Biobased Aromatic-Aliphatic Polyols from Cardanol by Thermal Thiol-Ene Reaction

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ABSTRACT: Cardanol is a natural phenol which is obtained from high vacuum distillation of cashew nut shell liquid. It contains a hydrocarbon chain of 15 carbon atoms in the *meta* position, either with one, two or three non-conjugated double bonds. This article describes thermal thiol-ene reaction to synthesize new cardanol-based polyols for polyurethanes with aromatic-aliphatic structure. Phenolic hydroxyl group was blocked by alkoxylation and 2-mercaptoethanol was added to the double bonds of propoxylated cardanol. The resultant product is a mixture of polyols that may contain one, two, three or four hydroxyl groups, as a function of the number of double bonds reacted with 2-mercaptoethanol. Similar polyols, but with much higher functionality, were also synthesized from condensation of cardanol-based novolacs with formaldehyde. These cardanol-based polyols were further utilized to prepare rigid polyurethane foams (PUs) with excellent physical and mechanical properties, useful for various applications in chemical and food industries.

KEYWORDS: Thiol-ene, mercaptans, cashew nut shell liquid, polyurethanes

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1 INTRODUCTION

Cashew nut shell liquid (CNSL) is a compound containing about 90% of anacardic acid, a product from cashew nut. Anacardic acid is a natural phenol with a carboxyl group at *ortho* position and a hydrocarbon chain of 15 carbon atoms in the *meta* position. Anacardic acid is easily decarboxylated by high vacuum distillation at 200–220 °C to obtain cardanol, a natural phenol possessing a hydrocarbon chain of 15 carbon atoms in the *meta* position with one, two or three non-conjugated double bonds [1–4].

Cardanol has been used as one of the most interesting biobased raw materials to synthesize new polyols for polyurethanes, novolac resins, epoxy resins, non-ionic surfactants, antioxidants, plasticizers, coatings, paints, etc. [5–20]. Previously [17, 18] we described a preparation of biobased Mannich polyols by reacting cardanol with 1,3-*N*-hydroxyethyl oxazolidine (product obtained from condensation of diethanolamine with formaldehyde) followed by propoxylation. The Mannich polyols lead to rigid polyurethane foams with excellent physical-mechanical, thermal and flame proofing properties [17–20]. These foams are useful especially as "spray" foams due to their high reactivity. Cardanol-based polyols for rigid polyurethanes were also prepared by epoxidation of double bonds in hydrocarbon chain followed by ring opening of epoxy groups with alcohols [11–13].

The present study describes the synthesis of new cardanol-based polyols from thermally initiated thiol-ene reaction by adding 2-mercaptoethanol to the C=C double bond of the hydrocarbon chain of cardanol. It is a known fact that the phenolic group has a strong inhibitory effect on radical reaction which facilitates a transfer of reactive species from the reaction system and generates aryloxy radicals stabilized by conjugation. Therefore, the phenolic group of cardanol was blocked by alkoxylation with propylene oxide (or ethylene oxide). With this new compound (propoxylated cardanol) in hand, thiol-ene reaction involving C=C double bonds of hydrocarbon chain can be carried out safely in high yield. Further, the functionality of polyols was also increased by using propoxylated cardanol novalocs (cardanol novaloc is a product obtained from condensation of cardanol with paraformaldehyde in the presence of acidic catalyst) with 2-mercaptoethanol (ME) in thiol-ene reaction. These new groups of cardanol-based polyols were transformed into rigid polyurethane foams using a polymeric methylene

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diisocyanate (MDI). The properties of resultant foams were also analyzed.

2 EXPERIMENTAL

2.1 Materials

Cardanol (trade name Cardolite NC-700), a dark brownish-red liquid with iodine value of 220 g I_2/100 g and color Hazen around 18, was kindly supplied by Cardolite Corporation [21]. Based on the literature data, the molecular formula of cardanol is $C_{21}H_{30}O$ with average molecular weight 297–298. Propylene oxide (PO), 99.8%, and 1,1,3,3-tetramethylguanidine (TMG), 99%, (catalyst for propoxylation of phenolic group) were purchased from Acros Organics. 2-Mercaptoethanol (ME), 99.5%, was kindly supplied by Chevron Phillips Chemical Company LP, Bartlesville, Oklahoma, under the trade name BME, as a colorless liquid with sulfur content of 41.0% and thiol equivalent weight EW = 39.1. Paraformaldehyde powder, 95%, and AIBN [2,2′-Azobis (2-methyl propionitrile)], 99%, the radical initiator, were purchased from Sigma-Aldrich. Voranol 490, a sucrose-glycerol polyether polyol with hydroxyl number OH#=490 mg KOH/g was kindly supplied by DOW. Silicone surfactant Tegostab B8404 was obtained from Evonik Industries, Inc., Niax™ A-1 catalyst bis(2-dimethylaminoethyl) ether was purchased from Momentive Performance Materials Inc. and DABCO T-12 (dibutyltin dilaurate) was obtained from Air Products and Chemicals Inc.; Rubinate M, a polymeric MDI (4,4′-diphenyl methane diisocyanate) having 31% NCO group and functionality 2.7 (EW=135) was obtained from Huntsman Corporation.

2.2 Methods

Hydroxyl numbers were determined by *p*-toluenesulfonyl isocyanate method (ASTM 1899). Polyol acid values were determined by titration with 0.1N NaOH in toluene-isopropanol mixture (ASTM D4662). Viscosity was measured at 25 °C on an AR 2000ex rheometer (TA Instruments). Iodine value (IV) was determined by Hanus method and is expressed as g I_2/100 g.

A size exclusion chromatography (SEC) system consisting of a Waters 515 HPLC pump (Waters Corp., Milford, MA), with a set of five Phenogel™ columns from Phenomenex Inc. (Torrance, CA) covering a MW range of 100 to 5×10^5, were used for assessing molecular weight and MW distribution. Calibration was carried out using a range of triglycerides, diglycerides and fatty acid esters of similar structure.

The IR spectra were taken in a Fourier transform infrared (FTIR) spectrophotometer (IRAffinity-1 from Shimadzu). ^{1}H NMR experiments were performed on a Bruker Avance DPX-300 spectrometer at 300 MHz with a 5 mm broadband probe using deuterated chloroform as a solvent.

Differential scanning calorimetry (DSC) measurements were performed with differential scanning calorimeter model Q100 from TA Instruments (New Castle, DE, USA) in nitrogen (50 mL/min flow) at a heating rate of 10 °C/min from −80 °C to 200 °C. Dynamic mechanical analysis (DMA) measurements were conducted using a DMA 2980 dynamic mechanical analyzer from TA Instruments (New Castle, DE) with a heating rate of 3 °C/min from −80 °C to 170 °C at 10 Hz. Density of foams was determined according to ASTM D1622. Compressive properties were measured on a Q-Test 2 tensile machine (MTS, USA) according to ASTM 1621. Close cell content of foams was measured by HumiPyc™ volumetric and RH analyzer from InstruQuest, Inc. (Coconut Creek, FL), according to ASTM D2856. The cellular structure and morphology of foams were observed via scanning electron microscopy (SEM) Phenom G2 Pro SEM (Netherlands). Before testing, the samples were gold-coated in a 108 Sputter Coater (Kurt J. Lesker Co.).

