drops with the percentage of polyester used. However, this decrease is fairly slight, about 10 °C. Regarding the mechanical properties, it can be shown that the incorporation of polyester has a significant impact on the ability of the film to elongate before breaking (Scheme 34). With 10 % w/w, PLA film with DMA-based polyester plasticizer gave best higher elongation at break. Otherwise, this incorporation decreases the Young modulus and the tensile strength. These results are in

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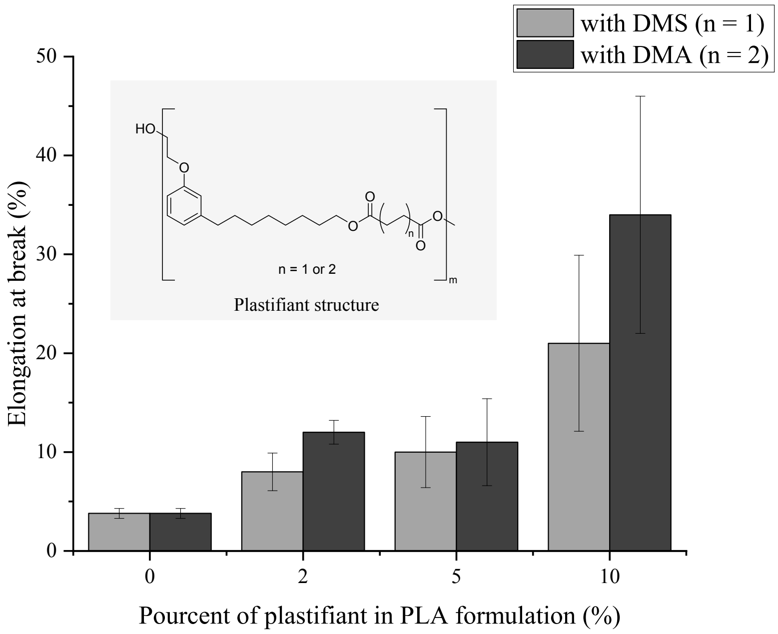
agreement with the literature (177). In fact, plasticizer provides higher free volume between the polymer chain and therefore enhances chain mobility and film flexibility.



Scheme 34: Influence of the percentage of plasticizer in the PLA film formulation on the elongation at break

d. Conclusion

There are very few articles on the synthesis of polyesters from CNSL-based polyols. This can be explained by the recent interest in CNSL derivatives and also by the difficulty encountered in performing polycondensation. The development of cardanol-based monomers for polyester synthesis has been widely studied, where they are used to drastically improve the solubility of bisphenol A-based polyesters as an example. These monomers can also be added in the formulation of alkyd resins to enhance the thermal stability and increase the renewable carbon content. An example shows the possibility of using a low molecular mass cardanol-base polyester as a plasticizer for PLA. Finally, there is still a lot of researches to be done regarding the development of polyesters based on cardanol and also cardol in order to obtain new aromatic biobased polyesters. The use of polyesters for the synthesis of polyurethanes could also be considered.

3) Applications and properties of miscellaneous polymers from CNSL-based polyols

CNSL-based polyols are mainly used for the polymerization of polyurethanes or polyesters as previously described. However, some CNSL-based polyols were also reported in the literature for the development of other polymers such as polyethers or phenolic foams. More *et al.* (178) synthetized a cardanol-based bisphenol (Figure 5A) for the synthesis by polycondensation of poly(ether ether ketone) (PEEK) and poly(ether ether ketone ketone) (PEEKK).

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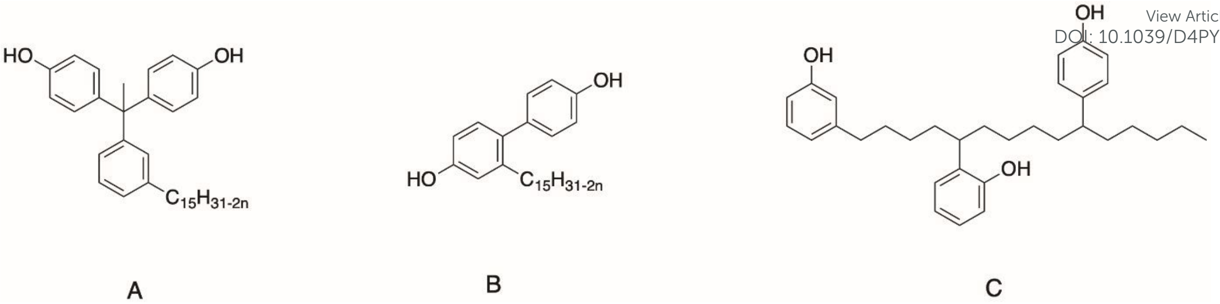

