

Biobased Aromatic-Aliphatic Polyols by Thiol-Ene Reactions of Propoxylated Mercaptanized Cardanol

Maha L. Shrestha^{1,2*}, Mihail Ionescu¹, Xianmei Wan¹ and Thomas Upshaw³

¹Kansas Polymer Research Center, Pittsburg State University, 1701 South Broadway, Pittsburg, Kansas, USA 66762

²Department of Chemistry, Pittsburg State University, 1701 South Broadway, Pittsburg, Kansas, USA 66762

³Chevron Phillips Chemical Company LP, Bartlesville Technology Center, Bartlesville, Oklahoma, USA 74003

Received October 02, 2017; Accepted January 10, 2018

ABSTRACT: Aromatic-aliphatic polyols were obtained previously from the thiol-ene reactions of propoxylated cardanol with hydroxyalkyl mercaptans; these aromatic-aliphatic polyols were then utilized in the preparation of rigid polyurethane foams with excellent properties. The current work describes a variant of cardanol polyol synthesis by thiol-ene reactions in three steps. The first step is propoxylation of cardanol by reacting cardanol with propylene oxide; the second step is mercaptanization of propoxylated cardanol by reacting double bonds with hydrogen sulfide; and the third step involves the addition of the thiol groups of mercaptanized propoxylated cardanol to the double bonds of allyl alcohol, glycerol-1-allyl ether, and trimethylolpropane allyl ether. Thus, obtained polyols were characterized by standard analytical methods. Rigid polyurethane foams prepared from these polyols show promising physical-mechanical properties. The rigid polyurethane foams can be used for various applications such as thermo-insulation of freezers, storage tanks and pipes for food and chemical industries, wood substitutes and flotation materials.

KEYWORDS: Cardanol, mercaptanized propoxylated cardanol, photochemical thiol-ene reaction, allyl alcohol, glycerol-1-allyl ether, trimethylolpropane allyl ether

1 INTRODUCTION

One of the most promising routes to obtaining renewable polyols for polyurethanes has been the thiol-ene reaction [1–4] of hydroxyalkyl mercaptans with biobased compounds containing double bonds, such as vegetable oils, limonene and cardanol [5–25]. Following the same protocol, synthesis of biobased aromatic-aliphatic polyols from thiol-ene reaction of propoxylated cardanol with 2-mercaptoethanol and 1-thioglycerol has been reported previously [10]. The present work describes the photochemical reaction of propoxylated cardanol (PO-Cardanol) with hydrogen sulfide, resulting in mercaptanized propoxylated cardanol (MPO-Cardanol), which can be transformed into new polyols via photochemical thiol-ene reaction. Three different alkenes containing hydroxyl groups were chosen for this purpose: glycerol-1-allyl ether (GAE), trimethylolpropane allyl ether (TMPAE) and allyl alcohol (AA). The intermediates, resultant

polyols and rigid polyurethane foams from cardanol-based polyols were characterized by standard methods.

Cardanol is a mixture of phenols with a C15 hydrocarbon chain in the *meta* position having one, two or three double bonds. Similar to the composition of cardanol, propoxylated cardanol (PO-Cardanol) may also contain the same number of double bonds, i.e., 2 double bonds/mol on average. Addition of hydrogen sulfide to the C=C bonds of PO-Cardanol, initiated by UV light in the presence of photoinitiator, leads to mercaptanized propoxylated cardanol (MPO-Cardanol). Photochemical thiol-ene addition of –SH groups of MPO-Cardanol to the C=C bonds of GAE or TMPAE generates cardanol-based polyols with higher functionality. Thus, synthesized cardanol-based polyols were utilized for the preparation of rigid polyurethane foams. These rigid polyurethane foams can be used for various applications in thermo-insulation of freezers, pipes and storage tanks in food and chemical industries. They can also be used as wood substitutes and flotation materials.