2.3 Polyols Synthesis

2.3.1 *Propoxylation of Cardanol*

The phenolic group of cardanol was blocked by alkoxylation with propylene oxide [22]. Propoxylation was carried out in a 450 mL stainless steel Parr reactor by stepwise addition of propylene oxide to cardanol in the presence of TMG (0.2% against cardanol), an organic superbase, as a catalyst at 105–110 °C and a pressure of 3 bars. After the addition of the entire quantity of propylene oxide (molar ratio [PO]/[cardanol] of 1.1/1), the reaction temperature was maintained at 105–110 °C, under continuous stirring for about 2 hours, to ensure the consumption of unreacted monomer. Then the pressure was decreased slowly from 3 bars to 0.5 bars. Traces of volatiles, mainly unreacted PO, were removed by using a medium vacuum (50–60 mmHg) for about 1 hour at 100–105 °C. Thus obtained propoxylated cardanol is a brownish-red color liquid with low viscosity of 0.6 Pa.s at 25 °C, hydroxyl number of 151.7 mg KOH/g and iodine value of 193 g I_2/100 g.

2.3.2 *Thermal Thiol-Ene Reaction of Propoxylated Cardanol and 2-Mercaptoethanol (ME)*

Due to the relatively dark color of cardanol and propoxylated cardanol, we preferred to use thermal thiol-ene reaction over the photochemical initiation. A solution of 2-mercaptoethanol (ME) and AIBN (0.5%) was added slowly to cardanol at 60–65 °C, under a protective nitrogen atmosphere. The molar ratio of [ME]/[double bonds] = 2/1 was used. The addition was complete within 2 hours. Then, the reaction mixture was stirred continuously, maintaining the temperature between 60–65 °C, for 3 hours. The unreacted 2-mercaptoethanol was removed by high vacuum distillation (2–5 mmHg) at 100–110 °C. After about 2 hours of vacuum distillation, a cardanol-based polyol was obtained which is transparent, light brown-red color, with hydroxyl number 310 mg KOH/g and low viscosity 0.8 Pa.s at 25 °C. However, thus formed polyol is a complex mixture, probably due to the reaction with cardanol containing one, two, three and four hydroxyl group/mol. The average functionality of the polyols calculated based on a total conversion of double bonds is in the range of 3–3.5 OH group/mol. This polyol containing aromatic-aliphatic structure was used for preparation of rigid polyurethane foams.

2.3.3 *Preparation of Cardanol-Based Novolacs by Condensation of Cardanol with Paraformaldehyde*

To increase the functionality of cardanol-based polyols, condensation of cardanol with paraformaldehyde was performed in the presence of oxalic acid as a catalyst. Water resulted from the reaction was removed by vacuum distillation (50–60 mmHg) at 100–105 °C. Thus, viscous, red-brown color novolacs based on cardanol were obtained which contained 2–4 cardanol units. Preparation of novolacs from cardanol and polyols from cardanol novolacs has been previously reported [9, 10, 23]. Our objective was to use a novel and efficient method to prepare propoxylated cardanol and cardanol novolacs simply in the presence of TMG, an organic superbase.

2.3.4 *Propoxylation of Cardanol-Based Novolacs*

The phenolic hydroxyl group of cardanol-based novolacs was also blocked with propylene oxide by using the same procedure described in propoxylation of cardanol (see Section 2.3.1). Propylene oxide was added to cardanol-based novolacs at 105–110 °C and 3–3.5 bars in the presence of TMG (0.2%). After completion of reaction, the unreacted PO was removed by vacuum distillation. These polyols have a hydroxyl number in the range of 140–153 mg KOH/g; unfortunately, the viscosity of these polyols is high, 10–83 Pa.s at 25 °C. Despite not having a very high functionality and long dangling chains, propoxylated novolacs of cardanol were proven to be excellent polyols for rigid polyurethane foams.

2.3.5 *Thiol-Ene Reaction between Propoxylated Cardanol-Based Novolacs and 2-Mercaptoethanol*

The functionality of propoxylated cardanol-based novolacs was increased by utilizing thermal thiol-ene reaction of 2-mercaptoethanol with C=C double bonds of C_{15} hydrocarbon chain of propoxylated cardanol novolacs. The reaction was performed by the same procedure as in the thiol-ene reaction using cardanol (see Section 2.3.2).

2.4 Preparation of Rigid PU Foams

Rigid polyurethane foams were prepared by using a mixture of cardanol polyols (50%) and a sucrose polyol Voranol 490 (50%). Initially, a polyol component was prepared from a mixture of polyols, silicone surfactant, amine catalyst, tin catalyst and water in a polystyrene cup. Polyol component was then mixed vigorously with polymeric MDI (Rubinate M) (isocyanate index 105) at 3000 rotations/minute for 10 seconds.

3 RESULTS AND DISCUSSION

3.1 Synthesis of Cardanol-Based Polyols

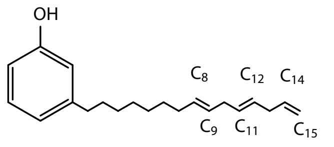
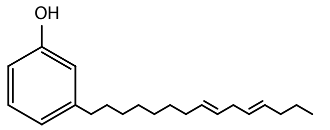
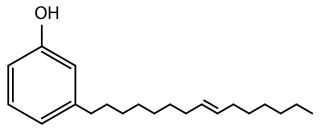
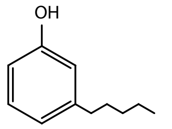
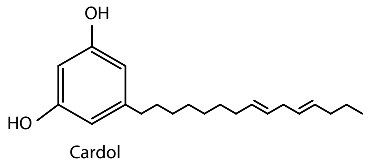
Cardanol is a complex mixture of species with no double bond, and/or with one, two or three double bonds (3-n-pentadecadienyl phenols). In general, the composition of cardanol is as presented in Table 1. The major component (30–41%) is the structure with C_{15} hydrocarbon chain in the *meta* position containing three non-conjugated double bonds. The second major species (25–36%) is the structure with C_{15} chain containing only one double bond [1–4]. However, the composition of cardanol varies depending upon the origin of cashew nut shell liquid (CNSL). Vietnam, India, Nigeria and Brazil are the highest CNSL producing countries [17–20].

Cardanol-based polyols are prepared by carrying out the thermal thiol-ene reaction using AIBN as a radical initiator. Thiol-ene reaction is the anti-Markovnikov addition of thiol group of mercaptans to the C=C double bond of alkenes (Scheme 1) [23–33].

Thermal thiol-ene reaction is initiated with decomposition of AIBN into two radicals, followed by transfer of radical to the thiol group to generate thiyl radicals (Scheme 2).

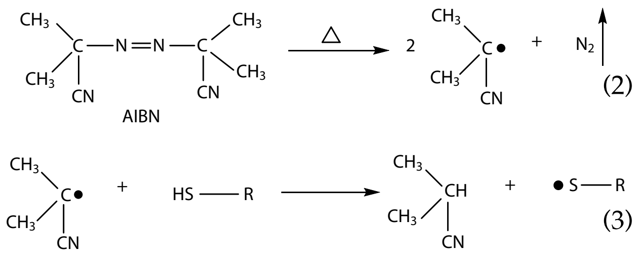
Thus formed thiyl radicals are added to the C=C double bonds [20, 24–31]. The newly formed carbon

Table 1 Average composition of cardanol.

No.	Structure	Percentage, %
1		30–41
2		16–22
3		25–36
4		2–3
5		~4

$$R{-}SH + CH_2{=}CH{-}R' \xrightarrow[60\text{–}65\ ^\circ C]{AIBN} R{-}S{-}CH_2{-}CH_2R' \qquad (1)$$

Scheme 1 General thiol-ene reaction.



Scheme 2 Initiation of thermal thiol-ene reaction with AIBN.

radical can react with the thiol group again (reaction 5) to generate new thiyl radicals; hence, the radical chain reactions continue (Scheme 3).

Thiyl radical acts as an active species in thiol-ene reaction, which can be inhibited if phenolic group is present. As described previously, phenolic group can be easily transformed into an aryloxy radical and stabilized by conjugation, hence becomes less reactive (Scheme 4).

