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# Aromatic Biobased Polymer Latex from Cardanol

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## Abstract

We present for the first time the aqueous emulsion radical polymerization of cardanol derived methacrylic monomer (CAMA) in order to pave the way for the replacement of styrene. This monomer was synthesized in two-step routes by epoxidation of cardanol prior to methacrylation. Polymerization of CAMA was studied both in toluene solution and in aqueous emulsion. Radical aqueous emulsion homo- and co-polymerization of CAMA with methyl methacrylate (MMA) were performed with sodium dodecyl sulfate as surfactant. Stable latexes were obtained with particle size between 25-75nm. CAMA and MMA conversions were monitored versus time. Influence of radical initiator was studied on gel content, showing transfer to monomer in the case of persulfate as initiator. Glass transition temperature of homoPoly(CAMA) was determined and is suitable for coating application. Photo-crosslinking was performed by thiol-ene chemistry and allowed yielding cross-linked biobased aromatic coatings.

## Keywords

Cardanol; thiol-ene; water emulsion; latex; coatings

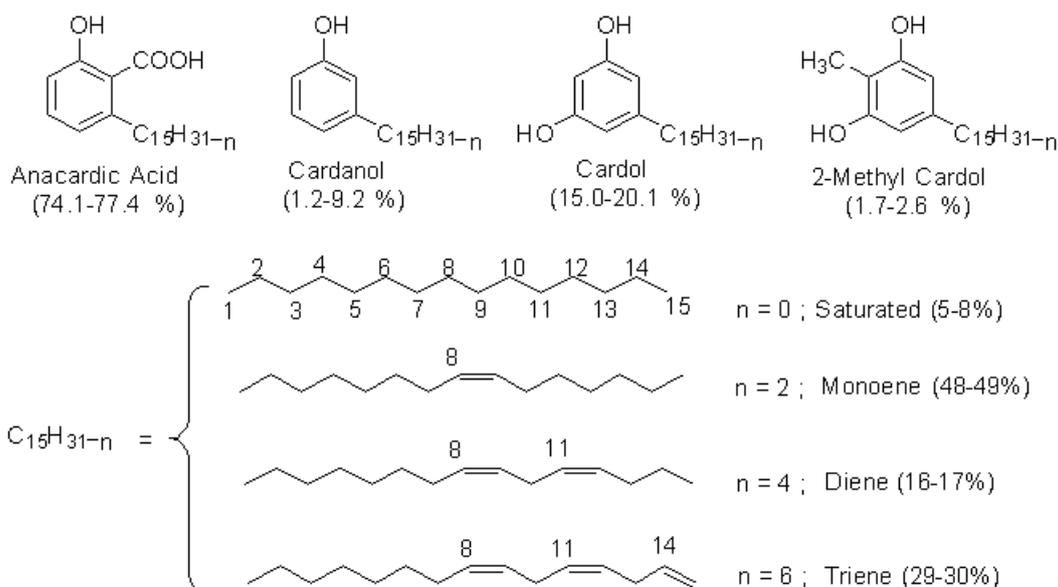
## Introduction

Synthetic latexes are a very important class of polymers with an increasing global production of more than 10 Mt p.a. for various applications, such as paints, varnishes, coatings. The increasingly stringent environmental regulations and market preferences have provoked a shift toward water-based systems. Thus, the use of a sustainable technology such as emulsion polymerization, where water is the dispersed medium, gives an added value to the polymerization process and to the final product. Nevertheless, producing waterborne full biobased polymeric materials is still a challenge nowadays. Only a handful of studies deal with this topic; and they were essentially focused on fatty acid derivatives<sup>1,2</sup>. A crucial requirement in conventional emulsion polymerization is the monomer transport through the aqueous phase from the monomer droplets to the polymer particles where the polymerization takes place; therefore, a minimal threshold monomer solubility in water is required. This represents a severe limitation for highly hydrophobic monomers, such as, precisely, fatty acid derivatives. Some works achieved the polymerization of fatty acid derivatives but they

had adapted processes such as miniemulsion, in which the polymerization occurs mainly in very small preformed monomer droplets<sup>3,4,5</sup>. For example, vegetable oil macromonomers<sup>6,7</sup>, acrylated methyl oleate for pressure sensitive adhesives<sup>8</sup>, and oil-acrylate hybrids<sup>9,10</sup> have been successfully polymerized via miniemulsion polymerization.

However, one of the main stakes in latex industry remains the replacement of styrene and also the access to low Tg aromatic latex for coatings. Indeed, accessing to biobased aromatic-containing radically-polymerizable monomers is a key issue, particularly for the substitution of styrene which is present in 75% of synthetic latex<sup>11</sup>. Styrene is a pervading monomer in synthetic latex. It is relatively cheap, is aromatic and thus confers good mechanical properties and solvent resistance to polymers. Polystyrene also possess a relatively high glass transition temperature which can be useful to tune the thermal properties of latex, but which needs to be decreased by addition of low-Tg acrylic monomers in order to meet suitable Tg for coatings. Moreover in the field of emulsion polymerization, styrene is very interesting for its nucleation property in *ab initio* emulsion polymerization.

In spite of these useful properties, styrene presents numerous drawbacks: it is toxic and suspected to be carcinogenic (and its main metabolite, styrene 7,8 oxide is classified as carcinogen and mutagen), it is produced from fossil resources<sup>12</sup> and is non-functional (and difficult to functionalize)<sup>13,14</sup>. Therefore, most recently, much focus is being placed on the substitution of styrene by non-harmful biobased aromatic monomers. Even if there has been some very interesting works on natural flavonoids<sup>15</sup> or lignin<sup>16,17</sup>, these resources exhibit strong drawbacks. Indeed, low purity and high molar masses of these resources limit their development in chemistry. Moreover, even if depolymerization of lignin<sup>18</sup> is an alluring route to give access to biobased aromatics needed by chemical industry, this route remains deceptive. In contrast, cardanol, extracted from cashew nut shell liquid, is really a promising aromatic non edible renewable source. It is a waste of the culture of Cashew nuts and does not compete with food. Cashew nut shell liquid (CNSL) is directly extracted from the shell of the cashew nut, fruit from cashew tree, *Anacardium occidentale* L. This tree is mainly grown in India and also in East Africa and Brazil<sup>19</sup>. The total production of CNSL approaches one million tons annually<sup>20</sup> and CNSL is one of the few major and economic sources of naturally occurring phenols.<sup>21</sup> CNSL can be regarded as a versatile and valuable raw material for polymer production and represents a good natural alternative to petrochemically derived phenols<sup>22</sup>.



**Figure 1. Components of CNSL**

CNSL constitutes nearly 25% of the total weight of the nut and is composed of anacardic acid (3-n-pentadecylsalicylic acid) and smaller amounts of cardanol (3-n-pentadecylphenol), cardol (5-n-pentadecylresorcinol), and methylcardol (2-methyl-5-n-pentadecylresorcinol), the long aliphatic side-chain being saturated, mono-olefinic (position 8), di-olefinic (positions 8 and 11), and tri-olefinic (positions 8, 11 and 14) with an average value of two double bonds per molecule (Figure 1). The thermal treatment of cashew nuts and CNSL induces the partial decarboxylation of anacardic acid, which is completed by a subsequent distillation. The result is an industrial grade of cardanol, in the form of a yellow oil containing mainly cardanol (about 90%), with a small percentage of cardol and methylcardol<sup>23</sup>. Cardanol is a yellow pale liquid composed of four meta-alkyl phenols differing by the degree of unsaturation of their aliphatic chain: fully saturated chains (SC) 8.4%, monoolefinic (MO) 48.5%, diolefinic (DO) 16.8% and triolefinic (TO) 29.33% chains (Figure 1).