*Corresponding author: mshrestha@pittstate.edu

DOI: 10.7569/JRM.2018.634106

2 EXPERIMENTAL PART

2.1 Materials

Cardanol (Cardolite NX-2023), supplied from Cardolite Corporation, is a light yellow-brown color liquid (Gardner Color 5), with an iodine value of 220 g I₂/100 g. 1,1,3,3-Tetramethylguanidine (TMG), 99.0%, and propylene oxide (PO), 99.8%, were purchased from Acros Organics. Mercaptanized propoxylated cardanol (MPO-Cardanol) was synthesized by Chevron Phillips Chemical Company from photochemical addition of H₂S to the double bonds of propoxylated cardanol (Cardanol-PO). Jeffol SG-360 (sucrose-glycerol polyether polyol), containing hydroxyl number OH# = 360 mg KOH/g, was obtained from Huntsman Corporation. Allyl alcohol (AA), 98%, glycerol-1-allyl ether (GAE), 98%, and trimethylolpropane allyl ether (TMPAE) were purchased from Alpha Aesar, Acros Organics and Aldrich, respectively. 2-Hydroxy-2-methylpropiophenone, 96% (photoinitiator), was obtained from TCI America. Silicone surfactant Tegostab B 8404 and NiaxTM A-1 catalyst bis(2-dimethylaminoethyl) ether were obtained from Evonik Industries Inc. and Momentive Performance Materials Inc., respectively. Dabco T-12 (dibutyltin dilaurate) was purchased from Air Products and Chemicals, Inc. Rubinate M, a polymeric MDI having 31% NCO groups and functionality 2.7 (EW = 135), was obtained from Huntsman Corporation.

2.2 Analytical Methods

Size-exclusion chromatography (SEC) was used to determine number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (M_w/M_n) of polyols. The SEC consists of a pump (Waters 515 pump from Waters Corporation, Milford, MA) and a set of five columns (PhenogelTM from Phenomenex). Tetrahydrofuran was used as an eluent. The SEC can be used to determine compounds with molecular weight ranges from 100 up to 5×10^5 .

Viscosity was recorded using an AR2000 EX rheometer (TA Instruments) at 25 °C. Hydroxyl numbers were analyzed using the *p*-toluenesulfonyl isocyanate method (ASTM 1899), and the acid values were measured using the titration method (ASTM D4662).

A Fourier transform infrared (FTIR) spectrometer (IRAffinity-1 from Shimadzu) was utilized to analyze the functional group of the polyols. NMR experiments were performed on a 300 MHz Bruker Avance DPX-300 spectrometer using a 5 mm broadband probe. Samples were prepared by using deuterated chloroform as a solvent.

Compression strength of the foams was determined by QTest-2 (MTS[®]). Closed-cell content of the foams was determined by HumiPycTM Volumetric and RH analyzer (InstruQuest Inc.). Glass transition temperatures were measured using a 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.

Cellular structure and morphology of the foams were observed via scanning electron microscopy (SEM), Phenom G2 Pro SEM (Netherlands). Samples were gold-coated in a 108 Sputter Coater (Kurt J. Lesker Co.) prior to testing.

2.3 Synthesis of Polyols

2.3.1 Synthesis of Propoxylated Cardanol (PO-Cardanol)

Cardanol (300 g) and tetramethyl guanidine (TMG, 0.4 g) catalyst were mixed in a 450 mL metallic Parr reactor. The reactor was purged with nitrogen and heated up to 100–105 °C, maintaining ~10 psi pressure. Propylene oxide (60–65 g) was added slowly to the reaction mixture at a pressure 30–40 psi. The addition of propylene oxide (PO) was complete within 1.5 hours. Then the reaction mixture was stirred continuously for ~1.5 at 100–105 °C for consumption of PO. At the end, traces of unreacted PO were removed by vacuum distillation (60–65 mmHg) at 100–105 °C.