The phenolic group of cardanol was blocked by alkoxylation with propylene oxide to obtain hydroxypropyl group [22] (Scheme 5). Thus, the low reactivity of phenolic hydroxyl towards isocyanates was transformed to a highly reactive aliphatic hydroxyl. Due to the complexity of cardanol structure, the propoxylated cardanol also contains a complex mixture with the structures of C_{15} chains from *meta* position with one, two, three or no double bonds.

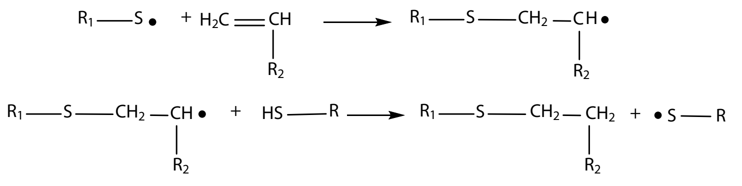
As mentioned previously, the thiol-ene reaction of propoxylated cardanol with 2-mercaptoethanol resulted in a complex mixture of polyols, which was due to various compositions of the starting material. Considering the quantitative addition of thiol group to double bonds, following are the major structures of products (Scheme 6, reactions 8, 9 and 10).

Size exclusion chromatograms of cardanol and cardanol-PO are displayed in Figure 1, which shows that cardanol was completely reacted.

Cardol also contains 2 phenolic hydroxyls which can react with 2 mols of propylene oxide. After thiol-ene reaction of propoxylated cardol and 2-mercaptoethanol, it is highly possible to obtain a tetrafunctional polyol, as shown in Scheme 7.

Scheme 8 shows a general chemical pathway for synthesis of cardanol-based polyols from thiol-ene reaction. Abbreviated names are used for these polyols.

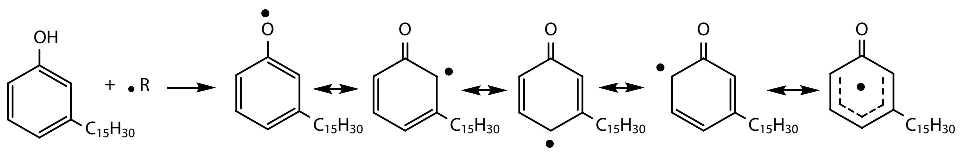
Figure 2 presents ^{1}H NMR of Cardanol-PO-ME, the product obtained after thiol-ene reaction, including the starting materials. ^{1}H NMR of cardanol shows a presence of methyl group at 0.89 ppm and methylene groups at 1.31 ppm,1.58 ppm, 2.03 ppm, 2.55 ppm and 2.80 ppm. The peaks range from 4.96–5.09 ppm and a multiplet at around 6.25 ppm corresponding to vinyl protons of terminal C=C double bonds (structure 1,



(4)

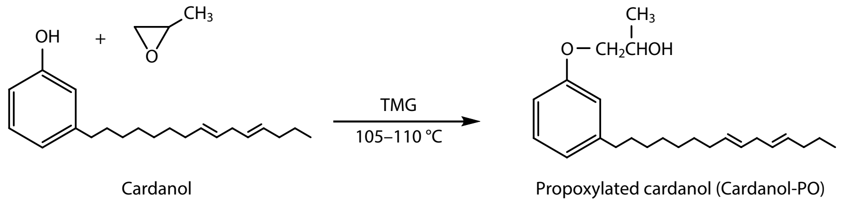
(5)

Scheme 3 Anti-Markovnikov addition of thiyl radical to double bonds (4) and the transfer reaction of formed radical with thiol groups (5).



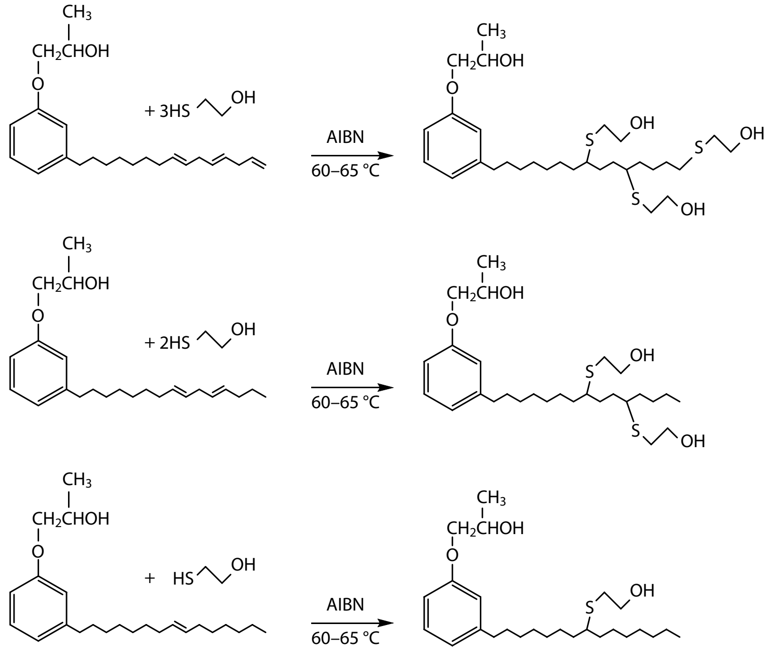
(6)

Scheme 4 Resonance structures of aryloxy radicals derived from cardanol.



(7)

Scheme 5 Phenolic group of cardanol blocked by alkoxylation with propylene oxide.



(8)

(9)

(10)

Scheme 6 Possible structure representing various functionalities of cardanol-based polyols after thiol-ene reaction of propoxylated cardanol with 2-mercaptoethanol (reactions 8, 9 and 10).

Table 1). Similarly, peaks at around 5.35 ppm show the presence of vinyl protons of structure 2. Aromatic protons are observed at 6.66 ppm, 6.77 ppm and 7.14 ppm respectively. Thus, these results suggest that the cardanol contains a mixture of compounds as shown in Table 1. A multiplet centered at 4.19 ppm of the ^{1}H NMR of Cardanol-PO shows a presence of methine proton. Methylene protons observed in the range from 3.83–3.94 ppm suggests a reaction occurred between cardanol and PO. Further, absence of terminal double bonds (4.96–5.09 ppm and 6.25 ppm) in ^{1}H NMR of Cardanol-PO-ME shows the thiol-ene reaction carried out between Cardanol-PO and mercaptoethanol. The peak at 5.38 ppm is still observed, which suggests the incomplete reaction with internal double bond. However, the absence of a characteristic -SH peak, a triplet at 1.41 ppm in the ^{1}H NMR of Cardanol-PO-ME, also confirms the thiol-ene reaction.

Figure 3 shows the FTIR spectrum of polyol Cardanol-PO-ME. A broad peak of hydroxyl groups is observed at 3400 cm^{-1}. Weak absorption at 3006 cm^{-1} corresponds to some unreacted double bonds. The absorption of thiol groups at 2550 cm^{-1} is practically absent because some unreacted ME was vacuum

