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CNSL oxyacetic derivatives, new bio-based binders for paint preparation

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The global coating industry produces tens of millions of metric tonnes of paints each year, and this quantity continues to grow. Most of these paints are obtained totally or partially from fossil resources, and many of them still use volatile organic compounds (VOCs) and/or other harmful chemicals. This paper describes the use of the cashew nutshell liquid (CNSL) as a raw material for synthesis of paint binders (sustainable materials). These binders are obtained in a single chemical step without tedious separation. These new bio-based materials (renewable resources) form stable films (green coatings) in a short drying time. The formulated paints are 100% aqueous, have low toxicity and ecotoxicity and require no additional drying agents or VOCs. Oxidative coupling of the alkylidene chain and addition of carboxylic acid to the carbon-carbon double bonds are implemented. The products obtained can be applied on different kinds of surfaces, such as glass slides, metal, wood or concrete, and exhibit good stability against various solvents and tropical conditions.

Keywords: green coatings/renewable resources/surface/sustainable materials

Notation

M_n	number average molecular weight
M_w	mass average molar weight
R_f	retention factor
δ	chemical shift (parts per million)

1. Introduction

The chemical industry, including detergents, packaging, plastics, cosmetics, fibers and coatings, is facing very strong pressure due to economic and regulatory developments. On the one hand, erratic price variation and availability of fossil resources need the most appropriate technologies. On the other hand, social demands and regulations driven by ecological concerns require new approaches, new bio-sourced raw materials and finally new products. Agribusiness waste is usually available on a large scale and is considered a normal production process result. This potential raw material is therefore particularly interesting from both an economic and an ecological point of view.¹ Cashew nutshell liquid (*Anacardium occidentale* L.), or CNSL, is one of the main wastes from cashew farming and is probably one of the most attractive. Indeed, this by-product alone represents, potentially, several hundreds of thousands of metric tonnes per

year,²⁻⁵ and most of the time, they are buried or burned. This figure is constantly increasing due to the cashew market boom and to the great interest in cashew trees during reforestation processes.^{6,7} The interest in CNSL can be explained by the high content of phenolic derivatives in its composition. 'Natural CNSL' from shell solvent extraction contains anacardic acid, cardol, cardanol and methyl cardol.⁸⁻¹¹ This mixture can be simplified by thermal decarboxylation of anacardic acid, giving 'technical CNSL',¹²⁻¹⁴ rich in cardanol. Even better, a single product could be obtained in high yield by reduction of the alkenyl chain and aromatic ring.¹⁵ Admittedly, renewable raw material use meets the new requirements of the chemical industry, but it is insufficient because the manufacturing process and products must also have low ecological impact; toxic reagents and solvents are unacceptable. For example, in coating and paint factories, volatile organic compounds, toxic pigments and additives are to be avoided. In consequence, it is to provide alternatives to these prohibited substances that new binders have been synthesized for more environment-friendly paints using CNSL as a raw material. Some works, including the authors' previous investigation, have shown that anacardic acid and natural CNSL can be easily transformed into diacids to give a non-toxic

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mixture of amphiphilic molecules with non-negligible surfactant properties.^{16,17} For example, surfactants of anacardic acid and cardol diacids are readily obtained through Williamson's reaction using sodium chloroacetate as an alkylating agent. These reactions have good yield and selectivity.¹⁷ Many important binders in coatings are polyesters from diacids and polyols.^{18–21} There are also 'green binders' from linseed oil, historically used as a binder in artistic paint.^{22,23} The structure of the CNSL alkylidene chain is close to that of linseed oil. Therefore, products originally created for their amphiphilic properties may also become a diacid monomer and part of useful new materials in the coating industry. Paint binders are mainly polymers with a molecular weight greater than 50 000 Da. That is why in this work, the authors studied some polyesters of diacids from CNSL and were also interested in monomers.

2. Experimental section

2.1 General information

Cashew nutshells were harvested in the Boeny region of Madagascar (16°23'34.6812" south, 47°0' east) in November 2019. Sodium chloroacetate, potassium hydroxide, *p*-toluenesulfonic acid (*p*TSA), potassium carbonate, tetrabutylammonium sulfate, 1,3-propanediol, tin (II) octanoate, ethylene carbonate, monobutyltin oxide (MBTO), boron trifluoride ether, methanesulfonic acid and activated charcoal were purchased from Sigma-Aldrich and VWR. Solvents and other materials were obtained from local commercial suppliers (Chimidis) and used without further treatment and purification. Fillers and pigments were generously given by Aurlac, the most important paint factory in Madagascar. Reactions were monitored by thin-layer chromatography (TLC) using silica gel (60 F254) on an aluminum plate. This technology was one of the main tools in developed countries about 40 years ago. Now it has been replaced by liquid chromatography (LC) coupled with mass spectroscopy (MS) or nuclear magnetic resonance (NMR), which are currently available in most university laboratories. This is not the case in Madagascar, where TLC remains a very powerful technology allowing qualitative and semiquantitative assessment when 'authentic samples' are available. For this study, NMR, MS, infrared (IR) spectroscopy and differential scanning calorimetry (DSC) were carried out at the Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), University of Lyon 1. NMR spectra were recorded using a Bruker ALS 500 spectrometer. For NMR interpretation, the abbreviations were defined as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. A GC 7890B gas chromatograph (Agilent Technologies) coupled to a 7200 quadrupole time-of-flight mass spectrometer (Agilent Technologies) and the LC-electrospray ionization mass spectra were used. The IR spectrometer used was a Nicolet iS 10 Smart iTR with a diamond attenuated total reflectance accessory. DSC analyses were carried out using a 3000 Mettler Toledo apparatus. At first, the temperature was maintained at 25–10°C and then increased to 300°C. Then, a cooling segment from 300 to –10°C and finally an increase from –10 to 300°C were implemented. The carrier gas was dinitrogen (200 ml/min for the cell and 50 ml/min for the internal oven). The molecular weight

distributions of the final polymers were determined using an Agilent gel permeation chromatography (GPC) instrument (model 1260 Infinity) consisting of a pump, a refractive index detector and one MesoPore PL1113-6325 (300 × 7.5 mm) column, using *N*-methyl-2-pyrrolidone as an eluent and a flow rate of 0.5 ml/min at 50°C. The GPC results were calculated with the Addon software using a linear polystyrene-based calibration curve.

2.2 Experimental part

2.2.1 Extraction of CNSL from cashew nutshells

Cashew shells were crushed and extracted by hot maceration with butyl acetate. Into a 1 liter flask, 500 g of crushed shells and 310 ml of butyl acetate were introduced. Then, they were heated at 80°C for 1 h. After the time was up, the mixture was filtered. The filtrate was recovered, and shell residues were macerated again with 310 ml of butyl acetate for a second hot maceration. The same procedure was carried out for a third extraction. At the end, the three filtrates were evaporated, and after weighing, 39% yield of CNSL was obtained (Figure 1). The yield and composition were similar to those obtained by other researchers.^{8,9} The CNSL composition (Figure 2) was determined by LC–MS.