2.3.2 Synthesis of Mercaptanized Propoxylated Cardanol (MPO-Cardanol)

PO-Cardanol was reacted with an excess amount of hydrogen sulfide (molar ratio H₂S/double bond = 21/1) in the presence of UV light. The photochemical thiol-ene reaction was performed by Chevron Phillips using their in-house procedure [26, 27]. The resultant MPO-Cardanol was obtained as a low-viscosity liquid.

2.3.3 Synthesis of Polyols by Thiol-Ene Reaction of Mercaptanized Propoxylated Cardanol with GAE, TMPAE and AA

MPO-Cardanol, synthesized by Chevron Phillips Chemical Company LP, was reacted with double bonds of GAE, TMPAE or AA in the presence of a photoinitiator (2-hydroxy-2-methylpropiophenone). A ratio of SH/double bond = 1.1/1 was used for the reaction. The photochemical thiol-ene reaction was carried out using a 365 nm wavelength UV lamp at room temperature for 6 hours. Thus, prepared polyols

based on MPO-Cardanol were characterized using the analytical methods described in Section 2.2.

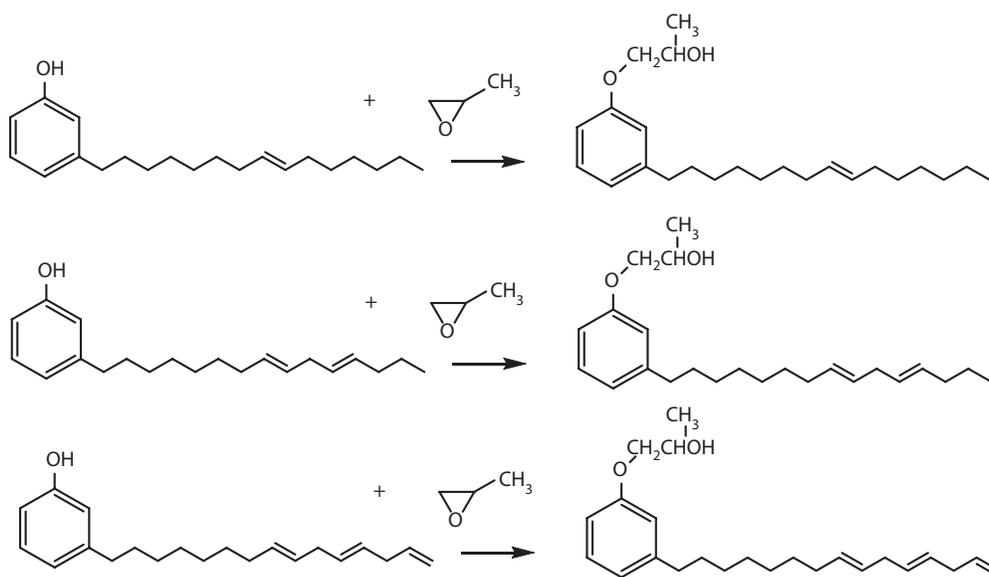
2.4 Preparation of Rigid Polyurethane Foams

Polyol component A was prepared by mixing polyols, silicone surfactant (Silicone B 8404), amine catalyst (Niax A-1), tin catalyst (Dabco T-12) and water in a plastic cup, using a stirrer rate of 3000 rot/min. Rubinate M (isocyanate), also referred to as component B, was added to component A and mixed vigorously for 10 seconds. Foaming process was characterized by recording cream time, rise time and tack-free time. Thus, prepared foams were left at room temperature for a week. After maturation, properties of rigid polyurethane foams were determined by using standard procedures (see Section 2.2 – Analytical Methods).

3 RESULTS AND DISCUSSION

Mercaptanized propoxylated cardanol (MPO-Cardanol)-based polyols were synthesized by alkoxylation of cardanol followed by thiol-ene reactions with hydrogen sulfide and then with C=C bonds of hydroxyalkyl allyl ethers (GAE, TMPAE and AA). However, the polyols obtained from three-step synthesis were a complex mixture, which could be due to various species already present in cardanol, the initial biobased compound.