Among the plant oil resource materials, CNSL is considered as an important starting material due to its unique structural features, abundant availability and low cost. Structurally diverse compounds have been developed starting from CNSL by taking advantage of the three reactive sites, namely, phenolic hydroxyl, aromatic ring and unsaturation(s) in the alkenyl side chain. Cardanol has been utilized as a starting material for the synthesis of condensation monomers. Wadgaonkar et al. have explored the synthesis of various CNSL-based difunctional condensation monomers such as aromatic diamines, diacids, diols, dialdehydes, diacylhydrazide, etc<sup>24</sup>. Our team also reported a platform approach on the synthesis of cardanol for the synthesis of di- and poly-functional monomers for polyepoxide and vinyl esters<sup>25</sup>. Most of the studies so far, focused on the functionalization of cardanol to propose monomers for thermoset polymers; and these studies were only investigating bulk or solvent borne processes.

Thanks to the phenol group and its long alkyl chain, cardanol is an obvious starting material for the synthesis of surfactants to be used in polymerization in dispersed media. It is therefore surprising that cardanol-derivatives have in fact, only seldom been used as emulsion stabilizers or comonomers. Polycardanol microcapsules were produced by enzymatic polymerization of the phenol moieties<sup>26</sup> under emulsion

conditions. Cardanol-based surfactants were used as stabilizers and dopant for the interfacial polymerization of aniline<sup>27,28,29,30</sup>. Unmodified cardanol was also used directly as a comonomer in the suspension polymerization of MMA or styrene, however the poor reactivity of the C<sub>15</sub> unsaturations limited its incorporation in the final copolymer<sup>31</sup>. Finally, cardanyl acrylate and methacrylate were polymerized in solution using conventional polymerization and ATRP<sup>32,33,34</sup>. To the best of our knowledge, there is only one report describing the use of cardanyl acrylate in homopolymerization or copolymerization with methyl methacrylate or styrene under suspension polymerization conditions<sup>35</sup> and the use of unmodified cardanol in emulsion polymerization<sup>36</sup>. Therefore our paper proposes a pioneering route to the synthesis of cardanol derived biobased aromatic latex. We functionalized cardanol into methacrylated cardanol and studied homopolymerization and copolymerization with methyl methacrylate in emulsion polymerization. We also proposed the feasibility of coating application with UV cross-linking via thiol-ene chemistry.

## **Experimental**

### **Materials and methods**

Cardanol was kindly supplied by Cardolite, Sodium hydroxide was purchased from Carlo Erba, epichlorohydrine from Fluka, methyl methacrylate (MMA), Ammonium persulfate, 4,4'-azobis(4-cyanovaleric acid) (ACVA), Azobisisobutyronitrile (AIBN), tetrabutyl ammonium chloride, methacrylic acid, hydroquinone, triphenylphosphine, potassium bicarbonate, chloroform, tert-dodecyl mercaptan, sodium dodecyl sulfate (SDS), bis(trimethylsilyl) benzene, 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (IRGACURE 2959), Bis-(mercaptoethyl) ether and laboratory reagent grade hexane, diethyl ether and ethyl acetate, (purity>95%) were purchased from Sigma Aldrich and used as received unless otherwise stated.

### **Nuclear magnetic resonance (NMR)**

The Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AC 400 instrument. Deuterated chloroform was used as the solvent in each sample. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording <sup>1</sup>H NMR, spectra were as follows: flip angle 90°, acquisition time 4.5 s, pulse delay 2 s.

### **Differential Scanning Calorimetry (DSC)**

DSC measurements were performed on 10–15 mg samples on a Netzsch DSC 200 F3 instrument using the following heating/cooling cycle: first heating ramp from room temperature (ca. 20 °C) to 150 °C at 10 °C/min, cooling stage from 150 °C to –100 °C at 10 °C/min, isotherm plateau at –50 °C for 3 min, second heating ramp from –100 °C to 150 °C at 10 °C/min, and last cooling stage from 150 °C to room temperature (ca. 20 °C). Calibration of the instrument was performed with noble metals and checked before analysis with an indium sample.

### **Thermogravimetric analysis (TGA)**

TGA analyses were carried out on 10-15 mg samples on a TGA Q50 apparatus from TA Instruments from 20 °C to 590 °C, in an aluminum pan, at a heating rate of 10 °C/min, under air.

### **Dynamic Light Scattering (DLS)**

Light scattering measurements were recorded on a VASCO-3 particle size analyzer from Cordouan Technologies. 1 mL samples were introduced into the cell after filtration through 0.45  $\mu\text{m}$  PTFE microfilters.

### **CryoTEM**

Cryo-TEM analyses were conducted using a JEOL 2200FS microscope operating at 200 kV equipped with an Omega energy filter. To prepare samples, 3.0  $\mu\text{L}$  of copolymer solution were placed onto a glow-discharged R2/2 Quantifoil grid (Quantifoil Micro Tools GmbH, Jena, Germany) and then quickly frozen in liquid ethane using a CP3 cryo-plunge (Gatan, inc.) with a blotting time of 0.50 s under a controlled moisture atmosphere. Images were recorded in the zero-energy-loss mode with a slit width of 20 eV at a nominal magnification of  $\times 30000$  to  $\times 50000$  using a 4k  $\times$  4k slow-scan CCD camera (Gatan, inc.) with defocus values ranging from 1.0 to 2.5  $\mu\text{m}$ .