Separations of anacardic acid, cardanol and cardol were performed using a procedure already described.^{24,25}

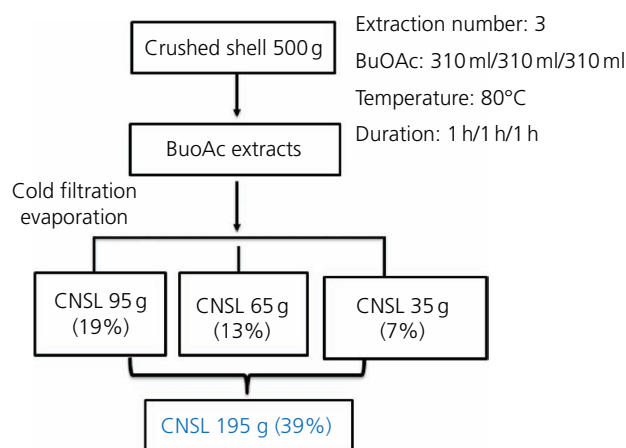


Figure 1. CNSL extraction yields. BuOAc, butyl acetate

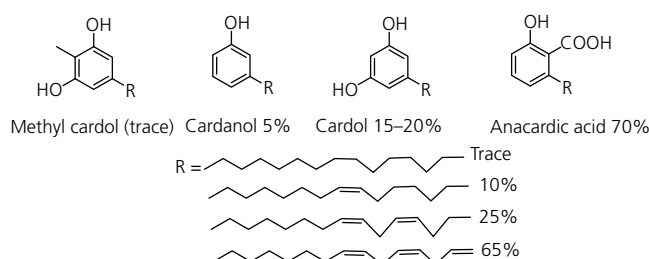


Figure 2. Composition of CNSL

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2.2.2 Synthesis of monomers and polyesters

2.2.2.1 SYNTHESIS OF POLYESTER 3: OXYACETIC ACID OF ANACARDIC

ACID 1/1,3-PROPANEDIOL

Anacardic acid (3.42 g, 10 mmol) was treated with 2 mol/mol of potassium hydroxide (KOH; 1.12 g or 20 mmol) and 1.8 mol/mol of sodium chloroacetate (2.1 g or 18 mmol) in 2 M ethanol at 70°C for 24 h. Ethanol was then evaporated, and the crude mixture was acidified with hydrochloric acid (HCl) until pH = 3 to be treated with water (H₂O)/ethyl acetate (EtOAc) (50 ml each). The organic phase was then distilled under vacuum to give 90% oxyacetic acid of anacardic acid **1**. Then, 2 g (5 mmol) of diacid was used for reaction with 2 mol/mol of 1,3-propanediol (0.7 ml or 10 mmol) at 150°C for 3 h to give a diester of 1,3-propanediol **2**. This diester **2** was added to 5 mol% *p*TSA and heated under vacuum at 150°C for 5 h to form insoluble polyesters, easily recoverable by filtration and washing with 20 ml of EtOAc (10 ml/g). Evaporation of the EtOAc phase led to 80% soluble polyester, which was analyzed using TLC and hydrogen-1 (¹H) NMR. The remaining 20% was intractable and insoluble and decomposed at around 200°C.

Solubility tests were tried with different solvents available in the authors' laboratory (water, methanol, ethanol, isopropanol (IPA), butanol, acetone, methylene chloride, cyclohexane, *N,N*-dimethylformamide, chloroform, toluene, tetrahydrofuran, chlorobenzene, acetic acid) without success.

Hydrogen-1 NMR of oxyacetic acid of anacardic acid **1** (300 MHz, CDCl₃, tetramethylsilane (TMS)): δ (parts per million (ppm)) 7.25–6.7 (m, 3H, CH aromatic); 5.6–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4.7 (s, 2H, –O–CH₂–COOH–); 2.6 (m, 2H, Ar–CH₂–); 2.4–1.1 (m, 16H, –CH₂– chain).

Hydrogen-1 NMR of diester of 1,3-propanediol **2**: (300 MHz, CDCl₃, TMS): δ (ppm) 7.45–6.7 (m, 3H, CH aromatic); 5.6–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4.75 (s, 2H, –O–CH₂–COO–); 4.25 (t, 4H, –COO–CH₂–); 4.7 (t, 4H, –CH₂–OH); 2.6 (m, 2H, Ar–CH₂–); 2.4–1.1 (m, 16H, –CH₂– chain); 1.8 (q, 4H, –COO–CH₂–CH₂–CH₂–OH).

Hydrogen-1 NMR of polyester **3** (300 MHz, CDCl₃, TMS): δ (ppm) 7.25–6.7 (m, 3H, CH aromatic); 5.6–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4.7 (s, 8H, –O–CH₂–COO– in the pattern); 4.3 (t, 8H, –COO–CH₂– in the pattern); and 4 (t, 2H, –CH₂–O–); 3.5 (t, 2H, –CH₂–OH) 2.6 (m, 2H, Ar–CH₂–); 2.4–1.1 (m, 16H, –CH₂– chain); 1.7 (2H, CH₂–CH₂–CH₂–OH).

2.2.2.2 SYNTHESIS OF POLYESTER 6: CARDOL DIOXYACETIC ACID 4/1,3-PROPANEDIOL

In the same way, 3.18 g of cardol (10 mmol) was treated with 2 mol/mol of potassium hydroxide (1.12 g or 20 mmol) and 2.4 mol/mol of sodium chloroacetate (2.8 g or 24 mmol) in 2 M ethanol at 70°C for 24 h. Ethanol was evaporated to obtain the

crude extract, which was acidified with hydrochloric acid until pH = 3 and washed with a water/EtOAc (50 ml each) mixture. The organic phase was then distilled under vacuum to obtain oxyacetic acid of cardol **4** with purified yield of 88%. This diacid (2.2 g) was added to 2 mol/mol of 1,3-propanediol (0.7 ml) at 150°C for 3 h to obtain a diester of 1,3-propanediol **5**. Diester **5** and 5 mol% *p*TSA were heated for 5 h at 150°C under vacuum. The product formed was recovered with 20 ml of EtOAc (~10 ml/g) to obtain 40% compound **6**. Melting point measurement and DSC analysis of the insoluble fraction (60%) were carried out without interpretable results. Only product decomposition was observed at around 200°C. Compound **6** was the unreactive residue of the starting diester according to TLC analysis. The same solubility tests as before were performed on the insoluble fraction, but no results were obtained; it remained insoluble.

Hydrogen-1 NMR of oxyacetic acid of cardol **4** (300 MHz, CDCl₃, TMS): δ (ppm) 6.45–6.29 (s, 3H, CH aromatic); 5.7–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4.66 (s, 4H, –O–CH₂–COOH–); 2.8 (m, 2H, Ar–CH₂–); 1.3–2.6 (m, 16H, –CH₂– chain).

Hydrogen-1 NMR of diester of 1,3-propanediol **5**: (300 MHz, CDCl₃, TMS): δ (ppm) 7.45–6.7 (m, 3H, CH aromatic); 5.6–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4.75 (s, 4H, –O–CH₂–COO–); 4.25 (t, 4H, –COO–CH₂–); 3.6 (t, 4H, –CH₂–OH); 2.6 (m, 2H, Ar–CH₂–); 2.4–1.1 (m, 16H, –CH₂– chain); 1.8 (q, 4H, –COO–CH₂–CH₂–CH₂–OH).

2.2.2.3 SYNTHESIS OF POLYESTER 8: DIETHYL OXYACETATE OF CARDOL 7/1,3-PROPANEDIOL

According to the authors' previous results,¹⁷ 7.9 g or 25 mmol cardol was treated with 2.2 mol/mol of potassium carbonate (7 g or 55 mmol), 10 mol/mol of ethyl chloroacetate (25 ml) and a small amount of quaternary ammonium (10 mol% or 875 mg tetrabutylammonium sulfate) at 80°C for 24 h to obtain diethyloxyacetate of cardol **7** with 92% purified yield. Then, 4.9 g or 10 mmol of diester **7** was reacted with 1 mol/mol of 1,3-propanediol (0.7 ml or 10 mmol) and 5 mol% tin (II) octanoate at 195°C for 8 h under vacuum. At the end of the reaction, 50 ml of toluene (~10 ml/g) was added to recover the polyester formed. Some insoluble product was observed. Evaporation of the soluble phase (toluene phase) produced 57% polyester **8**, which was analyzed using GC (Figure S5 in the online supplementary material). The insoluble part (43%) was analyzed using DSC, and its melting point was measured, but no significant result was recorded. Its decomposition temperature was found to be around 200°C. The same solubility tests as previously were performed.