Figure 5: Structure of cardanol-based bisphenol used in A) polycondensation of PEEK by More et al.[178] *B) polycondensation of poly(arylene ether) by Tawade et al.* [179] *and C) in phenolic foam by Jing et al.*[97]

Tawade *et al.* (179) introduced another cardanol-based bisphenol (Figure 5B) in the polycondensation of PEEK.

It is well-known that conventional PEEK derived from bisphenol-A or 4,4'-biphenol are insoluble in common organic solvents. In this study, the authors demonstrated that PEEK containing pendant pentadecyl chains were soluble in common organics solvent such as chloroform, dichloromethane, tetrahydrofuran and pyridine at room temperature. The good solubility of these polymers in both studies may be attributed to the pendant pentadecyl chains which led to increase the free volume and then, it was easy for the solvent to penetrate through the polymer chains. Thus, PEEK and PEEKK could be considered as good candidates for applications such as gas separation and microelectronic devices where the combination of solubility and good thermal properties is desired. Furthermore, a decrease of the Tg of the polymers was observed and may be attributed to the pentadecyl chain in polymer backbone acting as "internal plasticization". Moreover, a large difference between the T_g (35-78 °C) and the initial decomposition temperature (378-455 °C) was observed, thus offering PEEK and PEEKK a wide processing window.

Jing *et al.* (97) modified cardanol with a phenol to obtain a bisphenol (Figure 5C) which was then used to synthetize phenolic foams with paraformaldehyde. The addition of cardanol increased the viscosity of prepolymer, which was obvious when the dosage of cardanol was over 5 wt %. Moreover, phenolic foams with 5 $_{wt}$% cardanol had slight improvement on the mechanical performance. Noticeably, phenolic foams modified by 10 $_{wt}$% cardanol increased by 22 % in flexural strength and 28 % in bending modulus compared to pure phenolic foams, which indicates that the incorporation of cardanol improved the toughness of phenolic foams.

4) Applications and properties of surfactants from CNSL-based polyols

Surfactants are amphiphilic molecules which means they are composed of both lipophilic and hydrophilic parts (180-182). They are chemical compounds that decrease the surface tension or interfacial tension between two liquids, a liquid and a gas, or a liquid and a solid allowing the solubilization of two immiscible phases. Moreover, depending on the nature of the hydrophilic part, surfactant compounds are classified into four groups: non-ionic (the molecule has no charge), anionic (hydrophilic part negatively charged), cationic (hydrophilic part positively charged), and zwitterionic (hydrophilic part has a positive charge and a negative charge, the overall charge is zero). Consequently, they have a wide range of applications such as detergent, solubilizing agent, foaming agent, wetting agent, dispersing agent (to avoid flocculation), emulsifying agent, or antibacterial agent (183, 184). In the literature, numerous