### **Synthetic procedures**

#### ***Epoxy cardanol synthesis***

30 g (0.10 mol) of cardanol were epoxidized with 150 g (1.62 mol) of epichlorohydrin in the presence of 3 g (13.00 mmol) of tetrabutylammonium chloride. The reactants were placed into a round bottom flask, and the mixture was stirred for 1 h at 30  $^{\circ}\text{C}$  and then at 80 $^{\circ}\text{C}$  for 1 h. The non-reacted epichlorohydrin was removed under vacuum. To close the opened epoxy ring, the resulting product of the previous step, was mixed with 80.0 g of a 20 wt % of sodium hydroxide aqueous solution (0.40 mol) and stirred for 30 minutes at room temperature. The epoxy cardanol was extracted from the aqueous solution with ethyl acetate, and the organic phase was washed 3 times with DI water. The organic phase was dried using sodium carbonate and the solvent was removed under vacuum. A dark yellow-brown liquid was obtained. Yield: 92%. Note: The starting cardanol contained about 5 mol % of cardol. The epoxy cardanol thus also contained about 5 mol % of diepoxide compound.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.2 (t, 1 H, aromatic proton b Figure 2), 6.72-6.81 (m, 3H, aromatic protons a, c, and c' Figure 2), 6.38-6.41 (3H, d, cardol aromatic protons), 5.8-5.9 (m, 1H,  $\text{C}_{15}$  chain, protons 6 Figure 2),  $\delta$  5.3-5.5 (m, 4H,  $\text{C}_{15}$  chain, internal double bond protons 5 Figure 2), 5-5.1 (m, 2H,  $\text{C}_{15}$  chain, protons of the terminal double bond 1' Figure 2), 3.9-4.25 (m, 3H, protons j and k Figure 2),  $\delta$  3.35 (m, 1H, protons l Figure 2), 2.8-2.9 (m, 1H, protons m Figure 2), 2.7-2.8 (3H,  $\text{C}_{15}$  chain, protons 7 Figure 2), 2.6 (t, 2H,  $\text{C}_{15}$  chain, protons 4 Figure 2),  $\delta$  2.07 (m, 2H,  $\text{C}_{15}$  chain, protons 8 Figure 2), 1.64 (m, 2H,  $\text{C}_{15}$  chain, protons 3 Figure 2), 1.36 (m, 2H,  $\text{C}_{15}$  chain, protons 2 Figure 2), 0.95 (m, 3H,  $\text{C}_{15}$  chain, terminal  $-\text{CH}_3$ , protons 1 Figure 2).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)): 158.5 (aromatic,  $-\text{CH}-\underline{\text{C}}(\text{OH})-\text{CH}-$ ), 145 (aromatic,  $\text{CH}-\underline{\text{C}}(\text{C}_{15}\text{H}_{31-n})-\text{CH}-$ ), 136.8 ( $\text{C}_{15}$  chain,  $=\text{CH}-\text{CH}_2-\underline{\text{C}}\text{H}=\text{CH}_2$ ), 130.4 ( $\text{C}_{15}$  chain,  $-\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}-\text{C}_6\text{H}_{13}$ ), 130 ( $\text{C}_{15}$  chain,  $-\text{CH}_2-\underline{\text{C}}\text{H}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{C}_3\text{H}_7$ ), 129.9 ( $\text{C}_{15}$  chain,  $-\text{CH}_2-\underline{\text{C}}\text{H}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{C}_3\text{H}_5$ ), 129.8 ( $\text{C}_{15}$  chain,  $-\text{CH}=\text{CH}-\text{CH}_2-\underline{\text{C}}\text{H}=\text{CH}-\text{C}_3\text{H}_5$ ), 129.35 (aromatic,  $-\text{CH}-\underline{\text{C}}\text{H}-\text{CH}-$ ), 128.14 ( $\text{C}_{15}$  chain,  $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\underline{\text{C}}\text{H}-\text{C}_3\text{H}_5$ ), 128 ( $\text{C}_{15}$  chain,  $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\underline{\text{C}}\text{H}-\text{C}_3\text{H}_7$ ), 127.6 ( $\text{C}_{15}$  chain,  $-\text{CH}=\text{CH}-\text{CH}_2-\underline{\text{C}}\text{H}=\text{CH}-\text{C}_3\text{H}_7$ ), 126.8 ( $\text{C}_{15}$  chain,  $-\text{CH}=\underline{\text{C}}\text{H}-\text{CH}_2-\text{CH}=\text{CH}-\text{C}_3\text{H}_7$ ), 121 (aromatic,  $-\text{CH}-\underline{\text{C}}\text{H}-\text{C}(\text{C}_{15}\text{H}_{31-n})-$ ), 115.3 (aromatic,  $-\text{C}(\text{O}-\text{CH}_2-\text{C}_2\text{H}_3\text{O})-\underline{\text{C}}\text{H}-\text{C}(\text{C}_{15}\text{H}_{31-n})-$ ), 114.7 ( $\text{C}_{15}$  chain, terminal  $=\text{CH}_2$ ), 112.5 (aromatic,  $-\underline{\text{C}}\text{H}-\text{C}(\text{O}-\text{C}_3\text{H}_5\text{O})-\text{CH}-\text{C}(\text{C}_{15}\text{H}_{31-n})-$ ), 68.6 (epoxy,  $-\text{O}-\underline{\text{C}}\text{H}_2-\text{CH}(\text{O})\text{CH}_2$ ), 50.1 (epoxy,  $-\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}(\text{O})\text{CH}_2$ ), 44.7 (epoxy,  $-\text{O}-\text{CH}_2-\text{CH}(\text{O})\underline{\text{C}}\text{H}_2$ ), 35.7 ( $\text{C}_{15}$  chain,  $=\text{CH}-\underline{\text{C}}\text{H}_2-\text{CH}=\text{}$ ), 31.8 ( $\text{C}_{15}$  chain, aromatic  $-\underline{\text{C}}\text{H}_2-$ ), 31.5

(C<sub>15</sub> chain, -CH<sub>2</sub>-C<sub>2</sub>H<sub>5</sub>), 31.2 (C<sub>15</sub> chain, aromatic-CH<sub>2</sub>-CH<sub>2</sub>-), 29.7 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH<sub>2</sub>-CH=), 29.6 (C<sub>15</sub> chain, aromatic-C<sub>4</sub>H<sub>8</sub>-CH<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-CH=), 29.2 (C<sub>15</sub> chain, aromatic-C<sub>3</sub>H<sub>6</sub>-CH<sub>2</sub>-), 28.9 (C<sub>15</sub> chain, aromatic-C<sub>2</sub>H<sub>4</sub>-CH<sub>2</sub>-), 27.2 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-CH<sub>2</sub>-), 25.5 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH=C<sub>4</sub>H<sub>8</sub>), 22.6 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH<sub>3</sub>), 14 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 13.8 (C<sub>15</sub> chain, terminal -CH<sub>3</sub>). This spectrum is shown in Figure S2.