Hydrogen-1 NMR of diethyl oxyacetate of cardol **7** (300 MHz, CDCl₃, TMS): δ (ppm) 6.3 (s, 3H, CH aromatic); 5.8–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4.7 and 4.55 (s, 4H, –O–CH₂–C=O); 4.3 (m, 4H, O–CH₂–CH₃); 2.8 (m, 2H, Ar–CH₂–); 2.5–1.1 (m, 16H, –CH₂– chain).

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2.2.2.4 SYNTHESIS OF POLYESTER 10: CARDOL DIOXYETHANOL 9/ DIMETHYL SUCCINATE

Cardol (3.18 g, 10 mmol) was reacted with 2.4 mol/mol of ethylene carbonate (2 g or 24 mmol) in the presence of 2 mol/mol of potassium carbonate (35 mg or 0.25 mmol) for 2 h at 150°C. Once the reaction completed, the medium was cooled. A 95% gross yield was calculated. TLC analysis (using EtOAc/hexane (8/2, v/v) as the eluent system) and chromatographic column purification (with 100% hexane as eluent) were performed. Finally, after evaporation of the pure fractions, an isolated dioxyethanol **9** with 52% of yield was obtained. Then, diol **9** (cardol dioxyethanol) was treated with 2.2 mol/mol of methyl succinate in the presence of 0.1 mol% MBTO at 150°C for 5 h under vacuum. The product formed was dissolved in 20 ml of EtOAc, and after evaporation, it produced 75% polyester **10**, which was analyzed using TLC and hydrogen-1 NMR. The remaining 25% insoluble part was either not treatable or remained insoluble in other used solvents.

Hydrogen-1 NMR of cardol dioxyethanol **9** (300 MHz, CH₂Cl₂-d₂, TMS): δ (ppm) 6.45–6.29 (s, 3H, CH aromatic); 5.7–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4 and 3.8 (m, 8H, OH–CH₂–CH₂–O); 2.8 (m, 2H, Ar–CH₂–); 2.5–1.1 (m, 16H, –CH₂– chain).

Hydrogen-1 NMR of polyester **10** (300 MHz, CH₂Cl₂-d₂, TMS): δ (ppm) 6.5–6.3 (s, 3H, CH aromatic); 5.7–5 (m, 7H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂); 4.3 and 4 (m, 64H, O–CH₂–CH₂–O– in the pattern); 3.6 (s, 3H, –O–CH₃); 2.8 (m, 2H, Ar–CH₂–); 2.6 (32H, –OOC–CH₂–CH₂–COO– in the pattern); 1.3–2.5 (m, 128H, –CH₂– chain).

2.2.2.5 SYNTHESIS OF OXYACETIC ACID OF CNSL 11

Into a 250 ml flask, 34.2 g of CNSL (approximately 100 mmol if considering anacardic acid as the main constituent) was mixed with 1.8 mol/mol of sodium chloroacetate (20.8 g or 180 mmol) in the presence of 2 mol/mol of potassium hydroxide (11.2 g or 200 mmol) in 100 ml of ethanol at 70°C for 24 h. After cooling, evaporation of ethanol and addition of 200 ml water and acidification by 80 ml of 2 N hydrochloric acid were carried out until pH of up to 3. Liquid/liquid separation using EtOAc/water (200 ml/200 ml) was carried out, followed by three times successive washing with water (200 ml) to remove the salts. Then, the EtOAc phase was evaporated, and 98% crude oxyacetic acid of CNSL **11** was obtained. Discoloration was performed using 50% by mass of activated charcoal (FE12510F) in 100 ml of EtOAc. The suspension was stirred at room temperature (RT) for 5 h. After successive filtration, EtOAc washing and evaporation, partially discolored CNSL oxyacetic acids **11** were recovered with 76% yield.

Hydrogen-1 NMR of oxyacetic acid of CNSL **11** (300 MHz, deuterated methanol, TMS): δ (ppm) 6.25–7.4 (m, 9H, CH aromatic for anacardic acid, cardol and cardanol); 5.8–4.8 (m, 21H, –CH₂CH=CHCH₂–CH=CHCH₂–CH=CH₂ for anacardic

acid, cardol and cardanol); 4.6–4.8 (3s, 8H, –O–CH₂–COOH– for anacardic acid, cardol and cardanol); 2.7 (m, 6H, 3Ar–CH₂– for anacardic acid, cardol and cardanol); 1.3–2.6 (m, 48H, –CH₂– chain for anacardic acid, cardol and cardanol).

2.2.2.6 SYNTHESIS OF OXYACETIC ACID OF CNSL WITHOUT TRACES OF CNSL 11'

Into a 2 l double-membrane reactor, 100 g (~293 mmol) of CNSL, 57.4 g or 1.025 mol of potassium hydroxide (3.5 mol/mol) and 300 ml of IPA were mixed at 40°C. After complete dissolution of potassium hydroxide, 81.6 g or 703.2 mmol of sodium chloroacetate (2.4 mol/mol) was gradually added. The flask was closed, and the temperature was raised to 80°C for 2 h. After cooling, the mixture was poured into a 1 liter flask and evaporated. Three hundred milliliters of water was added to solubilize the obtained salt, and the pH was maintained at about 7. Then, the aqueous solution was subjected to two successive extractions with 200 ml of EtOAc to remove the remaining CNSL. After recovering and evaporation of EtOAc phases, the aqueous extract was treated with 55 ml of 11 N hydrochloric acid. When the pH was equal to 3, 250 ml of EtOAc was added to dissolve the oxyacetic acid **11'** formed from CNSL. Finally, liquid/liquid separation using EtOAc/water was carried out to obtain the 'pure' oxyacetic acid of CNSL **11'**, in the EtOAc fraction.

2.2.3 Evaluation of the drying properties of oligomers and monomers

The formation of stable films with the monomers and oligomers synthesized was carried out as follows. A drop of the tested product was placed on a glass slide and maintained at RT and in air or in the oven at 60°C. The stickness was manually observed as a function of time. Once the product became dry, the glass plate was kept 24 h under drying conditions and then soaked in water, hexane, ethanol, EtOAc and acetone to check its stability.

2.2.4 Preparation of paint samples and evaluation of film formation, drying properties and stability of paints

Paint results from the combination of many ingredients, including binders, fillers, pigments, diluent or solvent and additives. In this study case, the binder was the oxyacetic acid of CNSL; dolomite (CaMg(CO₃)₂), kaolin, talc (Mg₃Si₄O₁₀(OH)₂) and calcium carbonate (CaCO₃) were used as fillers; and iron oxide was used as a pigment and water was used as a paint diluent. As CNSL oxyacetic acids are not water soluble, sodium bicarbonate (NaHCO₃) or sodium hydroxide (NaOH) was used as a surfactant to obtain stable emulsions. Several tests were carried out. For example, the following formulation 16: 30 g or 75 mmol of CNSL 11 oxyacetic acids (binder) were introduced into 50 ml of water containing 45 mg NaOH, 1.5 mol %, then 12 g of 20 μ m dolomite (filler) and 8 g of red iron oxide PR 190 (pigment) were added with vigorous mechanical stirring. The solution was stirred mechanically (700 revolutions/min) at RT for 20–30 min until a stable emulsion was obtained.