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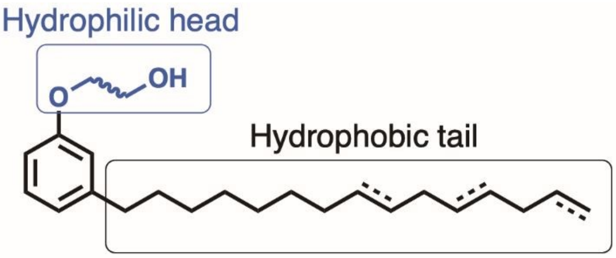
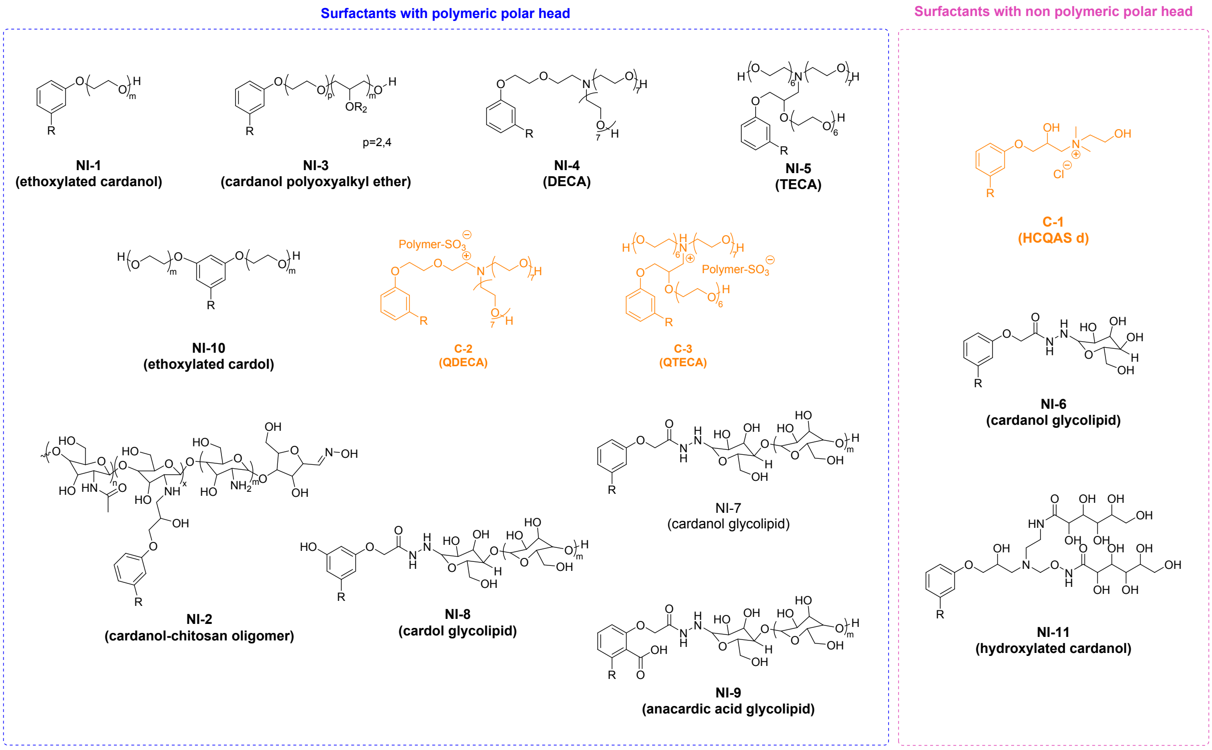
patents or articles have reported the synthesis of CNSL-based surfactants and a recent review lists them [24]. They have found various uses in many fields such as detergency, polymerization emulsion, enhanced oil recovery or antimicrobial applications. In the following section, only CNSL-based surfactants with hydroxyl functions are reported. Scheme 35 presented a general structure of cardanol-based surfactant with hydroxyl function. It should be mentioned that natural cardanol cannot be used as surfactant, the phenol had to be modified to obtain a polar head.



Scheme 35: general structure of cardanol-based surfactant with hydroxyl function.

The structures of CNSL-based surfactants are presented in Scheme 36. The relationships between structure and properties are discussed as well as the applications when they are mentioned by the authors. Critical micellar concentration (CMC) and surface tension at CMC (γ_{CMC}) are important parameters which could be discussed to analyze the structure-property relationship. Moreover, the nature of the hydrophilic group as well as the length had an influence on the previously mentioned parameters.