Propoxylation of cardanol (Scheme 1) provided a low-viscosity liquid (58.3 mPa) with hydroxyl number 155–165 mg KOH/g and iodine value 144 g I₂/100 g.



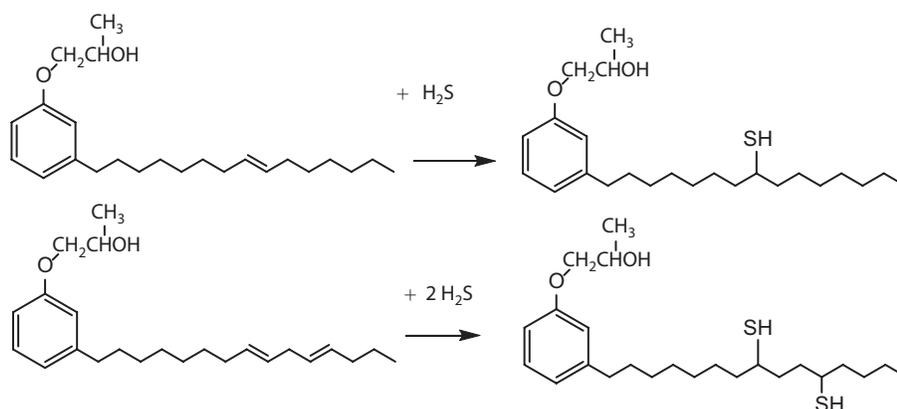
Scheme 1 Propoxylation of cardanol (showing major species present in cardanol).

Mercaptanized propoxylated cardanol (MPO-Cardanol) synthesized by thiol-ene addition of H₂S to the double bonds of PO-Cardanol (Scheme 2) is also a low-viscosity liquid with 10.1 wt% mercapto sulfur content. The thiol equivalent weight of MPO-Cardanol determined by Chevron Phillips is 318 g.

Figure 1 shows the SEC overlay of cardanol, propoxylated cardanol (PO-Cardanol) and mercaptanized propoxylated cardanol (MPO-Cardanol). The SEC curve of PO-Cardanol suggests the disappearance of the starting material, cardanol. Similarly, SEC of MPO-Cardanol shows PO-Cardanol completely reacted, suggesting thiol-ene addition of H₂S to the double bonds of PO-Cardanol.

The FTIR spectrum of MPO-Cardanol also supports the evidence that addition of H₂S to the C=C occurred successfully (Figure 2). A strong absorbance at 3010 cm⁻¹ corresponding to the C=C bond of C15 chain is observed in both cardanol and Cardanol-PO spectra, while this peak is absent in MPO-Cardanol. A strong absorbance for hydroxyl group at 3400 cm⁻¹ and absorbance for -CH₂ and -CH₃ groups of a C15 chain in the range of 1450 cm⁻¹ and 2920 cm⁻¹ are also observed.

MPO-Cardanol is a mixture of mercaptans, therefore the products obtained from thiol-ene reactions with GAE, TMPAE and AA were also obtained as a complex mixture of polyols. The starting materials (AA, GAE and TMPAE) containing C=C bond can be observed in the SEC of all three polyols, suggesting incomplete thiol-ene reactions. The calculated molecular weight of MPO-Cardanol is 403 g, while the thiol equivalent weight determined by Chevron Phillips is



Scheme 2 Synthesis of MPO-Cardanol (showing the reaction with one and two double bonds respectively).