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Supports of different natures (glass, metal, wood plate, cement) and even the outside wall of the authors' laboratory were brush-painted to test the paint effectiveness. After drying, water and organic solvent sensitivity tests were performed.

2.2.5 Study of the polymerization of the oxyacetic acid derivative of CNSL under acidic conditions

The oxyacetic derivative of CNSL **11** was treated either with 1 mol/mol of boron trifluoride ether or methanesulfonic acid overnight at 60°C. In both cases, a rubbery solid insoluble in any solvent was obtained. To control these acid-catalyzed transformations, 1% methanesulfonic acid/CNSL was used as a catalyst without a solvent at 60°C. Reactions were followed using GPC analysis.

3. Results and discussion

3.1 Synthesis of monomers and polyesters

3.1.1 Polyester **3**

The first step of the reaction – namely, monomer synthesis – led to 90% oxyacetic acid of anacardic acid **1**. Its polycondensation led to 80% soluble product and 20% insoluble black residue (Figure 3), which stayed insoluble in all solvents and had no melting point (decomposition above 200°C). The fraction soluble

in EtOAc **3** was analyzed by hydrogen-1 NMR and was found to be an oligomer with $n = 4$ (polymerization degree).

3.1.2 Polyester **6**

The first reaction step gave 88% oxyacetic acid of cardol **4**. After polycondensation, 60% of black insoluble fraction (Figure 4) was obtained and 40% soluble fraction. Based on the TLC analysis, the soluble product had the same R_f as the monomer (diester **5**). Thus, it was a diester of 1,3-propanediol **5** (Figure S3 in the online supplementary material).

3.1.3 Polyester **8**

Diethyl oxyacetate of cardol **7** (92%) was obtained. Polycondensation produced 57% soluble product and 43% black insoluble residue (Figure 5). Toluene-soluble fraction **8** was analyzed by GC (Figure S5 in the online supplementary material) and was identified to be an oligomer with $p = 6$ (polymerization degree) with $M_w \sim 1700$ g/mol.

3.1.4 Polyester **10**

The preceding sections have shown that polyester synthesis from oxyacetic acid derivatives of cardol and anacardic acid was difficult due to simultaneous formation of many insoluble products. The

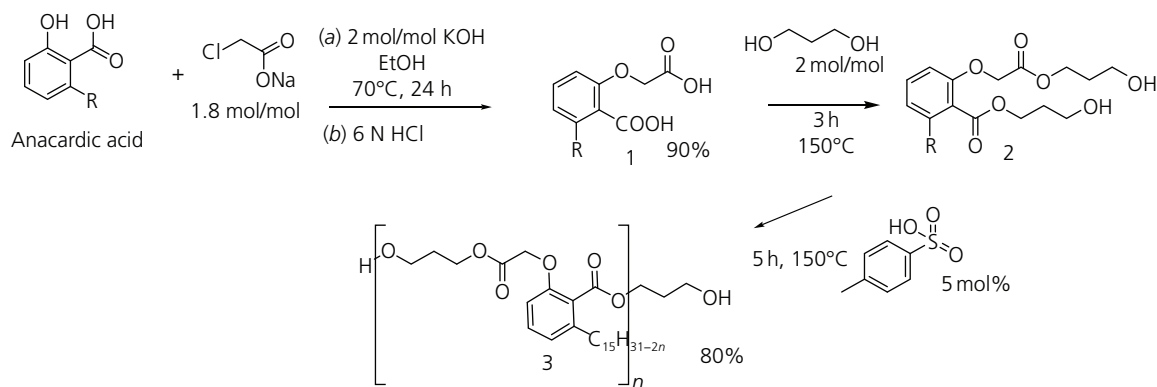


Figure 3. Synthesis of oligomers of oxyacetic acid of anacardic acid and 1,3-propanediol

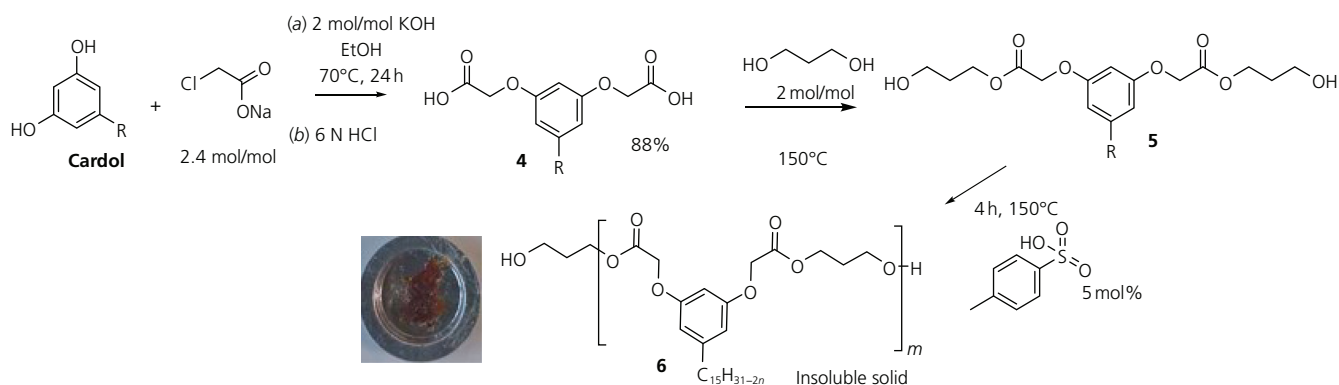


Figure 4. Synthesis of oligomers of oxyacetic acid of cardol and 1,3-propanediol

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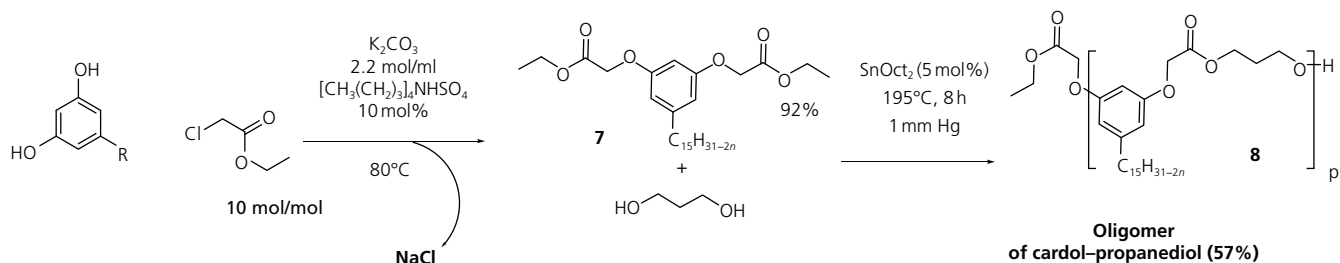


Figure 5. Synthesis of oligomers of diethyl oxyacetate of cardol and 1,3-propanediol

authors decided to evaluate the poly(ester) preparation by transesterification according to the method by Gioia *et al.*²⁶ (Figure 6). At first, the reaction led to 95 or 52% purified dioxyethanol of cardol **9**. After transesterification, 75% soluble oligomer **10** (Figure 6) in EtOAc with $m = 8$ was obtained.

3.1.5 Oxyacetic acid of CNSL **11**

CNSL oxyacetic acid **11** (98%) was obtained after modifying the pH with hydrochloric acid solution (Figure 7). Oxyacetic acid from CNSL **11** was a dark brown product. After discoloration, with 50% activated charcoal in EtOAc, 76% light brown wax product was obtained. However, traces of CNSL were still detected after TLC analysis.