Scheme 36: Structures of polyol CNSL-based cationic (C) in red and non-ionic (NI) in black surfactants

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a. Wetting agent

Non-ionic ethoxylated cardanol-based surfactants were also used in cement formulation as wetting agents, leading to the formation of fine, stable air bubbles to reduce internal pressure and thus avoid cracks, and also to improve its maneuverability (185). Tafardar *et al.* (186) claimed a cement composition containing ethoxylated cardanol surfactant for use in an oil-contaminated well (NI-1 Scheme 36). A low concentration of surfactant was introduced in an oil in water emulsion (70/30). The compressive strength is an important parameter studied in cement applications and the authors demonstrated that ethoxylated cardanol surfactants exhibited higher compressive strengths (> 1140 psi after 24 h) than a commercial ethoxylated phenol surfactant (Stabilizer 434^{TM}) (1000 psi after 24 h).

b. Emulsifying agent

Chapelle *et al.* (187, 188) showed that cardanol modified with chitosan oligomer (NI-2 Scheme 36) may be used as emulsifying agent to stabilize direct oil-in-water emulsions (60/40) . The authors demonstrated that the emulsion was stable for at least 24 h with 15 µm average size droplets. Unfortunately, the CMC and surface tension were not discussed. Eventually, the authors demonstrated promising potential as new biobased emulsifier for bituminous emulsions.

c. Detergent agent

CNSL surfactants can also be used in formulation of detergency solutions (189). Different cardanol poly(oxyethylene ether) (NI-1 Scheme 36), nonionic surfactants have been studied in several patents (190-193). Wang *et al.* (190) used it in detergents applications to reduce the surface tension of the solution with various ethylene oxide repetitive units (from 1 to 50). The authors demonstrated that the length of the poly(oxyethylene ether) (POE) head of those nonionic surfactants had an influence on the cloud point, temperature above which a sample becomes turbid, due to phase-separation between a rich-phase surfactant and the solution. This phenomenon is due to PEO chains, whose solubility in water decreases when the temperature is raised. Cloud point values of nonionic CNSL derivatives NI-1 rose from 48 to 62 °C with the number of ethylene oxide units in the polar head (from m comprised between 7 and 30). Moreover, the CMC increased with the increasing ethylene oxide number. Thereby, this study had showed that cardanol PEO had a high cloud point, a low CMC and were easily soluble in water which make them ideal for use in detergents. Nevertheless, CNSL-based PEO usually have a darker color and a pronounced smell. Therefore, it is particularly important to develop a cardanol PEO foaming agent with light color and low odor as well as strong foaming capacity. This is what Wang *et al.* (191) claimed in a recent patent three different cardanol POE with ethylene oxide number of 19, 15 and 14. Once introduced in formula of laundry detergent, they provided good foaming property. The results demonstrated that the higher the ethylene oxide number, the stronger the irritation was. Nevertheless, all the non-ionic cardanol-based surfactants claimed in this patent exhibited lower irritation compared to commercial anionic surfactant such as sodium lauryl tetradecanol PEO sulfate. Jin *et al.* (192, 193) prepared oil-in-water emulsions containing non-ionic cardanol poly(oxyalkyl ether) (NI-3 Scheme 36). They recorded the time required to observe a definite separated volume of water: the higher the time, the stronger the emulsification capability. Cardanol derivatives

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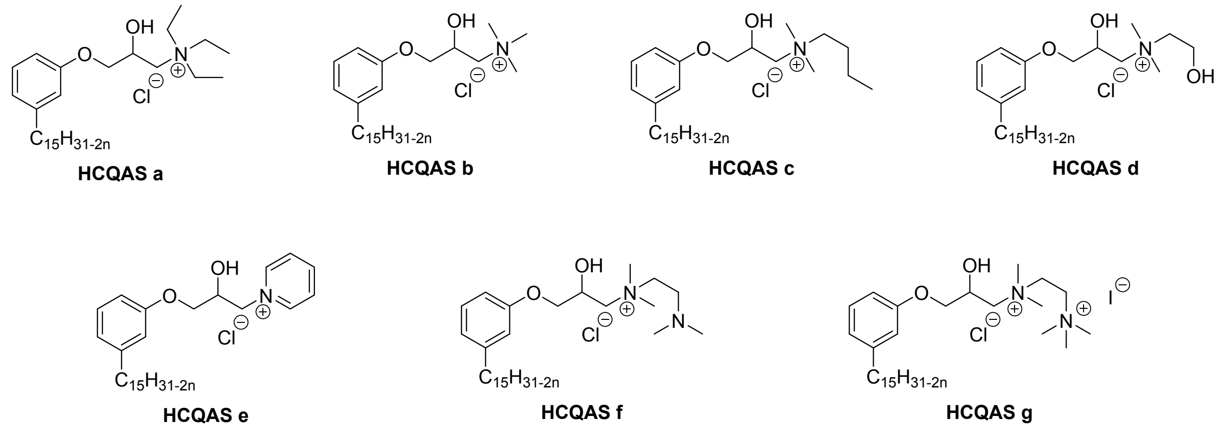
were able to stabilize O/W emulsions in the same range of time than commercial alkylphenol polyethoxylated surfactants (such as Tergitol^{TM} NP-10). A washing test on soiled cotton fabric proved that NI-3 had similar performances to petroleum-based Tergitol^{TM} NP-10.