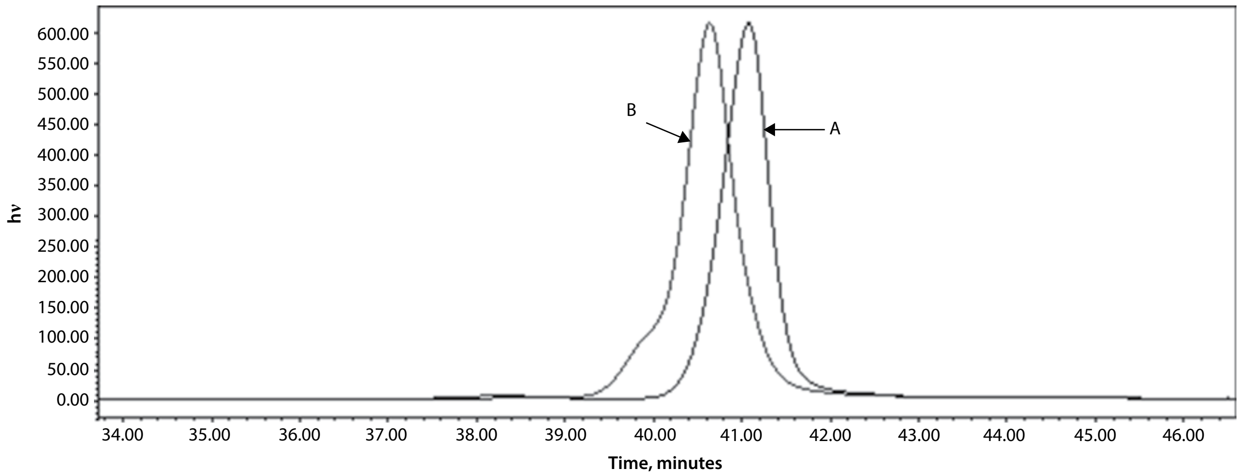
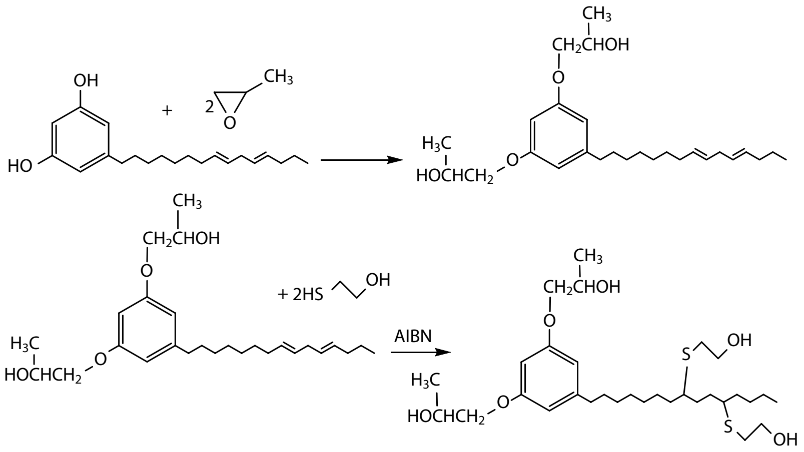


Figure 1 Size exclusion chromatogram of cardanol (A) and of propoxylated cardanol (B).



(11)

Scheme 7 Synthesis and structure of a tetrafunctional cardol-based polyol from thiol-ene reaction of propoxylated cardol and 2-mercaptoethanol.

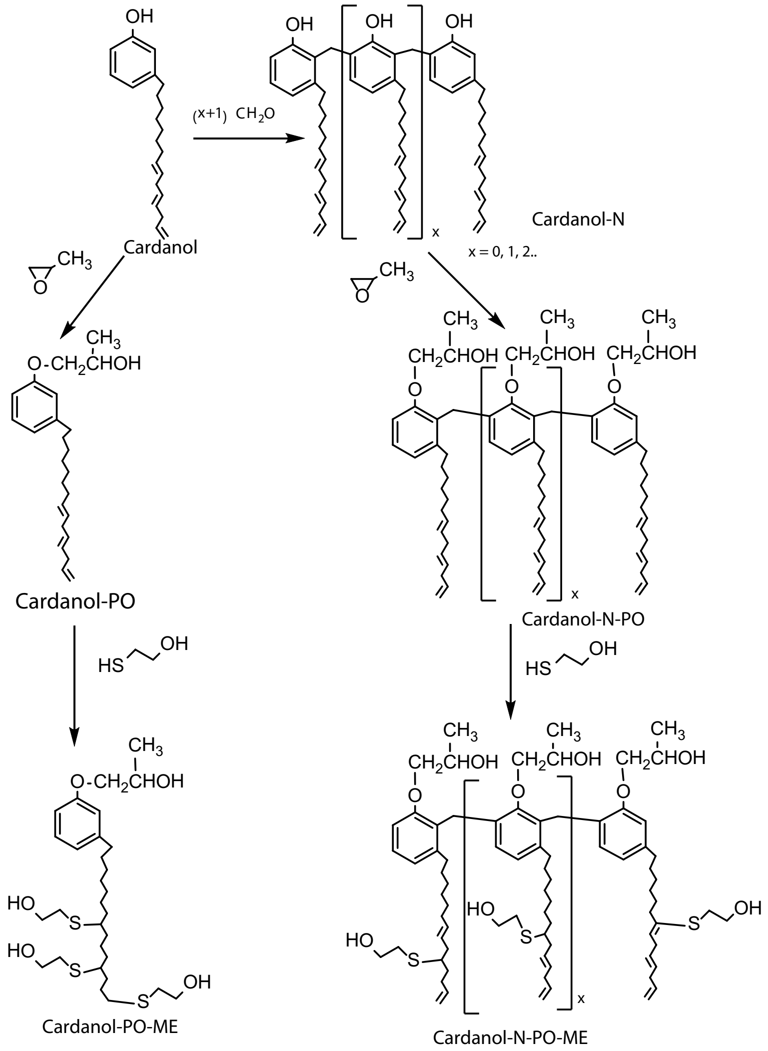
distilled. The chemical determination also proved that around 88% of the double bonds were reacted by thiol-ene reaction, consistent with ^{1}H NMR and FTIR spectra. Thus, the thiol-ene addition of 2-mercaptoethanol to double bonds of Cardanol-PO provided a high yield. Specific aromatic ring absorptions are between 680–810 cm^{-1} (aromatic CH bending) and 1500–1700 cm^{-1} (aromatic C=C bending).

Cardanol novolacs possess a very interesting structure which is synthesized from condensation of cardanol with paraformaldehyde at 100–105 °C. Oxalic acid was used as an acidic catalyst. Cardanol novolacs (Cardanol-N) were further propoxylated to obtain new polyols; propoxylated cardanol novolacs (Cardanol-N-PO) (Scheme 9).

Although Cardanol-N-PO has a relatively low hydroxyl number and long dangling chains (non-functionalized hydrocarbon chain of 15 carbon atoms at *meta* position), it reacts with polymeric MDI and provides rigid polyurethane foams with very good properties (Cardanol-N-PO-4, Table 3).

Furthermore, new aromatic-aliphatic polyols with higher hydroxyl number and higher functionality were also obtained from thiol-ene reaction of cardanol novolacs and 2-mercaptoethanol (Scheme 10).

Figure 4 shows the overlay of ^{1}H NMR spectra of Cardanol-N-PO-ME with Cardanol-N-PO and Cardanol-N respectively. As analyzed previously, ^{1}H NMR of cardanol clearly suggests that it is a mixture of compounds (Figure 2 and Table 1). Presence of a benzylic peak centered at 3.85 ppm in the ^{1}H NMR is a characteristic of Cardanol-N. ^{1}H NMR of propoxylated Cardanol-N (Cardanol-N-PO) shows a new peak at 4.19 ppm which corresponds to methine proton. Further,



(12)

Scheme 8 Synthesis of cardanol-based polyols by using thiol-ene reaction.
Abbreviations: Cardanol-PO = propoxylated cardanol; Cardanol-PO-ME = propoxylated cardanol reacted with ME; Cardanol-N = novolac based on cardanol; Cardanol-N-PO = propoxylated novolac based on cardanol; Cardanol-N-PO-ME = propoxylated cardanol novolac reacted with ME.

methylene protons are also observed in the range from 3.79–3.90 ppm. Similar to the ^{1}H NMR of Cardanol-PO-ME, ^{1}H NMR of Cardanol-N-PO-ME also suggests that the terminal C=C double bond reacted completely while the residue of internal double bonds is still present. These results confirm that the thermal thiol-ene reaction occurred between Cardanol-N-PO and mercaptoethanol, providing polyols with higher functionality.