3.1.6 Oxyacetic acid of CNSL **11'** without traces of CNSL

To remove all remaining CNSL in the final product, another way was proposed. IPA was chosen for its higher boiling point, allowing the use of high temperatures and having a faster reaction. Thus, phenolate was treated with sodium chloroacetate

in IPA. The remaining CNSL was selectively extracted at pH 7 using EtOAc (Figure 8). Then, the aqueous solution was acidified to pH 3 and extracted by butyl acetate to obtain 95% oxyacetic derivatives of CNSL without traces of CNSL **11'** (Figure S9 in the online supplementary material).

3.2 Evaluation of the drying capacity of CNSL derivative oligomers

3.2.1 Drying capacity of oligomers

The drying capacity of oligomer **8** was not evaluated due to the poor synthesis yield (presence of insoluble product ~50%). Only oligomers **3** and **10** were tested. They gave non-sticky films at different formation speeds. Oligomer **3** (product of oxyacetic acid of anacardic acid **1** and 1,3-propanediol) took 5 days to become non-sticky, while 2 days were necessary for oligomer **10** (product of diol from cardol **9** and methyl succinate) to dry at RT (Table 1). Both materials were stable in water and hexane but swelled in acetone and ethanol, although **10** was much less sensitive than **3**. Indeed, **10** was spread on a piece of bamboo, and

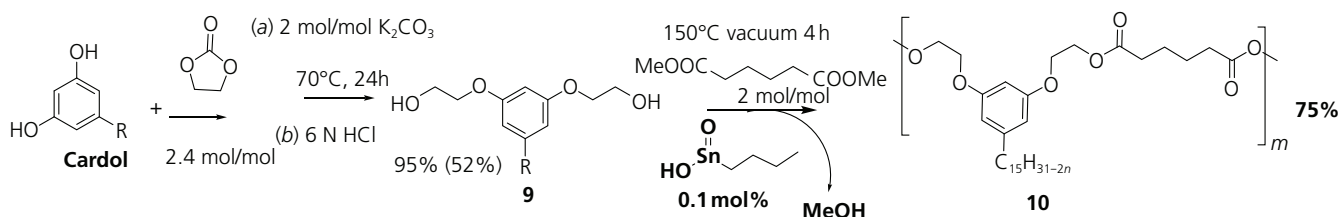


Figure 6. Synthesis of the oligomer of dioxyethanol cardol/dimethyl succinate

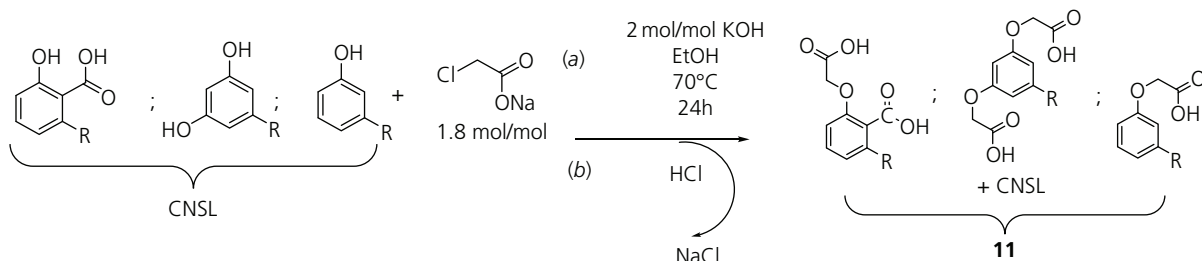


Figure 7. Synthesis of oxyacetic acid of CNSL **11**

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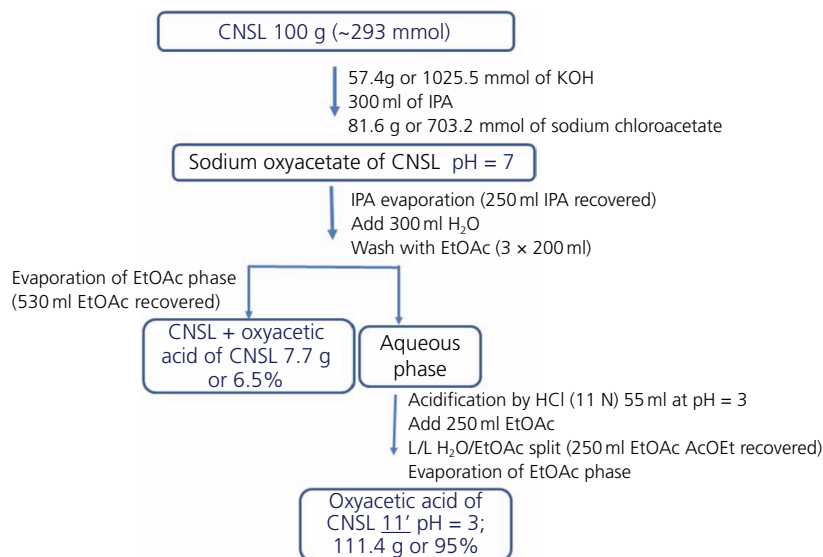


Figure 8. Synthesis and separation of oxyacetic acid of CNSL 11'

Table 1. Film formation with oligomers of CNSL derivatives

Oligomer	Formula	Drying time at RT: days	Solvent stability
Oxyacetic acid of anacardic acid 1 /1,3-propanediol		5	Water ++ Hexane ++ Ethanol + (swelling) Acetone + - (swelling)
Dioxyethanol of cardol 9 /dimethyl succinate		2	Water ++ Hexane ++ Ethanol ++ Acetone + (little swelling)

after a few days, it looked like a nice slightly colored varnish (Table S2 in the online supplementary material).

The results presented above show that the oligomers of CNSL derivatives can form stable and cross-linked films after open air-drying. Unfortunately, their synthesis is far from being acceptable from economic and ecological points of view. Acid-catalyzed polycondensation of monomers requires a long reaction time at 150°C and allows only the formation of small oligomers with a molecular weight much lower than that generally required in polyester binders such as glycerophthalic binders. Additionally, the reaction yield is low due to competitive formation of undesirable insoluble by-products. Polymerization and cross-linking occur during polycondensation due to the high level of CC double bonds, in a proportion similar to that of linseed oil. The best solution for polyester formation with CNSL derivatives

seems to be transesterification of diol derived from cardol **9**. Nevertheless, this material formation strategy giving a suitable yield has also significant drawbacks. First, diol synthesis is more expensive than that of diacid; second, it is available only from cardol, which must be separated; and finally, oligomer synthesis requires a tin catalyst and elimination of methanol, both of which have a strong ecological impact.

3.2.2 Film formation with CNSL constituents and derivatives

Formation of insoluble materials during polyester synthesis can be explained by alkenyl chain reactivity. Use of an inert argon atmosphere during the reaction does not alter insoluble product formation. IR spectroscopy offered no information on product structure, and further spectroscopic analyses were also useless due to their insolubility.