Zhao *et al.* (194) reported the synthesis of novel hydroxylated cardanol quaternary ammonium salts (HCQAS) (Scheme 37) used in detergent applications. Different cardanol quaternary ammonium salts were studied in direct emulsion. The best emulsifying ability for paraffin oil was obtained with HCQAS d (C-1 Scheme 36) and its two hydroxyl groups which induced more hydrogen bonds with water molecules, so that more time was needed to separate it from water. Moreover, with two hydroxyl groups, HCQAS exhibited low surface tension which facilitates foamability. The authors showed that HCQAS exhibited a contact angle less than 90 ° and an excellent wettability. Moreover, detergency studies demonstrated that HCQAS exhibited better results than with standard detergent.



Scheme 37: Structures of different HCQAS used for detergent application by Zaho et al.(194)

d. Demulsifier agent

Another application of CNSL surfactants was as demulsifier agents in crude oil emulsions. Demulsifiers are used to separate emulsions, usually in the processing of crude oil. Indeed, this process produced along with significant quantities of saline water which must be removed from the crude oil prior to refining. Moreover, is most of the salt water is not removed, significant corrosion problems can arise during the refining process. Atta *et al.* (195) reported the synthesis of two novel non-ionic cardanol-based surfactants containing amine group and oxyethylene unit: the di-etherified cardanoxy amine (DECA) (NI-4 Scheme 36) and the tri-etherified cardanoxy amine (TECA) (NI-5 Scheme 36). They exhibited different degrees of solubility in water, and were used to disperse asphaltene fractions of heavy crude oil. The former observed total demulsification for Arabic crude oil/water emulsions (90/10 vol %) formulated with 50 mg.L^{-1} of DECA. On the other hand, TECA showed high demulsification capabilities (at concentration ≥ 100 mg.L^{-1}) for crude oil/water emulsions with higher water contents (50/50 vol %). The authors demonstrated that the oxyethylene repetitive unit of TECA expands and interacts with water more than DECA to affect their hydrodynamic diameters at aggregation above their CMC. The strong hydrophobic interaction of alkyl phenoxy of cardanol at the core of its micelles and the packing of oxyethylene groups at the micelle shell more for DECA are more than TECA. In this study, the DECA showed a strong tendency to irreversibly adsorb at the water-oil interface. The lower adsorption of TECA on the asphaltene surfaces turned the asphaltene surfaces to be more polar and, hence,

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decreasing its capacity to interact with heptane aliphatic solvents. The good ability of DECA to act as asphaltene dispersants facilitated the demulsification of highly stable water in crude oil emulsions with low water contents.

Ezzat *et al.*(196) synthetized cationic cardanol-based surfactants with similar structures as the study of Atta *et al.* (195) previously discussed. Quaternized di-etherified cardanoxy amine (QDECA) (C-2 Scheme 36) and quaternized tri-etherified cardanoxy amine (QTECA) (C-3 Scheme 36) were also used to disperse asphaltene fractions of heavy crude oil. The demulsification data confirmed that the QTECA and QDECA achieved high separation performances and demulsifying action reached 100 % at low concentration, 10 mg.L^{-1} for crude oil / water (90/10 Vol %) emulsion. Moreover, lower dosages of QTECA and QDECA demulsifiers showed better demulsification performance with low water content of crude oil water emulsions. Increasing concentrations of QTECA and QDECA demulsifier reduced the water separation of emulsions which may be attributed to an overdosing effect. The surface tension measurements showed that the QDECA has greater tendency to reduce the surface tension of water more than QTECA. Thus, the high reduction of the water surface tension for QDECA, and more than QTECA, confirmed the weak intermolecular interaction between ions as well as the hydrophobicity of cardanol cations. As in Atta *et al.* study, the chemical structure of QDECA is less sterically hindered than QTECA which increases its tendency to irreversibly adsorb at the water-oil interfaces. Hence, the interfacial activity of QDECA increased more than QTECA when they dispersed in the water. To conclude, the cationic cardanol-based surfactants had greater ability to reduce the surface tension and could separate water more effectively and exhibited greater tendency to disperse asphaltene perform better as demulsifier than their non-ionic analogues.