### **CAMA (cardanol methacrylate) synthesis**

30.0 g (84.00 mmol) of epoxy cardanol, 72.3 g (0.84 mol) of methacrylic acid, 0.3 g (3.00 mmol) of hydroquinone and 0.75 g (0.30 mmol) of triphenylphosphine were placed in a round bottom flask, and the resulting solution was stirred at 80°C for 20 h. The excess methacrylic acid ( $\delta$  of the methacrylic proton of methacrylic acid: 5.66 ppm and 6.25 ppm) was then neutralized with an aqueous solution of potassium bicarbonate at room temperature. The cardanol methacrylate was extracted from the aqueous solution with chloroform and washed 3 times with DI water. The organic phase was dried using sodium carbonate and the solvent was removed under vacuum. A yellow-brown viscous liquid was isolated. Yield: 87%. Note: The resulting product contained about 5% of dimethacrylate compound (quantity determined from the <sup>1</sup>H NMR spectrum).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 7.2 (t, 1 H, aromatic proton b Figure 2), 6.7-6.85 (m, 3H, aromatic protons a, c, and c' Figure 2), 6.2-6.4 (3H, m, cardol aromatic protons), 6.18 (s, 1H methacrylate proton d, Figure 2), 5.8-5.9 (m, 1H, C<sub>15</sub> chain, protons 6 Figure 2), 5.6 (s, 1H methacrylate proton e, Figure 2), 5.3-5.5 (m, C<sub>15</sub> chain, internal double bond protons 5 Figure 2), 5-5.15 (m, 2H, C<sub>15</sub> chain, protons of the terminal double bond 1' Figure 2), 4.38 (m, 2H, protons f Figure 2), 4.3 (m, 1H, proton g Figure 2), 4-4.1 (m, 2H, protons h Figure 2), 2.8 (m, 2H, C<sub>15</sub> chain, protons 7 Figure 2), 2.6 (t, 2H, C<sub>15</sub> chain, protons 4 Figure 2), 2-2.1 (m, 2H, C<sub>15</sub> chain, protons 8 Figure 2), 1.98 (s, 3H, methacrylate -CH<sub>3</sub>, protons i Figure 2), 1.62 (m, 2H, C<sub>15</sub> chain, protons 3 Figure 2), 1.25-1.45 (m, C<sub>15</sub> chain, protons 2 Figure 2), 0.92 (m, 3H, C<sub>15</sub> chain, terminal -CH<sub>3</sub>, protons 1 Figure 2).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 167.4 (methacrylate, -O-C(O)-), 158.5 (aromatic, -CH-C(OMeth)-CH-), 145 (aromatic, -CH-C(C<sub>15</sub>H<sub>31-n</sub>)-CH-), 136.8 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH=CH<sub>2</sub>), 135.7 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH=CH<sub>2</sub>), 130.4 (C<sub>15</sub> chain, -CH=CH-C<sub>6</sub>H<sub>13</sub>), 130 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-CH=CH-C<sub>3</sub>H<sub>7</sub>), 129.9 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH=CH<sub>2</sub>-CH=CH-C<sub>3</sub>H<sub>5</sub>), 129.8 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH=CH-C<sub>3</sub>H<sub>5</sub>), 129.35 (aromatic, -CH-CH-CH-), 128.14 (C<sub>15</sub> chain, -CH=CH-CH<sub>2</sub>-CH=CH-C<sub>3</sub>H<sub>5</sub>), 128 (C<sub>15</sub> chain, -CH=CH-CH<sub>2</sub>-CH=CH-C<sub>3</sub>H<sub>7</sub>), 127.6 (C<sub>15</sub> chain, -CH=CH-CH<sub>2</sub>-CH=CH-C<sub>3</sub>H<sub>7</sub>), 126.8 (C<sub>15</sub> chain, -CH=CH-CH<sub>2</sub>-CH=CH-C<sub>3</sub>H<sub>7</sub>), 121 (aromatic, -CH-CH-C(C<sub>15</sub>H<sub>31-n</sub>)-), 115.3 (aromatic, -C(O-CH<sub>2</sub>-C<sub>2</sub>H<sub>3</sub>O)-CH-C(C<sub>15</sub>H<sub>31-n</sub>)-), 114.7 (C<sub>15</sub> chain, terminal =CH<sub>2</sub>), 112.5 (aromatic, -CH-C(O-C<sub>3</sub>H<sub>5</sub>O)-CH-C(C<sub>15</sub>H<sub>31-n</sub>)-), 68.6 (-O-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-O-C(O)-), 65.5 (-C(O)-O-CH<sub>2</sub>-CH(OH)-), 35.7 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH=), 31.8 (C<sub>15</sub> chain, aromatic-CH<sub>2</sub>-), 31.5 (C<sub>15</sub> chain, -CH<sub>2</sub>-C<sub>2</sub>H<sub>5</sub>), 31.2 (C<sub>15</sub> chain, aromatic-CH<sub>2</sub>-CH<sub>2</sub>-), 29.7 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH<sub>2</sub>-CH=), 29.6 (C<sub>15</sub> chain, aromatic-C<sub>4</sub>H<sub>8</sub>-CH<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-CH=), 29.2 (C<sub>15</sub> chain, aromatic-C<sub>3</sub>H<sub>6</sub>-CH<sub>2</sub>-), 28.9 (C<sub>15</sub> chain, aromatic-C<sub>2</sub>H<sub>4</sub>-CH<sub>2</sub>-), 27.2 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-CH<sub>2</sub>-), 25.5 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH=C<sub>4</sub>H<sub>8</sub>), 22.6 (C<sub>15</sub> chain, -CH<sub>2</sub>-CH<sub>3</sub>), 18.3 (methacrylate, -CH<sub>3</sub>), 14 (C<sub>15</sub> chain, =CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 13.8 (C<sub>15</sub> chain, terminal -CH<sub>3</sub>). This spectrum is shown in Figure S3.

### **Purification of CAMA by flash column chromatography**

10ml of unpurified CAMA were poured in 4ml of cyclohexane and 1ml of ethyl acetate. The solution were injected in a silica column (40 $\mu$ m, 120g provide by REVELERIS) and a cyclohexane:ethyl acetate 80:20 % v/v mixture was used as eluent with a flow of 80ml/min.

### **Emulsion polymerisation**

10 g of monomer (CAMA or CAMA/MMA mixture), 0.1 g (0.50 mmol) of tert-dodecyl mercaptan (transfer agent which reduces the molar mass and the risk of gel formation), 0.01 g (0.12 mmol) of calcium bicarbonate, 1.35 g (5.00 mmol) of sodium dodecyl sulfate, 0.28 g (1.25 mmol) of 1,4-bis(trimethylsilyl) benzene (NMR internal standard) and 24.4 g (1.36 mol) of water were placed in a round bottom flask, and the mixture was deoxygenated by nitrogen bubbling for 20 minutes. The reaction mixture was then heated up to 80°C over the course of 1h and stirred with a magnetic stirrer at 300 rpm. A solution of 0.02 g (0.09 mmol) of ammonium persulfate and 1.09 g (61.00 mmol) of deoxygenated DI water was injected in the media. After 2 h at 80°C, the solution was cooled down to room temperature. A light brown latex was obtained. Monomer conversions were calculated by NMR using 1,4-bis(trimethylsilyl) benzene (BTMBS) as reference (introduced in the reaction medium at the start of the emulsion polymerization, typically in a 5.5% molar ratio to the monomer) via the following equations.

$$(1) \quad \text{Conv}_{(\text{CAMA})} = 100 \times \left| 1 - \frac{N_{\text{D}} \text{ (CAMA)}}{N_{\text{D}} \text{ (BTMBS)}} \right|$$

$$(2) \quad \text{Conv}_{(\text{MMA})} = 100 \times \left| 1 - \frac{N_{\text{D}} \text{ (MMA)}}{N_{\text{D}} \text{ (BTMBS)}} \right|$$

### **Solution polymerization of CAMA**

2 g (4.5 mmol) of CAMA, 0.0148 g (0.09 mmol) of AIBN and 6 g of toluene were placed in a 20 mL round bottom flask and heated at 80°C for 7 h. PCAMA was then precipitated in methanol. The precipitated was filtered and dried in a vacuum oven at 50°C overnight.

### **Thiol-ene photocrosslinking**

Photocrosslinking was performed on films prepared from PCAMA latex (entry 1, Table 1). A polymer film was formed using a bar coater with a latex containing 0.5 eq. of bis-(mercaptoethyl)ether and 0.03 eq. of IRGACURE 2959 to 1 eq. of C<sub>15</sub> chain unsaturations. Typically, 0.093 g of Bis-(mercapto ethyl) ether and 0.0045 g of IRGACURE 2959 were added to 1g of latex and stirred vigorously. The aqueous solution was then coated at room temperature (ca. 20 °C) on a steel plate with a manual bar coater (200 $\mu$ m) and dried in an oven at 50°C. This flexible film was then irradiated under UV for 20 s (1800W, 120W/cm, 200-600 nm). This UV treatment is also likely accompanied by an elevation of T.