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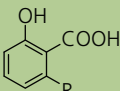
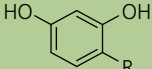
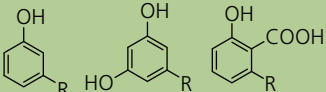
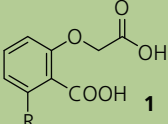
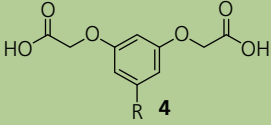
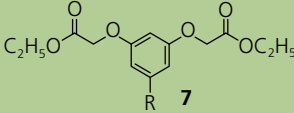
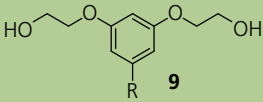
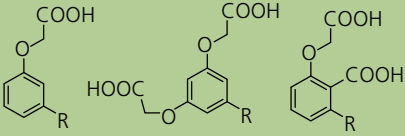
To understand this phenomenon, the drying capacity of CNSL derivatives was evaluated (Table 2). For that, drying tests were carried out. The stickiness of the film was manually checked regularly (Table 2). Thus, anacardic acid, cardol, cardanol and the mixture of these products did not form stable films on drying, even in an oven at 60°C after several days. Dioxyethanol derivative of cardol **9** behaved the same. Conversely, diacids **1** and **4** derived from anacardic acid and cardol became dry after 2 days and 1 day at RT, respectively. These two compounds dried even faster at 60°C in the oven. Moreover, ethyl ester **7** failed the drying tests even after 10 days at 60°C. In contrast, the authors were very pleased to observe that oxyacetic acid derivative from natural CNSL containing a high proportion of anacardic acid **11** gave a stable film after air-drying. This mixture of carboxylic acid

derivatives can therefore be used as a 'binder precursor' for paint formulation.

3.3 Proof of concept: paint formulation tests using CNSL oxyacetic acid **11** as a binder precursor

Formation of films, stable in water and in organic solvents, from carboxylic acid derivatives is somewhat difficult to explain by only oxidative mechanism as postulated for ester oligomers (see above). Nevertheless, this amazing behavior may be of practical interest, particularly in the case of the oxyacetic derivative of natural CNSL. As proof, the authors were able to formulate paint from CNSL oxyacetic acid **11** using the simplest possible way: combination of a binder, a filler, a pigment and water (Table 3). Clearly, compared with modern paint formulation resulting from painstaking

Table 2. Drying properties of CNSL derivatives

Product	Drying time at RT	Drying at 60°C	Film properties
Anacardic acid 	>10 days	>10 days	Soluble in hexane
Cardol 	>10 days	>10 days	Soluble in hexane
Natural CNSL 	>10 days	>10 days	Soluble in hexane
Oxyacetic acid of anacardic acid 	2 days	15 h	Stable in water and hexane Swelling in ethanol and acetone
Dioxyacetic acid of cardol 	24 h	6 h	Stable in water and hexane Slight swelling in ethanol and acetone
Diethyl oxyacetate of cardol 	>10 days	>10 days	Soluble in hexane
Dioxyethanol of cardol 	>10 days	>10 days	Soluble in hexane
Natural CNSL oxyacetic acid 	6 days	24 h	Stable in water and hexane Swelling in ethanol and acetone

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optimization by engineers over years, the authors' method was different. Oxyacetic derivative of CNSL **11** was used as a binder precursor. This material was not water soluble and formed a suspension that must be stabilized. For that, the amphiphilic properties of oxyacetic acid salt were taken advantage of by adding a small proportion of base (sodium bicarbonate or sodium hydroxide). Then, oxyacetic acid derivatives of CNSL **11** had two functions: binder and surfactant. One hundred grams of paint was prepared in each case using various fillers and pigments. After stirring, emulsion was applied with a brush to several supports: glass slides, wood, metal and concrete. Non-sticky films were obtained with all formulations tested after 1–3 days. Their stability with respect to the solvent, water, hexane, ethanol and acetone, were evaluated on depositing them on glass slides.

When using calcium carbonate as a filler, a solid film was formed, but it broke down quickly when treated with water, ethanol or acetone. In contrast, taking talc or dolomite as a filler, the layer was stable under all solvents, although some swelling was observed with ethanol and acetone. The best film formation was obtained by employing dolomite, a higher proportion of the binder (30%) and a lower proportion of the filler (12%). With 0.5% hydrogenocarbonate as the surfactant, phase separation was noticed after a few hours. The use of 2% sodium hydroxide gave stable emulsion formation (>1 day) but induced a strong increase in viscosity. Decreasing the amount of sodium hydroxide (line 5 formulation **16**) to 1% appeared to be a good compromise because it led to a paint with good stability with easy application on brush.

The authors demonstrated that the oxyacetic derivatives of natural CNSL could be a binder for paint formulation. All coatings obtained were matte, probably due to the brown color of the binder. However, it was possible to discolor it by treatment with

activated charcoal. The paint previously formulated was also used to coat the eastern part of the concrete wall of the International Associated Laboratory at Antananarivo. Some paintings were made more than 2 years ago and have experienced various climatic conditions, including two rainy seasons, alternating high temperatures, strong sunshine, heavy rains and several cyclones (coming from the east coast). Little or no degradation was observed, although conventional exterior paints generally suffered a lot under these conditions (Figure 9). This 'discovery' could have important applications even if real paint engineer intervention seemed very advisable to obtain an optimal coating.

3.4 Mechanism considerations

Oxidative polymerization and cross-linking of alkylidene chain are very well documented, and the CNSL derivative structure is really consistent with such phenomena.^{27,28} However, neither anacardic acid nor cardol nor ester **7** nor diol **9** leads to a cross-linked material on air-drying. Cardol and cardanol have both a highly oxidizable alkylidene chain and an antioxidant moiety (the alkylphenol^{29,30}); the second can inhibit the oxidation of the alkylidene chain (Figure 10).

Synthesis of oxyacetic acid from CNSL **11** was done without purification. Its conversion was almost complete, but traces of raw material (cardol, cardanol and anacardic acid) were still present at 5–7%. This starting material trace was eliminated by dissolving the crude mixture in a water solution of sodium hydroxide until pH 7 and then ethyl extraction of phenol derivatives. After acidification up to pH 3 of the aqueous solution, it was treated with EtOAc, and after evaporation, the purified CNSL oxyacetic acid **11'** was obtained with a good yield. Purified CNSL oxyacetic acid **11'** was used for a range of different formulations: the first is the optimal formulation **16'**; in the second, cobalt (II) octanoate was added as a drying agent at a

Table 3. Paint formulation tests using CNSL oxyacetic acid 11 as a binder precursor

Entry	Binder	Fillers	Pigment	Solvent	Viscosity	Solvent stability
12	Oxyacetic acid of CNSL 11 25%	Calcium carbonate 2Q Prochimad 25%	Blue iron oxide PU 48 10%	Water 40% Sodium bicarbonate 0.5%/binder	High	Water – Hexane + Ethanol – Acetone –
13	11 25%	Talc 20 µm 25%	Yellow iron oxide Py 42 10%	Water 40% Sodium bicarbonate 0.5%/binder	High	Water + Hexane + Ethanol + – Acetone + –
14	11 25%	Dolomite 20 µm 25%	Yellow iron oxide Py 42 10%	Water 40% Sodium bicarbonate 0.5%/binder	High	Water + Hexane + Ethanol + Acetone +
15	11 30%	Dolomite 20 µm 12%	Red iron oxide PR 190 8%	Water 50% Sodium hydroxide 2%/binder	High	Water ++ Hexane ++ Ethanol ++ Acetone ++
16	11 30%	Dolomite 20 µm 12%	Red iron oxide PR 190 8%	Water 50% Sodium hydroxide 1.5%/binder	Medium	Water ++ Hexane ++ Ethanol ++ Acetone ++

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Figure 9. Samples of formulated paintings

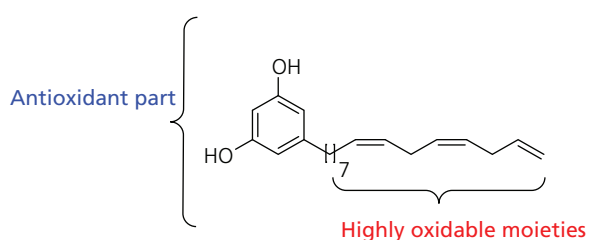


Figure 10. Oxidizable and antioxidant moieties of cardol

proportion of 5% **17** and 10% **17'**; the third had always the same optimal proportions but using a mixture of 90–80% **11'** and natural

CNSL 10% **18** or 20% **18'**. Each paint was spread on 400 cm² of concrete surface, and the drying time was determined (Table 4).