e. Antibacterial agent

Finally, some studies reported the antibacterial properties of CNSL-based surfactants. Prasad *et al.* (197) functionalized cardanol with glucose This glycolipid self-assembles to produce a gel in hydrophobic solvents and behaves as a surfactant in water by diffusion into air-water interface and reduces the surface tension of water. The authors showed that cardanol-based glycolipids NI-6 (Scheme 36) was able to disrupt biofilms formed by pathogens such as *Escherichia coli* and *Salmonella enterica* Typhimurium. These biobased products could be used for surface cleaning in hospital environments or food processing industries.

f. Miscellaneous

Otherwise, the surfactant properties of several non-ionic CNSL-based polyols were studied without giving specific applications. Franca *et al* . (198) synthetized CNSL-based surfactants through a glycosylation between cardanol (NI-7 Scheme 36), cardol (NI-8 Scheme 36) or anacardic acid (NI-9 Scheme 36) and saccharide. They demonstrated that the CMC values were low for those three surfactants. However, the concentration indicated that the aggregation behavior of alkylphenyl glycosides depends on their structural characteristics. Indeed, cardanyl oligoglycoside showed a lower CMC value followed by cardyl oligoglycoside and anacardyl oligoglycoside. Moreover, the area per molecule (A) values indicate that cardyl oligoglycosides (NI-8) are likely to form aggregates smaller than cardanyl oligoglycosides (NI-7) and anacardyl oligoglycosides (NI-9). Thus, cardyl oligoglycosides tend to shape inverted micelles whereas cardanyl and anacardyl oligoglycosides vesicles and bilayers. Tyman and

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Bruce synthetized novel polyethoxylated cardanol and cardol (NI-1 and NX-10 Scheme 36) surfactants with various number of ethoxylate (EO) units from 1 to 48 (199, 200). No specific application was mentioned but interesting analyzes were performed to compare the surfactant properties between cardanol and cardol. Moreover, the influence of the polar head length was studied as well as the impact of unsaturation of the side chains. The samples of polyethoxylated cardanol with an EO of 13 and polyethoxylated cardol with an EO of 10 exhibited the greatest reduction in surface tension. Nevertheless, polyethoxylated cardol exhibited a relatively smaller reduction in surface tension (25 Nm^{-1}) and, consequently, would be expected to be a less effective surfactant than polyethoxylated cardanol which showed a reduction in surface tension of 34 Nm^{-1}. The authors also demonstrated that polyethoxylated cardanol and its saturated analog appeared to be similar in surfactant behavior. However, biodegradation studies showed that hydrophobic chains with unsaturations were beneficial to biodegradation. Thus, even if the authors have not given precise applications for these surfactants, the study of the biodegradability and the performance of surfactants make it possible to highlight the strong potential of polyethoxylated cardanol in detergent formulations that are more respectful of the environment and commonly used in daily life, for example for laundry. Xu *et al.* (201) disclosed the synthesis of a non-ionic cardanol-based (NI-11 Scheme 36)surfactant with a high functionality of hydroxyl functions. The authors highlighted the low surface tension of this surfactant at the CMC, which make it very interesting for many applications. Nevertheless, no specific application was mentioned by the authors.

g. Conclusion

Table 3 summarized the name, the structure, the CMC, the surface tension, and the applications of different CNSL-based surfactants discussed in the above part. A wide range of CNSL-based polyol surfactants have been identified and studied. Indeed, numerous applications have been widely described in this paragraph for CNSL-based polyol surfactants. Once again most of the CNSL-compounds used were cardanol. This may be explained by the fact that the CMC was usually lower with cardanol-based surfactant than with its analogs cardanol or anacardic acid-based surfactants. Thus, it reduces the price of the formulation which it is an excellent commercial argument for industrial. Moreover, some of the CNSL-based polyol described in this part as surfactants could be used as monomers for the synthesis of polymers which required polyols such as polyesters or polyurethanes.