Figure 5 presents the FTIR spectrum of a representative propoxylated cardanol-novolac polyol (Cardanol-N-PO-ME). A strong absorption of hydroxyl groups at 3400 cm^{-1} and absorption at 3006 cm^{-1} due to some unreacted double bonds are observed as in the case of Cardanol-N-PO-ME. The absorption of thiol groups at 2550 cm^{-1} is very week. The chemical analysis of double bonds content proved that 50% from double bonds of Cardanol-N-PO reacted with 2-mercaptoethanol by thiol-ene reaction. Between 680–810 cm^{-1} and 1500–1700 cm^{-1} are the absorptions specific to aromatic rings (aromatic –CH bending and aromatic C=C bending respectively)

The characteristics of cardanol-based polyols, divided into three representative groups are presented in Tables 2, 3 and 4 respectively;

a. Polyols obtained from thiol-ene reaction of propoxylated cardanol and 2-mercaptoethanol, Cardanol-PO-ME (Table 2).
b. Polyols obtained from propoxylation of cardanol novaloc (condensation product of cardanol and paraformaldehyde), Cardanol-N-PO (Table 3).

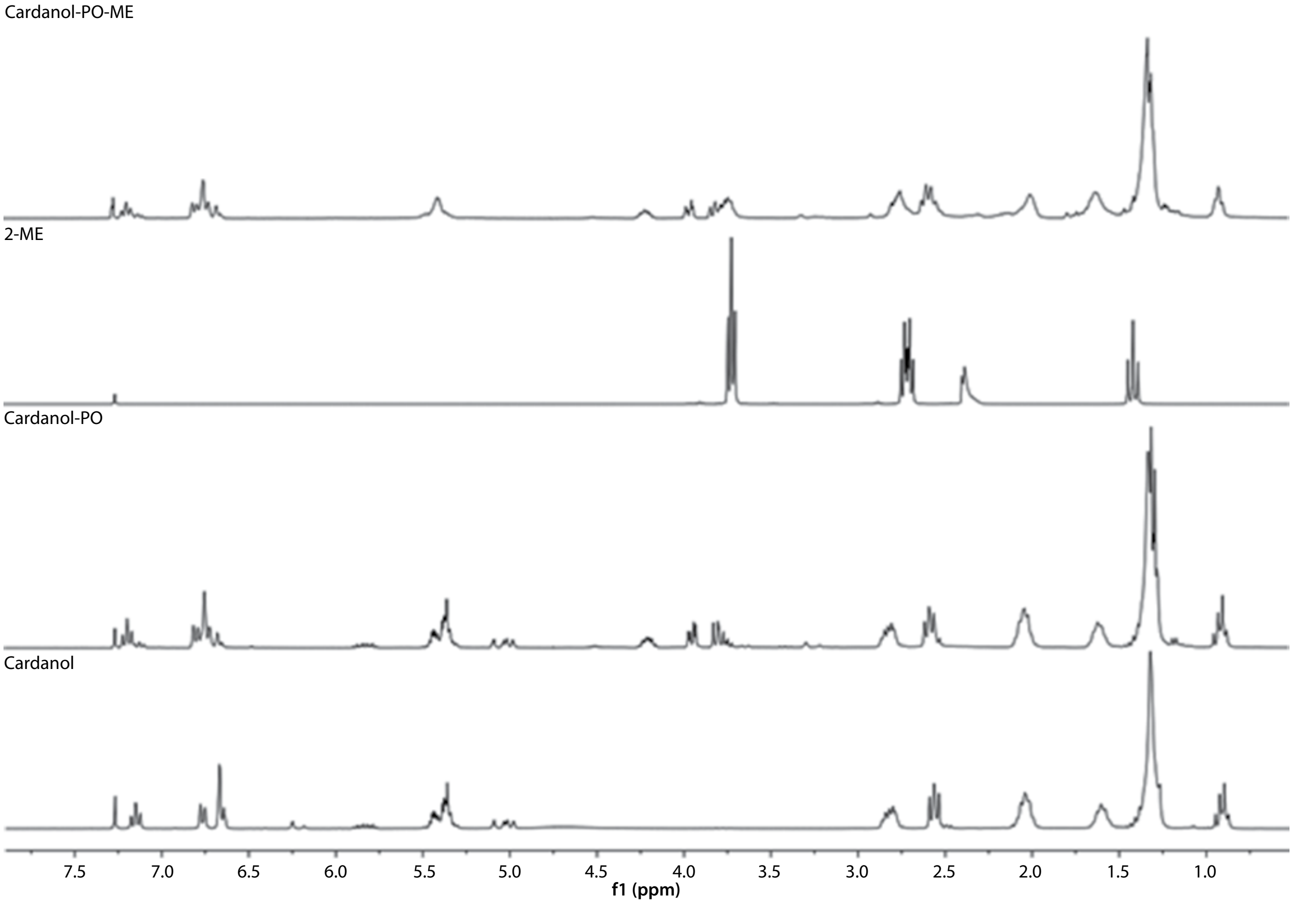


Figure 2 ^{1}H NMR overlay spectra of Cardanol-PO-ME, ME, Cardanol-PO and cardanol.

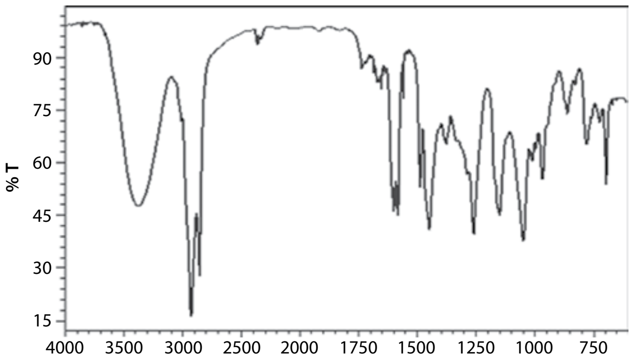


Figure 3 FTIR Spectrum of Cardanol-PO-ME polyol.

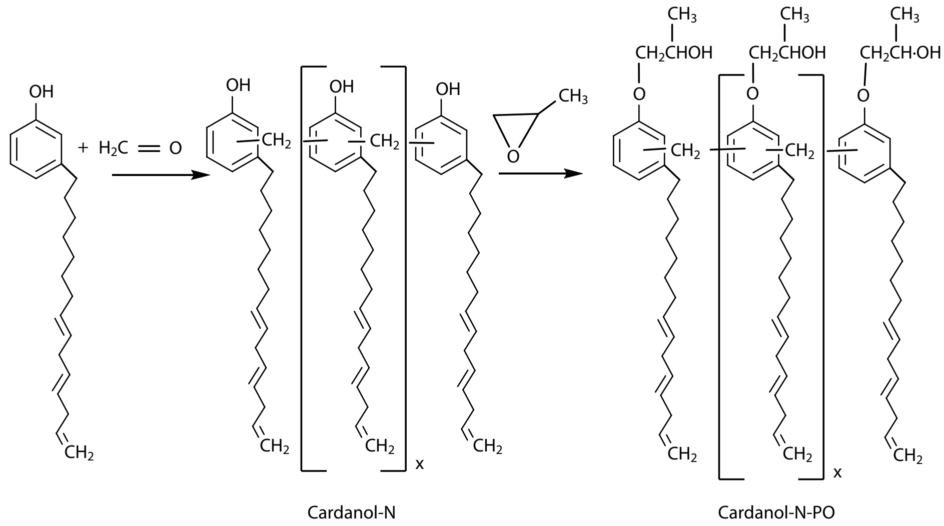
c. Polyols obtained from thiol-ene reaction of propoxylated cardanol novolac and 2-mercaptoethanol, Cardanol-N-PO-ME (Table 4).