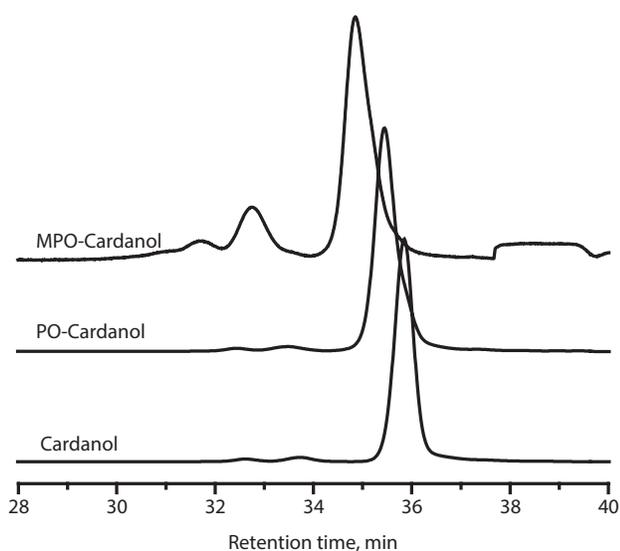


Figure 1 SEC overlay of cardanol, propoxylated cardanol (Cardanol-PO) and mercaptanized propoxylated cardanol (MPO-Cardanol).

318 g. Therefore, functionality of mercaptanized propoxylated cardanol available for thiol-ene reaction is 1.26 thiol groups/mol (functionality = 408 g/318 g). Considering the value of thiol functionality, the photochemical thiol-ene reactions provided approximately 65–67% conversion. The SEC results also show that the polyols obtained from thiol-ene reactions by using GAE or TMPAE contained 12–13% unreacted allyl ether derivatives (Figure 3). The presence of these unreacted allyl derivatives, however, is not detrimental, since GAE and TMPAE can act as chain extenders in rigid polyurethane foams. The polyol containing allyl alcohol was distilled using vacuum; therefore, only a trace of allyl alcohol remained in MPO-Cardanol-AA.

The structure with three double bonds may react in a different way. The terminal double bond, which is much more reactive compared to the internal double

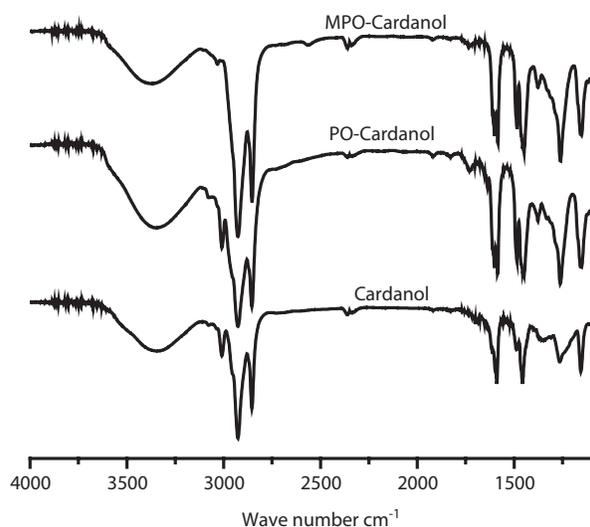


Figure 2 Overlay of FTIR spectra of Cardanol, PO-Cardanol and MPO-Cardanol.