Paint from CNSL oxyacetic acid without traces of CNSL **16'** was dry after 10 h. The same product was added with 5% (**17**) and 10% (**17'**) of a drying agent cobalt, (II) octanoate; stable films were obtained after respectively 8 and 4 h under the same conditions. Finally, adding 10 or 20% of CNSL delayed the film formation by several hours (16 h for **18** and over 48 h for **18'**), unlike the drying agent that accelerated it. Alkyl phenols such as cardol and cardanol made drying much slower. Oxidation mechanisms were certainly involved in the process, but they were far from being the only mechanisms because the phenol group (cardol and cardanol

Table 4. Effect of drying agents and CNSL on the drying speed of paint film

Entry	Binder	Drying agent	Drying time (sticky finger test): h	Stability in solvent after 24 h
16'	Oxyacetic acid of CNSL without traces of CNSL 11'	None	10	Water + Hexane + Ethanol + Acetone +
17	Oxyacetic acid of CNSL without traces of CNSL 11'	Cobalt octanoate 5% mol/binder	8	Water + Hexane + Ethanol + Acetone +
17'	Oxyacetic acid of CNSL without traces of CNSL 11'	Cobalt octanoate 10% mol/binder	4	Water + Hexane + Ethanol + Acetone +
18	Oxyacetic acid of CNSL 11' with 10% natural CNSL	None	16	Water + Hexane + Ethanol + Acetone +
18'	Oxyacetic acid of CNSL 11' with 20% natural CNSL	None	>48	Water + Hexane + Ethanol – Acetone –

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contained in the CNSL) acted as an antioxidant.³¹ First of all, it was observed that several products without phenolic group (ester **7**, diol **9** etc.) had the same alkylidene chain but did not form stable

films. Secondly, the binder precursors used were monomers with two carboxylic groups and only one alkylidene chain, unlike linseed oil and glycerophthalic (alkyd) binders. Thus, another

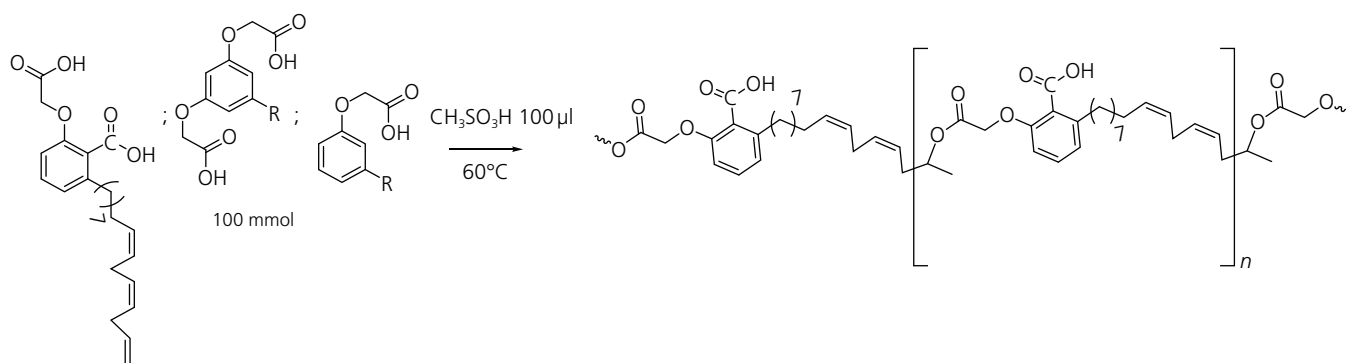


Figure 11. Polymerization of CNSL oxyacetic acid 11

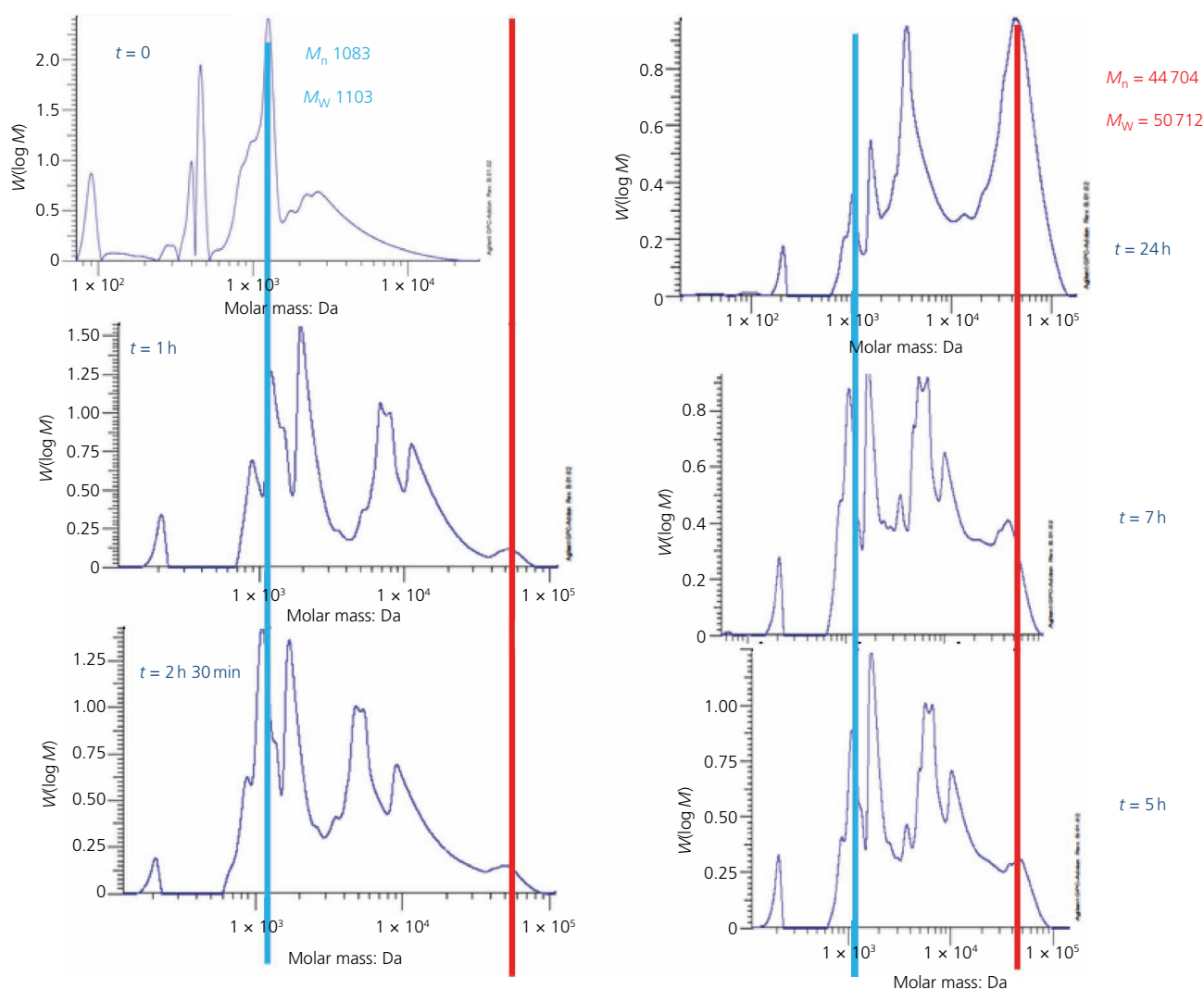


Figure 12. GPC analysis of acid catalysis of polymerization

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reaction could also occur: addition of carboxylic acid to CC double bonds. IR and DSC analyses were done to verify this.