### **Gel content measurements**

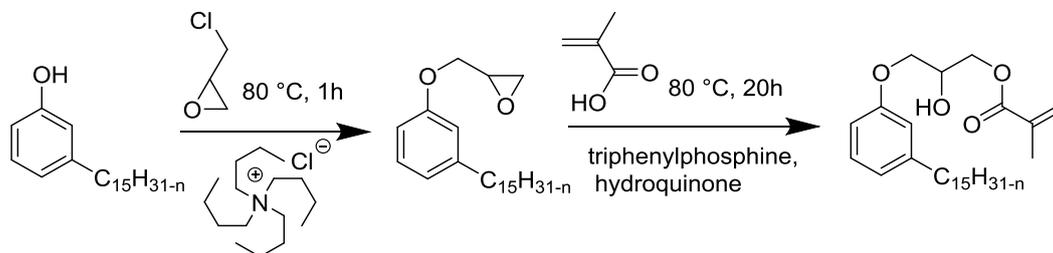
3 samples (30 mg each) were placed in Teflon pockets which were put separately into 30 ml of THF for 24 h then dried in a ventilated oven at 50°C during 24h. The gel content GC is given by the following equation.  $m_0$  is the initial mass and  $m_1$  is the mass after drying.

$$(3) \quad GC = \frac{m_1}{m_0} \times 100$$

## Results and discussion

### *Cardanol methacrylate monomer synthesis*

The cardanol methacrylate monomer was synthesized via a two-step procedure (Scheme 1) adapted from previously published protocols<sup>37</sup>. In the first step, cardanol was epoxidized using epichlorohydrin. Epoxide rings which were opened during the synthesis were closed by treatment with sodium hydroxide. The resulting epoxy cardanol was reacted with a large excess of methacrylic acid, in the presence of triphenylphosphine (as catalyst) and hydroquinone (as polymerization inhibitor) to afford the desired cardanol methacrylate monomer (CAMA) in high yields (>80 %). CAMA was easily isolated by simple solvent extraction from the aqueous reaction medium. However, it is important to note that starting cardanol contained about 5 mol % of cardol, therefore the final CAMA also contained about 5 mol % of dimethacrylate (as indicated by the <sup>1</sup>H NMR spectrum). Figure 2 shows the <sup>1</sup>H NMR spectra of the starting cardanol, the intermediate epoxy cardanol and the final CAMA. These NMR spectra clearly show the functionalization of the phenol moiety and the presence of about 5% of cardol and cardol derivatives in the starting cardanol and in the final CAMA respectively. The synthesis of CAMA could not be performed from technical epoxy cardanol purchased from cardolite (NC513), probably due to the lack of purity of the starting material. Direct methacrylation of cardanol, although probably easy to perform in high yield, was not attempted, because it leads to phenolic esters known for their low resistance to hydrolysis.

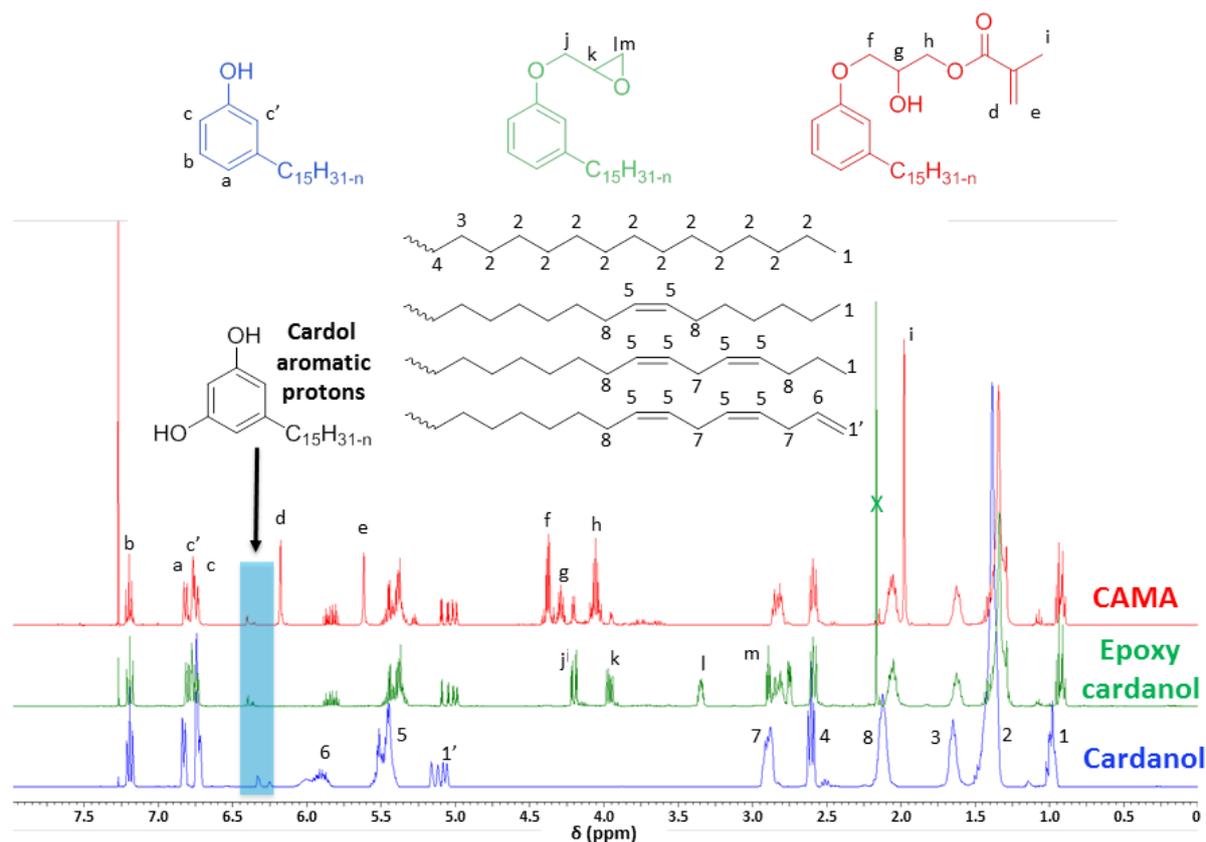


**Scheme 1. Synthesis of the cardanol methacrylate monomer (CAMA)**

### *Emulsion polymerization of CAMA*

The goal of this study was to assess the behaviour of a biobased methacrylate derived from cardanol in aqueous emulsion polymerization. CAMA was thus first used as the sole monomer in an aqueous emulsion formulation using sodium dodecyl sulfate as surfactant and ammonium persulfate as initiator at 30 % solids content. The polymerization was carried out in batch at 80 °C and in the presence of tert-dodecyl mercaptan in order to reduce the molar mass of the resulting polymer and of 1,4-bis(trimethylsilyl) benzene which provided useful <sup>1</sup>H NMR signals to calculate monomer conversion (Entry 1, Table 1). The emulsion polymerization was stopped after 2 hours and the resulting latex was analysed by <sup>1</sup>H NMR, DLS, cryo-TEM, TGA and DSC. The conversion of CAMA reached 91 % and the emulsion polymerization did not yield any significant amount of coagulum (< 2%). This PCAMA latex was, however, quite polydisperse with intensity hydrodynamic diameters, measured by DLS, ranging from 50 to 110 nm (entry 1, Table 1, and S4-S7). This rather small particle size is likely due to the large amount of surfactant used. These sizes and