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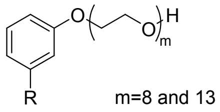
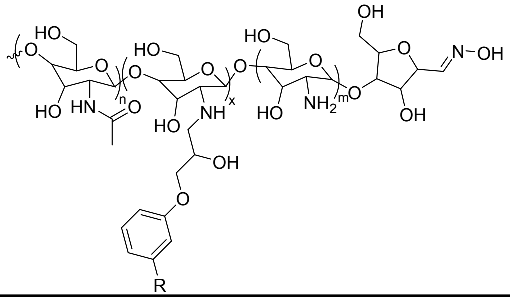
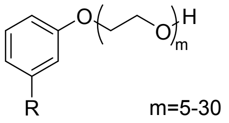
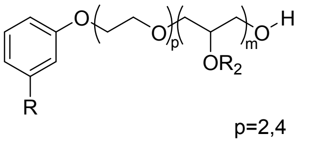
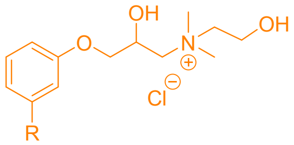
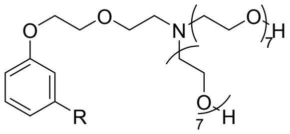
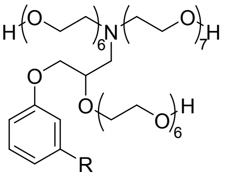
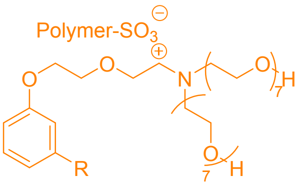
Table 3: Name (cationic surfactants are in red), structure, CMC, surface tension and applications of different CNSL-based surfactants

Name	**Structure**	**CMC (mol.L^{-1})**	**γ_{CMC} (mN.m^{-1})**	**Applications**
NI-1 **(186)**		-	-	Wetting agent in cement
NI-2 **(187, 188)**		-	-	Emulsifying agent for bituminous
NI-1 **(190)**		$5.50*10^{-6}$ – $2.40*10^{-5}$	31.90 – 46.16	Detergent
NI-3 **(192, 193)**		-	-	
C-1 **(194)**		$4.27*10^{-5}$	22.54	
NI-4 DECA **(195)**		$3.40*10^{-4}$	33.35	Demulsifier
NI-5 TECA **(195)**		$5.87*10^{-4}$	31.22	
C-2 QDEACC **(196)**		$4.90*10^{-4}$	35.60	

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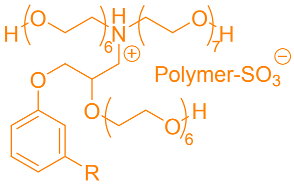
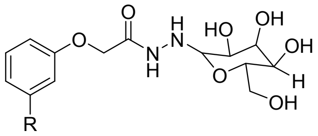
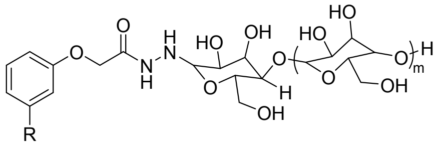
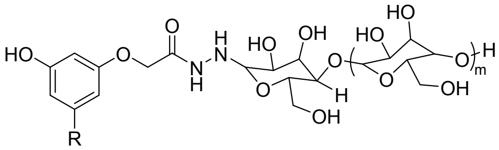
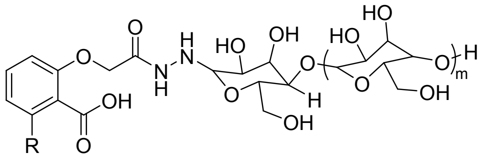
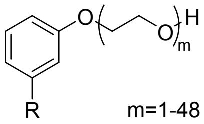
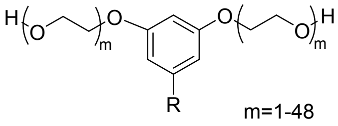
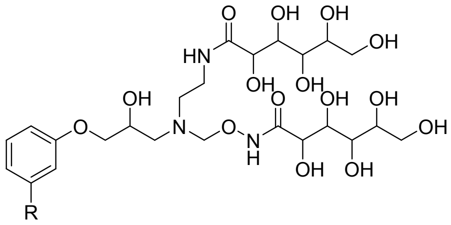
C-3 QTEACC -29 b **(196)**		$1.10*10^{-4}$	43.20	
NI-6 **(197)**		$2.10*10^{-3}$	51.00	Biofilms
NI-7 **(198)**		$6.90*10^{-4}$	42.00	Emulsion
NI-8 **(198)**		$8.20*10^{-4}$	49.00	
NI-9 **(198)**		$9.20*10^{-4}$	39.00	
NI-10 **(199, 200)**	 m=1-48	-	-	-
NX-10 **(199, 200)**	 m=1-48	-	-	-
NI-11 **(201)**		$5.00*10^{-3}$	35.27	-