Cardanol novolacs of lower viscosity (Cardanol-N-PO-1 and Cardanol-N-PO-2) are preferred for preparation of polyols. We observed that the viscosity of cardanol novolacs increased with an increase in molecular weight (or increase in degree of polycondensation). The molecular weights of Cardanol-N-PO depend on the molar ratio of [cardanol]/[formadehyde] used for synthesis of cardanol novolacs, which varies from 2/1 to 4/3.

3.2 Preparation of Rigid Polyurethane Foams from Cardanol-Based Polyols

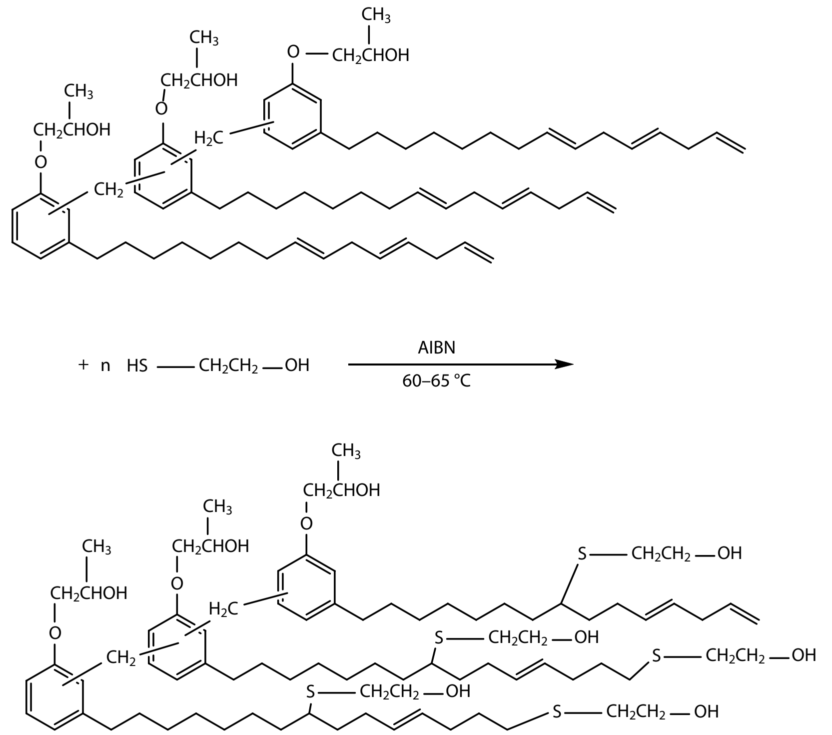
Rigid polyurethane foams were prepared by using a mixture of cardanol polyols (50%) with a conventional sucrose polyol, Voranol 490 from DOW (50%). A polymeric MDI, Rubinate M from Huntsman, was used as an isocyanate. The general formulation used for preparation of polyurethane foams is as follows (all the compounds in parts by weight):

1. Cardanol polyol	10
2. Voranol 490	10
3. Tegostab B8404	0.4
4. Niax A-1	0.12
5. DABCO T-12	0.04
6. Water	0.8
7. Rubinate M, index	105



(13)

Scheme 9 Synthesis and structure of propoxylated cardanol novaloc.



(14)

Scheme 10 Synthesis and structure of polyols prepared from thiol-ene reaction of propoxylated cardanol novolacs and 2-mercaptoethanol (Cardanol-N-PO-ME).

First, compounds 1–6 were well mixed to prepare the polyol component. The isocyanate was added to the polyol component followed by vigorous mixing at 3000 rotation/min for about 10 seconds. Cream time, rise time and tack-free time were recorded as 3–4 seconds, 40–50 seconds and 50–55 seconds respectively. The relatively high reactivity during foaming process is evidence of a catalytic effect on the reaction between isocyanate, polyols and water, due to the presence of tetramethyl guanidine (TMG), the catalyst used for propoxylation of phenolic hydroxyl groups. Nevertheless, the rigid PU foams from cardanol polyols have the normal appearance and a uniform cellular structure similar to the foams exclusively based on petrochemical polyols.

Characteristics of the resultant rigid polyurethane foams are presented in Table 5 (density, compression

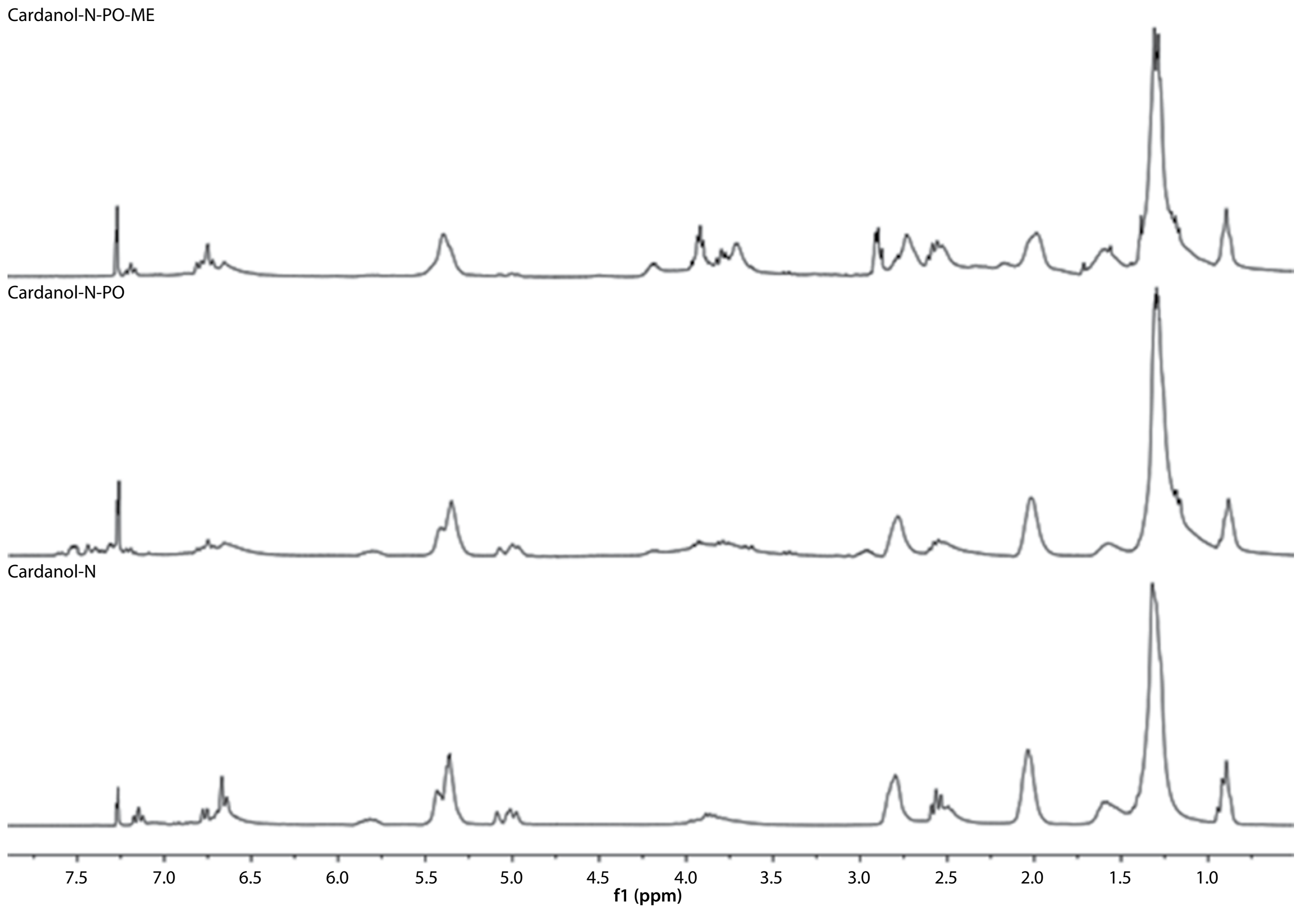


Figure 4 ^{1}H NMR overlay spectra of Cardanol-N-PO-ME with Cardanol-N-PO and Cardanol-N.