dispersities were partly confirmed by Cryo-TEM imaging (Figure S8a) which showed particles of smaller size (ca. 20 nm). In addition, the latex displayed rather high gel content (9.7%). The formation of gel may be ascribed to the presence of bismethacrylate (the cardol bismethacrylate derivative) in the CAMA or to the participation of the CAMA C<sub>15</sub> side chain unsaturations to the polymerization. The CAMA used here was synthesized from a cardanol containing roughly 5 mol % of cardol (bisphenol), and thus contained about 5 mol % of dimethacrylate.



**Figure 2.** <sup>1</sup>H NMR spectra of the starting cardanol (blue trace), the intermediate epoxy cardanol (green trace) and the final cardanol methacrylate (red trace)

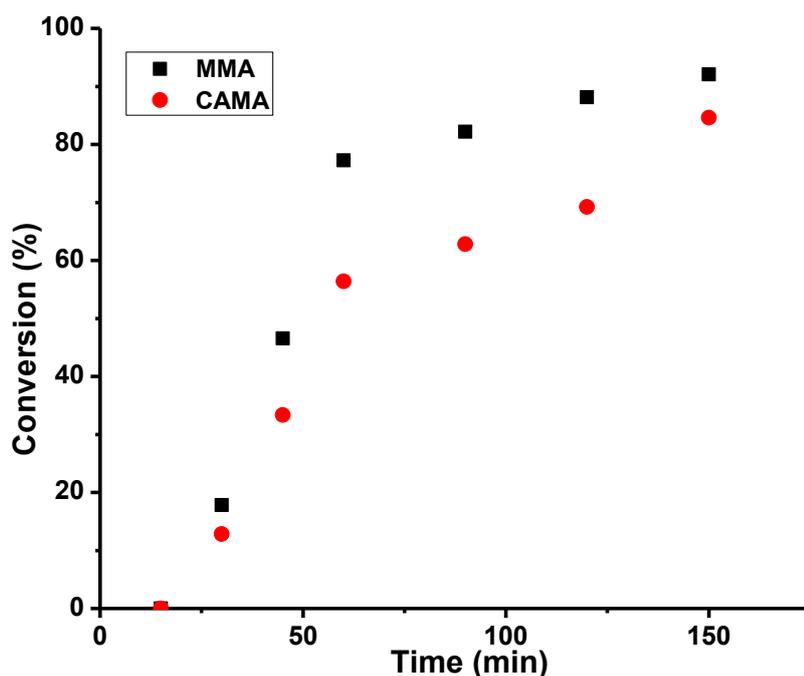
When MMA was polymerized in emulsion using the conditions used for CAMA (entry 2, Table 1), the polymerization proceeded to very high conversion (99 %) and yielded a very well-defined PMMA latex, with a narrow and monomodal particle diameter distribution centered at 62 nm (Figure S8b) and without any gel formation. These results also suggest that the gel content observed in the emulsion polymerization of CAMA was indeed caused by the bismethacrylate or the C<sub>15</sub> unsaturated side chains.

#### *CAMA/MMA latex*

A range of poly(CAMA-co-MMA) copolymer latex with contents of CAMA varying from 25 to 75 wt % was also prepared (entries 3 to 8, Table 1). Both monomers are methacrylates and they should copolymerize very well leading to statistical poly(CAMA-co-MMA) copolymer. The copolymerizability of the CAMA and MMA was estimated by monitoring the evolution (by <sup>1</sup>H NMR spectroscopy) of the conversions of both monomers versus time during a typical aqueous emulsion polymerization (Figure 3). CAMA was observed to be consumed slightly more slowly than MMA. While MMA conversion reached about 90 % in 150 minutes, the CAMA conversion only reached

80 % during the same period of time. This expected behaviour may be ascribed to the much higher steric hindrance (caused by the cardanol-derived pendent group) of CAMA compared to MMA, or to hydrogen abstraction (transfer reactions) to the allylic or doubly allylic protons of the C<sub>15</sub> unsaturated side chain leading to less reactive radicals<sup>38</sup>. The consequence of this slight difference in reactivity is that the synthesized latexes were slightly richer than targeted in MMA.

In all cases, the copolymer latexes showed relatively broad size distributions (Table 1, Figure 4 and Figure S4-S7). The gel content appears to increase with CAMA content (entries 4 and 5, Table 1) and with CAMA conversion (entries 3, 4 and 5, Table 1). Increasing CAMA content from 50 to 75 wt % (at conversion in CAMA around 80%) led to the increase of gel content from 2 % to 7.9 %. High CAMA conversion (99 %) but lower CAMA content also resulted into relatively high gel content (6.5 % for entry 3 compared to 2.0 % for Entry 4). This is consistent with previous studies which showed that in the case of difunctional methacrylates, the second methacrylate functional group only takes part to the polymerization reaction (and thus lead to intra- or inter-chain crosslinking) when relatively high (typically higher than 90 %) conversions are reached<sup>39</sup>. Another explanation for the relatively high gel content may be radical transfer to the polymer. The oxygen-centered radical (persulfate) used here is known to have a much higher capacity for H-abstraction than carbon-centered radicals such as those formed by thermal degradation of azo-initiators (AIBN or ACVA for



example<sup>40</sup>).

**Figure 3.** Evolution of the MMA (black squares) and CAMA (red circles) conversions versus time during a typical aqueous emulsion polymerization (CAMA / MMA = 75 / 25 wt %)

In addition CAMA and PCAMA possess an isopropyl alcohol proton quite prone to H-abstraction. The hypothesis that H-abstraction by radical transfer from the persulfate radicals to PCAMA was responsible for the microgel formation was thus tested (entries 4, 6, 7 and 8, Table 1). When poly(CAMA-co-MMA) (50:50 wt %) copolymer latexes were prepared using ammonium persulfate (APS) as the initiator, microgel formation was observed (entries 4 and 8, Table 1) When the same experiments were

performed using ACVA as the radical source (entries 6 and 7, Table 1), no microgel was observed. Moreover, when purified CAMA (i.e. CAMA treated with flash column chromatography and thus without bismethacrylate derivative) was used, the same observations were made: the use of APS led to microgel (entry 8, Table 1) whereas ACVA produced latexes without any microgel (entry 7, Table 1). These observations suggest that in the conditions used (relatively low conversion of CAMA, < 85 %, copolymerization of MMA and CAMA at 50 wt %), the microgel formation is uniquely caused by transfer reaction to the polymer (as depicted in Scheme 2).