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IV) Conclusion

In this review, we were able to highlight the versatility of cashew nutshell liquid (CNSL). This bioresource, and more particularly cardanol, allows, thanks to its particular chemical structure, a very large number of chemical modifications and makes it a precursor of choice for the synthesis of polyol. Thanks to their chemical structure of phenol lipids, the addition of a polar head with several hydroxy functions allows these CNSL polyol derivatives to be a good candidate in the field of surfactant, especially for non-ionic surfactants. These CNSL-based polyols are increasingly investigated as precursors for the synthesis of polyurethanes (foam and coating), polyesters or alkyd resins. In addition to increasing the ratio of biobased carbon to these polymers, CNSL derivatives impact the final properties of the resulting materials by increasing the thermal stability, the flexibility, and the hydrophobicity, due in large part to the presence of aromatic rings and unsaturations. Furthermore, this structure can provide faster drying to alkyd resins. However, this can also lead to yellowing or unwanted oxidation reactions. In order to limit some of the side effects, it is possible to functionalize these unsaturations or to add an antioxidant agent. Since the raw material itself is colored, this may also limit its use in certain applications. For this reason, many academic and industrial studies focus on the discoloration of CNSL (202).

However, despite the wide variety of polyol described in the literature, few are made from cardol or anacardic acid, a promising difunctional precursor also present in CNSL. In fact, only cardanol is currently being sold on a large scale. Currently, only a small number of companies market cardol or anacardic acid and only in small quantities at prices that make them unattractive for academic studies or industrial use. While CNSL is relatively inexpensive due to the availability of waste from the cashew nut industry, the techniques used to separate its different components may limit their industrial use at present. The origin of the raw material can also impact the CNSL composition and this could affect the properties of materials using these polyols. In order to overcome batch disparities linked to the unsaturation content, it is also possible to carry out a hydrogenation step to obtain a saturated alkyl chain. Additionally, all the polyol syntheses described in the literature are not necessarily economically viable for the applications targeted by companies, as they involve several synthesis steps and fairly expensive reagents. It is therefore important to take this into account when developing biobased polyols as an alternative for common applications.

Finally, the synthesized polyols are often only partially bio-based, the other reagents used in the synthesis steps remaining petroleum-based molecules. The toxicity of these reagents is sometimes questionable, and few reports focus on the toxicity, biodegradability or environmental impact of the resulting CNSL-based polyols described in this review. Efforts still need to be made in this area because “biobased” is not synonymous with “non-toxic” and the sustainability of a product is a complex character that concerns all the reagents and synthesis steps that lead to this product.

Despite the undeniable acceleration of the study and the use of CNSL and its derivatives in the chemical industry, there is still a long field of investigation and possible improvement concerning CNSL-based polyols. It is still easy to imagine many new polyol monomers from this abundant and available bioresource that does not conflict with crops intended for human or animal feed. Optimizations and a significant seriousness are still

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necessary in order to develop sustainable, efficient and relevant solutions for many and diverse applications, suggesting a promising future for CNSL derivatives for the years to come.

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No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Sylvain CAILLOL