IR spectroscopy of the oxyacetic derivative of CNSL was complicated, and no clear variation could be observed after drying. IR spectroscopy of the product **4** dioxyacetic derivative of cardol was much simpler due to the symmetry of this molecule. After overnight drying at RT, IR spectroscopy of a film of **4** showed a new band at 1735 cm^{-1} , which might attributed to the formation of the ester bond (Figure S10 in the online supplementary material).

DSC analysis of CNSL oxyacetic acid mixture **11** shows an endothermic transition at 114°C . This transition is not reversible, and the sample becomes a black residue (Figure S11 in the online supplementary material).

Addition of carboxylic acid on CC double bonds is a known reaction. Ethyl or isopropyl acetate can be easily obtained in good yield from corresponding alkene and acetic acid using aluminum-exchanged montmorillonite as a catalyst.³² The same reaction is performed with strongly acidic ion-exchange resin³³ or triflic acid.³⁴ Self-addition of oleic acid in the presence of a Brønsted

acid allows the preparation of bio-estolide.³⁵ Addition of carboxylic acid on alkene is also described with gold³⁶ and iron³⁷ complexes.

Although these reactions have relatively few synthetic applications, they can be performed at moderate to low temperatures and in most of the cases at RT. Brønsted acids, solid acids, Lewis acids or transition metal complexes can be used as catalysts.

Treatment of CNSL oxyacetic acid with 1 mol% methane sulfonic acid induced product oligomerization (Figure 11). Mass evolution was followed by GPC for 24 h (Figure 12).

The starting material **11** was placed at RT under argon. It was a brown, viscous liquid that became solid after a few days of storage. Its GPC analysis (Figure 12, $t = 0$) showed that the major component of monomers had $M_p = 399\text{--}405$ for anacardic oxyacetic acid **1** and $M_p = 429\text{--}435$ for cardol dioxyacetic acid **4** and also several others. The more important corresponded to a trimer ($M_w 1083$, $M_p 1103$), and some peaks were attributed to tetra-, penta- and hexamers. The oxyacetic derivative of CNSL oligomerized at RT without oxygen. This transformation stopped

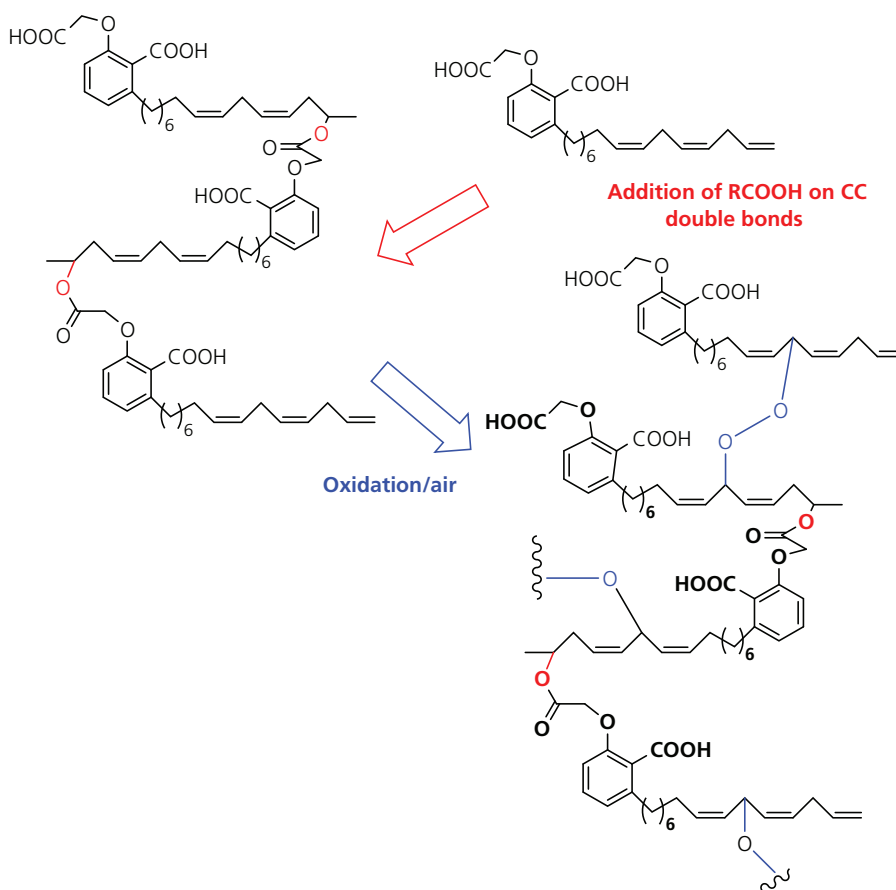


Figure 13. Proposed mechanism for polymerization and cross-linking of a CNSL oxyacetic binder

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as soon as the product became solid. Six months later, GPC analysis showed no difference. This was not the case when using 1% methane sulfonic acid at 60°C with stirring. Under these conditions, the disappearance of the monomer signal and a continuous decrease in trimers signals were observed. Simultaneously, the appearance and increase of oligomer signal with a mass of 44 704 g/mol were observed. After 24 h (Figure 12, $t = 24$ h), the latter became the main product (M_n 44 704, M_p 50 712), and the reaction mixture solidified. Hydrogen-1 NMR analysis was performed on this product that was slightly soluble in deuterated chloroform ($CDCl_3$). Broad signals were obtained; nevertheless, the carbon (C) sp^2 -hydrogen (H) peaks decreased drastically and vinyl proton signals disappeared (Figure S12 in the online supplementary material). Thus, the structures of the major products (two carboxylic groups and three CC double bonds) and the drying conditions (high concentration of monomers, presence of salts and metal oxide) allowed the formation of a three-dimensional (3D) network, thanks to both oxidative coupling and ester formation.

These experimentations show that the polymerization mechanism through addition of carboxylic acid is also responsible for film formation, together with oxidative processes (Figure 13).

4. Conclusion

Much work remains to be done to understand fully how small molecules (of even lower molecular weight than linseed oil) in mixtures of oxyacetic acid derivatives of natural CNSL form cross-linked films at RT. Nevertheless, there are at least two phenomena at work, the first being the oxidative process using a high level of unsaturation in CNSL derivatives and the second is the addition of carboxylic acid on CC double bonds. These hypotheses are supported by both examples from the literature and experimental results. Given the high level of functionality (two carboxylic groups and three CC double bonds in the major product), a 3D network can be formed. To the authors' knowledge, such an association of coupling reaction has never been used for material formation and may have more general applications. The authors have clearly found a potential new application for the main cashew industry waste. Paint formulations used in these experiments are so 'simplistic' that many improvements are to be expected from this point. The main practical result is that this new binder is easily obtained from natural CNSL without any separation and purification step. A single synthesis step is performed with a good yield. The reagents and solvent are relatively safe, and no hazardous waste is produced. It could be used in 100% water as solvent. This new binder is more than 90% bio-based. Finally, toxicity and ecotoxicity have already been assessed as very low for another application of the same product.¹⁷ Considering the potential production of CNSL, with over a hundred thousand metric tonnes, and the growing demand for sustainable materials and processes, this new application may meet the social and economic demand of customers.

Acknowledgements

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