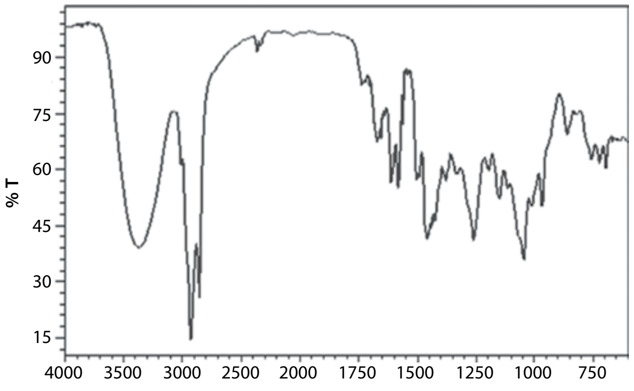


Figure 5 FTIR spectrum of Cardanol-N-PO-ME polyol.

strength and closed cell content). High compression strengths of the foams based on cardanol polyols are probably due to the presence of aromatic rings in the structure of polyols. Closed cell content is also high, ranging from 85–92%, which is ideal for application in thermal insulation. Densities of the resultant rigid PU foams are also in the normal range for thermal insulation of 32–38 Kg/m^3, except for one.

The DMA curves of foams from cardanol polyols (one for each mentioned category) are shown in Figures 6, 7 and 8 respectively. The glass transition temperature (T_g) of rigid PU foams based on cardanol polyols (from Tan δ curves) are high, in the range of 178–205 °C, the rigid PU foam from Cardanol-PO-ME polyol being the one with highest T_g.

The SEM images of rigid PU foams from cardanol-based polyols (Figures 9–11) show a uniform cellular structure with cell dimensions in the range of 124–290 µm. However, Cardanol-N-PO-ME possesses the lowest cell dimension.

The TGA curves of two rigid PU foams based on two representative cardanol polyols are presented in Figures 12 and 13: PU-Cardanol-PO-ME polyol (Figure 12) and PU-Cardanol-N-PO-ME polyol (Figure 13). Both foams lost 5% from initial weight at around 250 °C, proving a good resistance to thermo-oxidative degradation.

Table 2 Characteristics of polyol prepared from thiol-ene reaction of propoxylated cardanol and 2-mercaptoethanol.

Polyol	OH#, mg KOH/g	Acid value, mg KOH/g	Viscosity, 25 °C, Pa.s	Residual IV, g I_2/100 g
Cardanol-PO-ME	309.8	1.35	0.8	21.39

Table 3 Characteristics of polyols prepared from propoxylation of cardanol novolacs.

Polyol	OH# mg KOH/g	Acid value, mg KOH/g	Viscosity, Pa.s	M_n	M_w	M_w/M_n
Cardanol-N-PO-1	188.4	0.10	10.53	760	1980	2.6
Cardanol-N-PO-2	153.0	0.46	14.52	830	2080	2.5
Cardanol-N-PO-3	177.0	0.90	17.20	1030	2920	2.8
Cardanol-N-PO-4	179.0	0.78	83.10	1590	4400	2.8

Table 4 Characteristics of polyols prepared from thiol-ene reaction of propoxylated cardanol novolacs and 2-mercaptoethanol.

Polyol	OH#, mg KOH/g	Acid value, mg KOH/g	Viscosity, 25 °C, Pa.s	Residual IV, g I_2/100 g
Cardanol-N-PO-ME-1	246.7	1.33	15.7	80.8
Cardanol-N-PO-ME-2	249.8	1.90	68.4	85.0

Table 5 Characteristics of rigid polyurethane foams based on cardanol polyols.

Foam name*	Density, Kg/m^3	Compression strength @ 10% strain, kPa	Closed cell content, %	T_g, °C
PU-Cardanol-PO-ME-1	32	261	91	205
PU-Cardanol-N-PO-1	34	311	89	178
PU-Cardanol-N-PO-2	38	379	92	–
PU-Cardanol-N-PO-ME-1	38	377	85	198
PU-Cardanol-N-PO-ME-2	60	471	90	–

*Polyurethane foams are named by using abbreviation for polyurethane (PU) followed by name of cardanol polyol used (see Tables 2, 3 and 4).

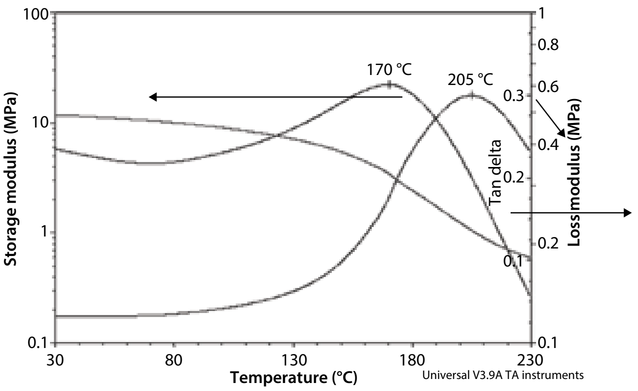


Figure 6 DMA curves: storage modulus, loss modulus and tan delta as function of temperature for rigid PU foam from polyol Cardanol-PO-ME-1.

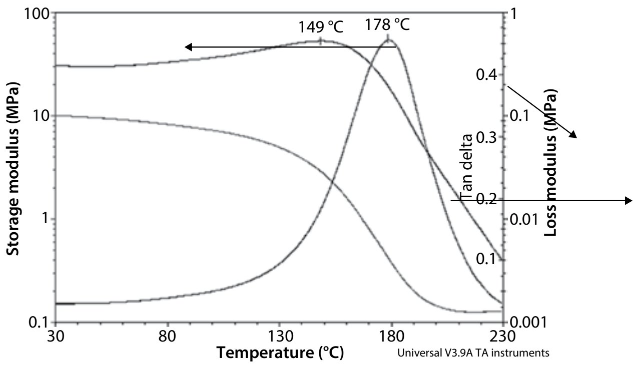


Figure 7 DMA curves: storage modulus, loss modulus and tan delta as function of temperature for rigid PU foam polyol Cardanol-N-PO-1.

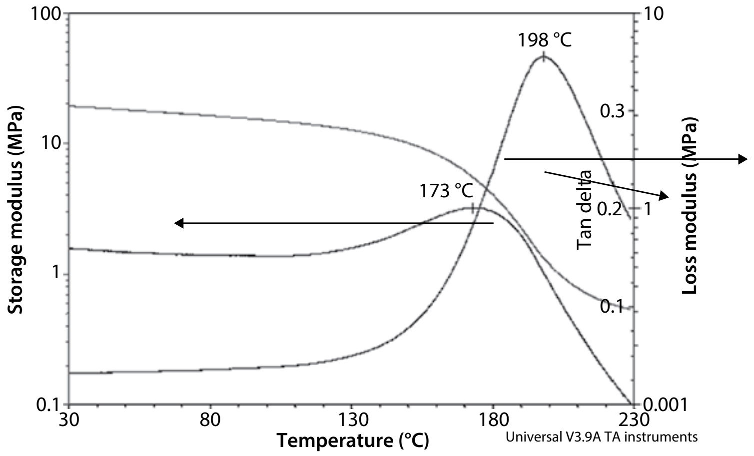


Figure 8 DMA curves: storage modulus, loss modulus and tan delta as function of temperature for rigid PU foam from polyol Cardanol-N-PO-ME-1.