**Table 1. Summary of the CAMA/MMA latex synthesized**

Entry	Initiator	Monomer feed (mol %)/ (wt %)		<sup>a</sup> Monomer conversion (%)		Polymer composition (mol %)/ (wt %)		<sup>b</sup> Average particles diameter (nm)	Gel content (%)
		CAMA	MMA	CAMA	MMA	CAMA	MMA		
	APS	CAMA	MMA	CAMA	MMA	CAMA	MMA		
1	APS	100 / 100	-	91	-	100 / 100	-	95	9.7
2	APS	-	100 / 100	-	99	-	100 / 100	44	0
3	APS	6.9 / 25	93.0 / 75	99	99	7 / 25.3	93 / 74.7	45	6.5
4	APS	18.4 / 50	81.6 / 50	83	98	16.8 / 46.2	84.2 / 53.8	46	2.0
5	APS	40.2 / 75	59.8 / 25	82	89	38 / 73.4	62.0 / 26.6	43	7.9
6	ACVA	18.4 / 50	81.6 / 50	66	74	16.8 / 47.2	83.2 / 52.8	72	0
<sup>c</sup> 7	ACVA	18.4 / 50	81.6 / 50	96	99	17.8 / 49.1	82.2 / 50.9	93	0
<sup>c</sup> 8	APS	18.4 / 50	81.6 / 50	76	88	16.3 / 46.3	83.7 / 53.7	40	10

*Reaction conditions:* Initiator: ammonium persulfate (APS) or 4,4'-Azobis(4-cyanovaleric acid) (ACVA), surfactant: Sodium dodecyl sulfate (SDS), chain transfer agent: tert-dodecyl mercaptan (TDM), <sup>1</sup>H NMR internal standard: 1,4-bis(trimethylsilyl) benzene (BTMBS). Typical emulsion formulation: [M] : [initiator] : [TDM] : [BTMBS] : [SDS]= 250 : 1 : 1.325 : 13.75 : 13.9, target solids content = 31.5 wt %. <sup>a</sup> Determined by <sup>1</sup>H NMR. <sup>b</sup> Determined by DLS (intensity average hydrodynamic diameter). <sup>c</sup> CAMA was purified by flash column chromatography.

In the conditions used to prepare the latexes, neither the C=C double bonds of the C15 side chains of CAMA nor the bismethacrylate derived from cardol took part in the crosslinking reaction.

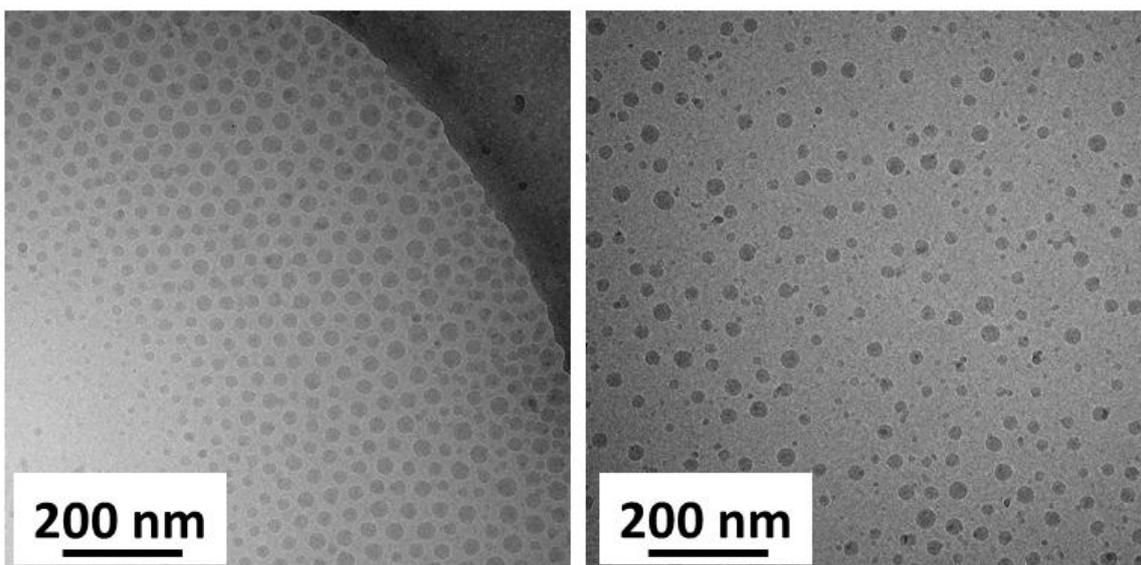
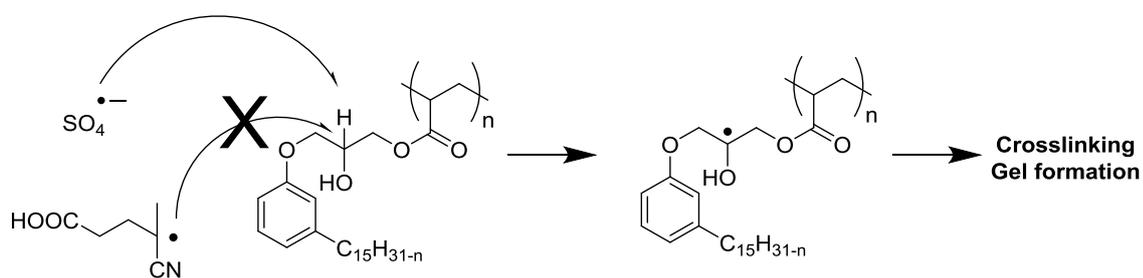


Figure 4. Cryo-TEM micrographs of poly(CAMA-co-MMA) latex (50:50 wt %), average diameter measured using ImageJ software: 22 nm (left image), 10 nm (right image).

#### *Thermogravimetric analyses of the CAMA-containing latexes*

The TGA of the PCAMA latex showed that this cardanol-derived polymer possesses a relatively high thermal resistance. The thermogram (Figure 5) of the 100 % PCAMA latex features a first decomposition step between 149 °C and 249 °C with  $T_{\text{Decomp}}(5\%) = 178\text{ °C}$  and a second very sharp decomposition step between 350 °C and 500 °C.



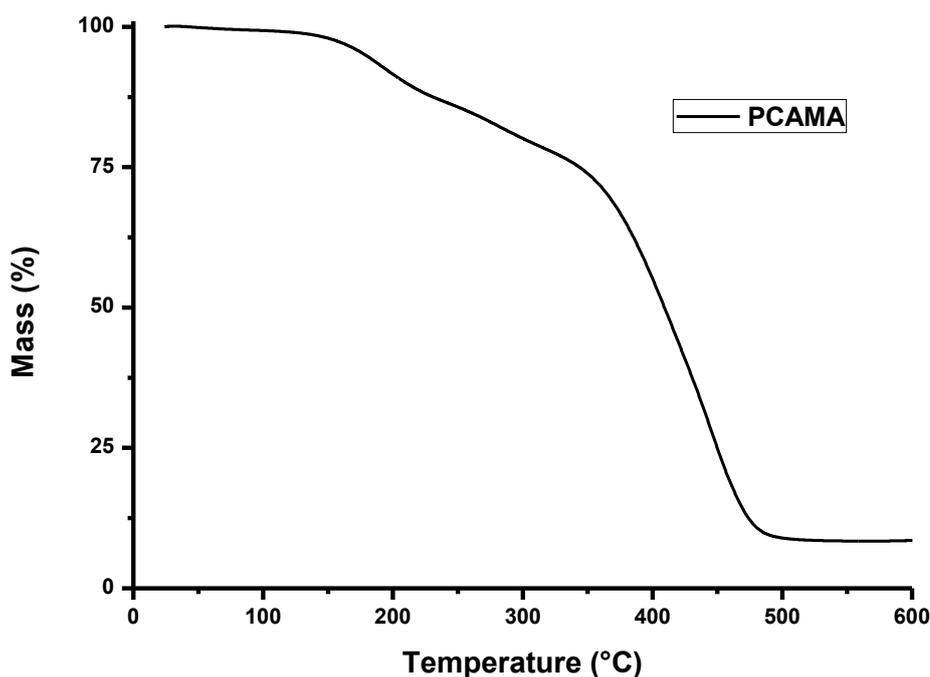


Figure 5. TGA thermogram of PCAMA latex under air.