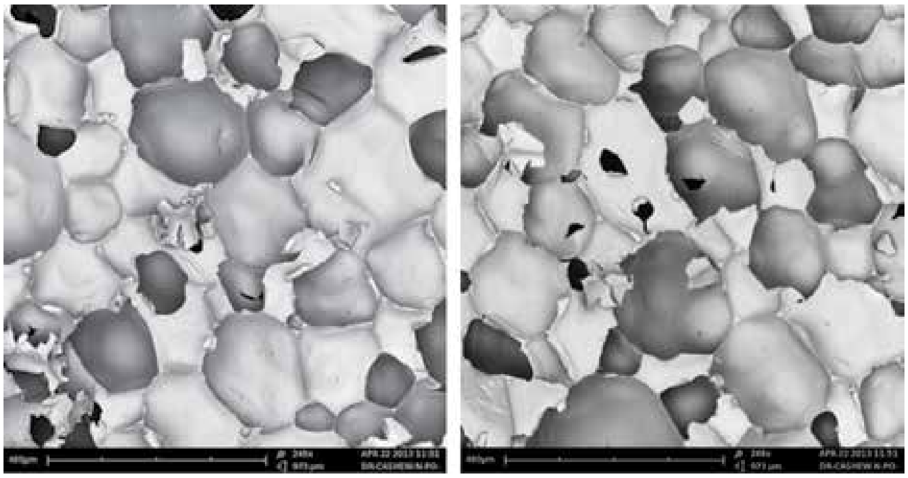


Figure 9 SEM images of two PU foams from Cardanol-PO-ME-1 polyol (average cell size 210 µm).

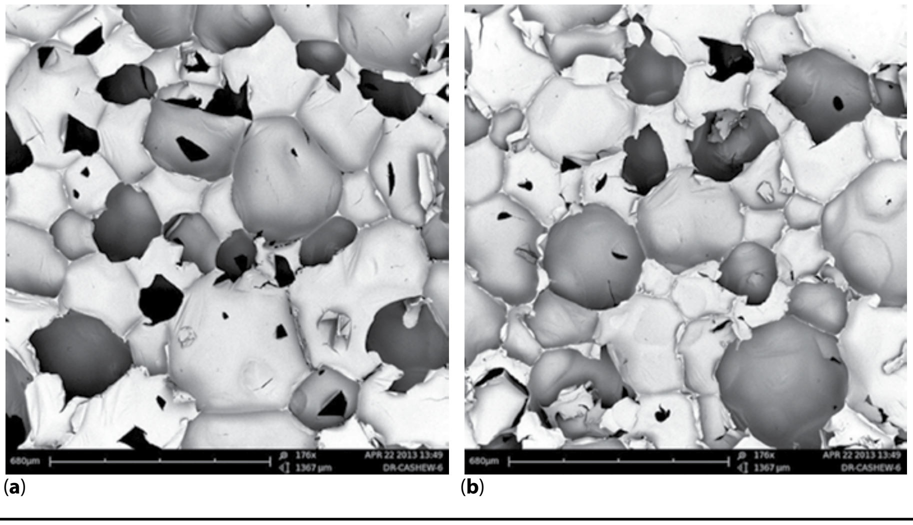

(**a**) (**b**)

Figure 10 SEM images of two PU foams from Cardanol-N-PO-1 (**a**) and Cardanol-N-PO-2 (**b**) polyols (average cell size 290 µm).

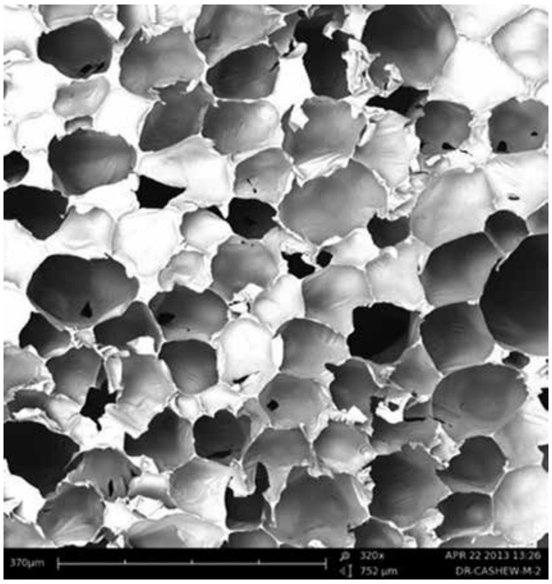


Figure 11 SEM image of rigid PU foam from Cardanol-N-PO-ME-1 polyol (average cell size 124 µm).

4 CONCLUSIONS

Cardanol was found to be an excellent biobased raw material for preparation of hybrid aromatic-aliphatic polyols for rigid polyurethane foams by using thiol-ene reaction of C=C double bonds at C_{15} chain of cardanol and 2-mercaptoethanol. Considering the strong inhibitory effect of phenolic group on thiol-ene radical reaction, the phenolic group was blocked by alkoxylation with propylene oxide. A new structure, propoxylated cardanol, was also used successfully as a partner in thiol-ene reaction without any inhibitory effect. Due to the relatively dark brown-red color of propoxylated cardanol, only thermal thiol-ene initiation was utilized when reacted with 2-mercaptoethanol. The functionality of cardanol-based polyols was increased by using cardanol novolac which has an oligomeric structure with 2–4 phenolic units linked by methylene bridges (prepared by condensation of cardanol with paraformaldehyde in the presence of an acid catalyst). Thus, two

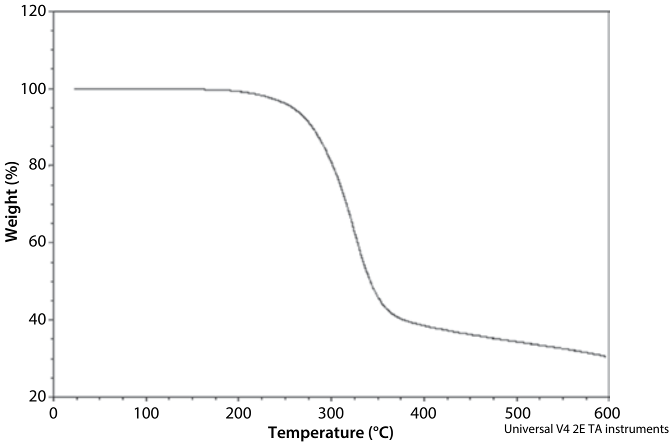


Figure 12 TGA curve of rigid PU foam from Cardanol-PO-ME polyol.

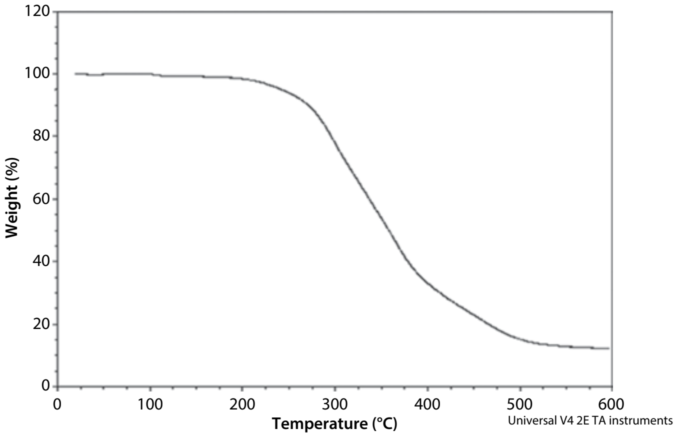


Figure 13 TGA curve of rigid PU foam from Cardanol-N-PO-ME polyol.

types of compounds—propoxylated cardanol and propoxylated cardanol novolacs—were used to prepare cardanol-based polyols. All the synthesized cardanol polyols led to rigid polyurethane foams with very good physical-mechanical properties, which is probably due to the presence of aromatic rings in their structure. These rigid polyurethane foams can be used for a wide range of applications in chemical and food industries such as thermal insulations of freezers, buildings, storage tanks and pipes. They can also be used as wood substitutes, packaging materials and flotation materials.

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