The results of the DSC analyses of the latexes made using different content of CAMA are plotted in Figure 6. These thermograms show a first transition around 15 °C for the poly(CAMA-co-MMA) (25/75 wt %) copolymer latex which increases with increasing content of CAMA in the copolymer to reach about 40 °C for the PCAMA latex. This transition is also visible in the CAMA at around 20°C (Figure S10) before polymerization and is thought to be the  $T_g$  of the  $C_{15}$  side chain. Surprisingly, the expected effect of the copolymer composition on the  $T_g$  was not observed here, in contrast to what has been reported by Kang et al.<sup>41</sup> A second transition which looked like a melting transition was observed around 90°C. This surprising thermal transition which could not be assigned to a  $T_g$  was investigated further and appeared to be caused by interaction between the latex and the SDS (the latex were purified prior to DSC analysis). Indeed, this transition was not observed on the DSC thermograms of SDS alone (Figure S11), of CAMA (Figure S10), nor on the DSC thermograms of PCAMA synthesized by conventional radical solution polymerization in toluene which showed a  $T_g$  at 20 °C (Figure S12) or on the DSC of the poly (CAMA-co-MMA) copolymer (CAMA:MMA = 50/50 wt %) microgel alone (Figure S13). It can clearly be seen, however, on the DSC thermogram of a mixture of SDS and of PCAMA prepared by polymerization in solution (Figure S14). This transition might be ascribed to the melting of crystals formed of  $C_{15}$  side chains of CAMA and SDS.

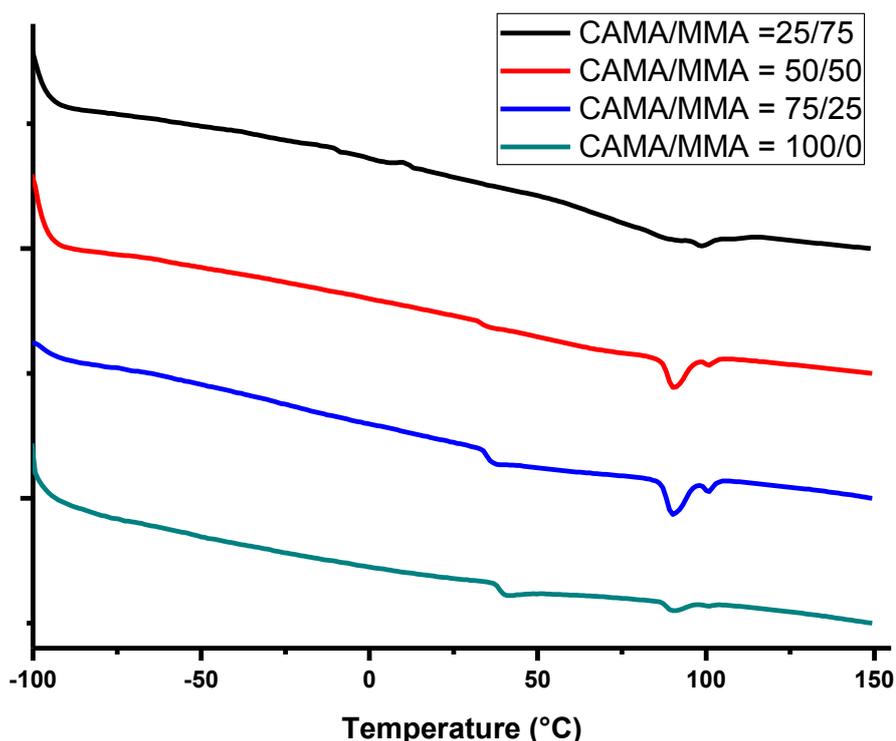


Figure 6. DSC thermograms of the CAMA-containing latex synthesized in Table 1

#### *Film formation and photo-crosslinking.*

To test the ability of the PCAMA latex to form films for potential application in coatings, PCAMA latex film were prepared and photo-crosslinked using thiol-ene chemistry. Films of PCAMA latex containing small amount of dithiols were then irradiated under UV light in the presence or absence of a photoinitiator and the insoluble content was measured. The film irradiated in the absence of photoinitiator displayed an insoluble content of 41 wt %, whereas the film irradiated in the presence of the photoinitiator showed an insoluble content of 86 wt %. This significant increase of the insoluble content (from 9.7 wt % in the starting latex to 86 wt % after irradiation) is likely caused by crosslinking of alkyl chains of cardanol by thiol-ene reaction between dithiol and the available C=C double bonds in the latex (C<sub>15</sub> side chains unsaturations and unreacted methacrylate functional groups from the cardol derivative).

#### **Conclusions**

This article presents the synthesis of CAMA, a novel phenolic methacrylic monomer derived from cardanol, a very interesting biobased and non-edible phenol source from cashew nut shell. This article reports for the first time the aqueous emulsion polymerization and copolymerization with MMA of this novel monomer. This biobased CAMA monomer can be prepared in very high yields in 2 steps: first the epoxidation of the phenol group of cardanol, followed by the methacrylation of the epoxy ring with methacrylic acid. This monomer contained about 5 % of dimethacrylate derived from cardol (a diphenol impurity of cardanol), but can be purified by column chromatography. In spite of the expected very hydrophobic character of this biobased

monomer which may have precluded the preparation of latex by emulsion polymerization in water, this cardanol methacrylate afforded stable latex. The latexes showed non negligible contents of microgel. These microgels were demonstrated to be formed by transfer to the monomer and polymer (likely by abstraction of the isopropyl proton of CAMA by the oxygen-centered radicals of the persulfate polymerization initiator used) rather than by the polymerization of the cardol dimethacrylate or the unsaturations of the C<sub>15</sub> side chains of cardanol. Using an azo-initiator instead of a persulfate eliminated the microgelation entirely. The CAMA containing latex showed T<sub>g</sub> increasing with CAMA content and ranging from 30 to 40 °C (when CAMA content increased from 25 wt % to 100 wt %). These latexes were also showed to be able to form films that could be efficiently photocrosslinked by thiol-ene chemistry. These preliminary results allowed to propose aromatic biobased latex without styrene that bode well for potential applications in the fields of paints and coatings. Further studies are underway in our team.

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