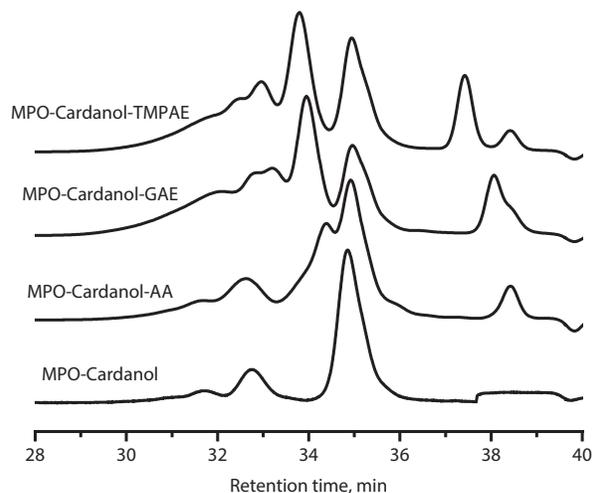
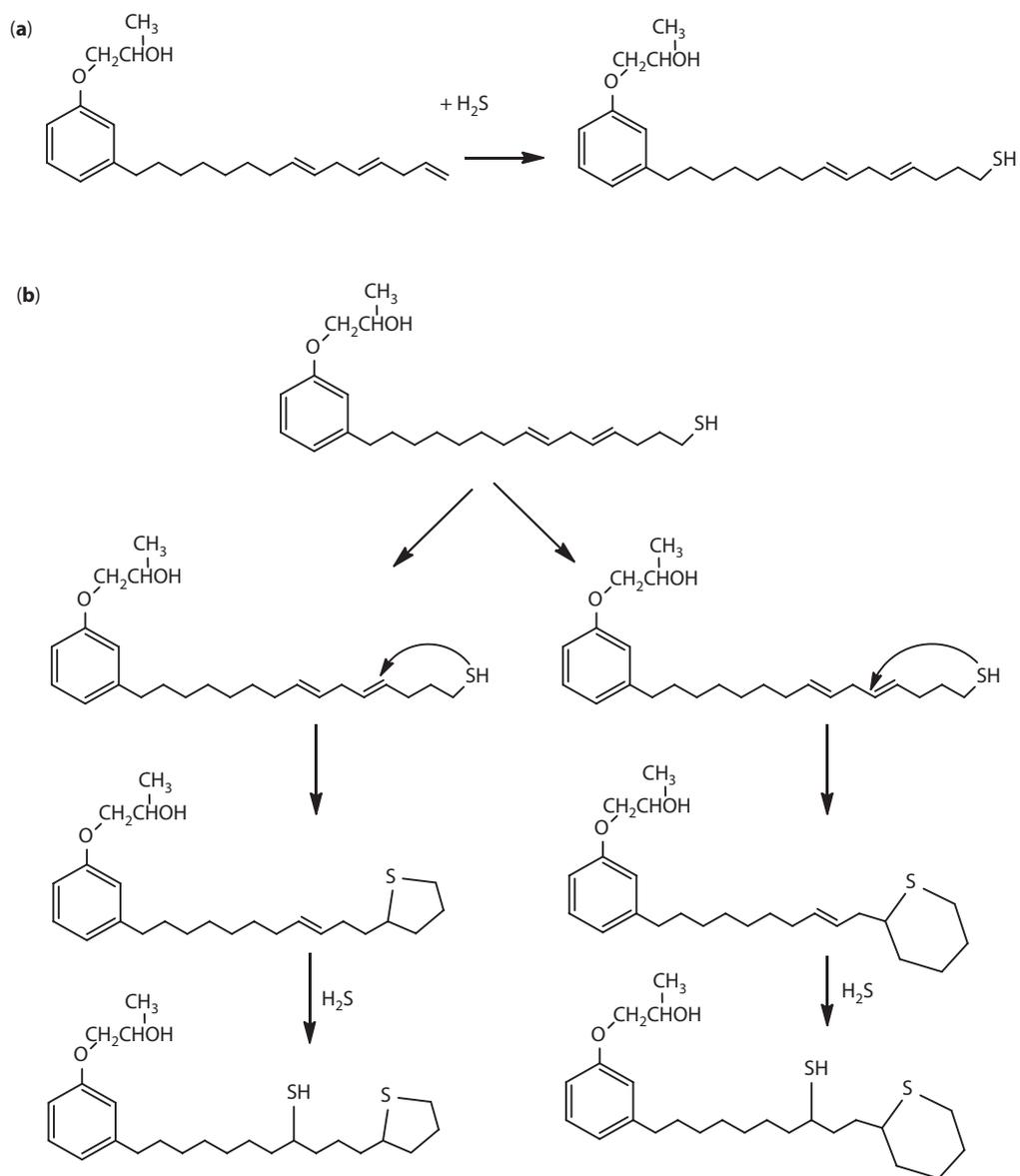


Figure 3 SEC overlay of MPO-Cardanol and polyols thereafter.



Scheme 3 Intramolecular thiol-ene reaction of MPO-Cardanol.

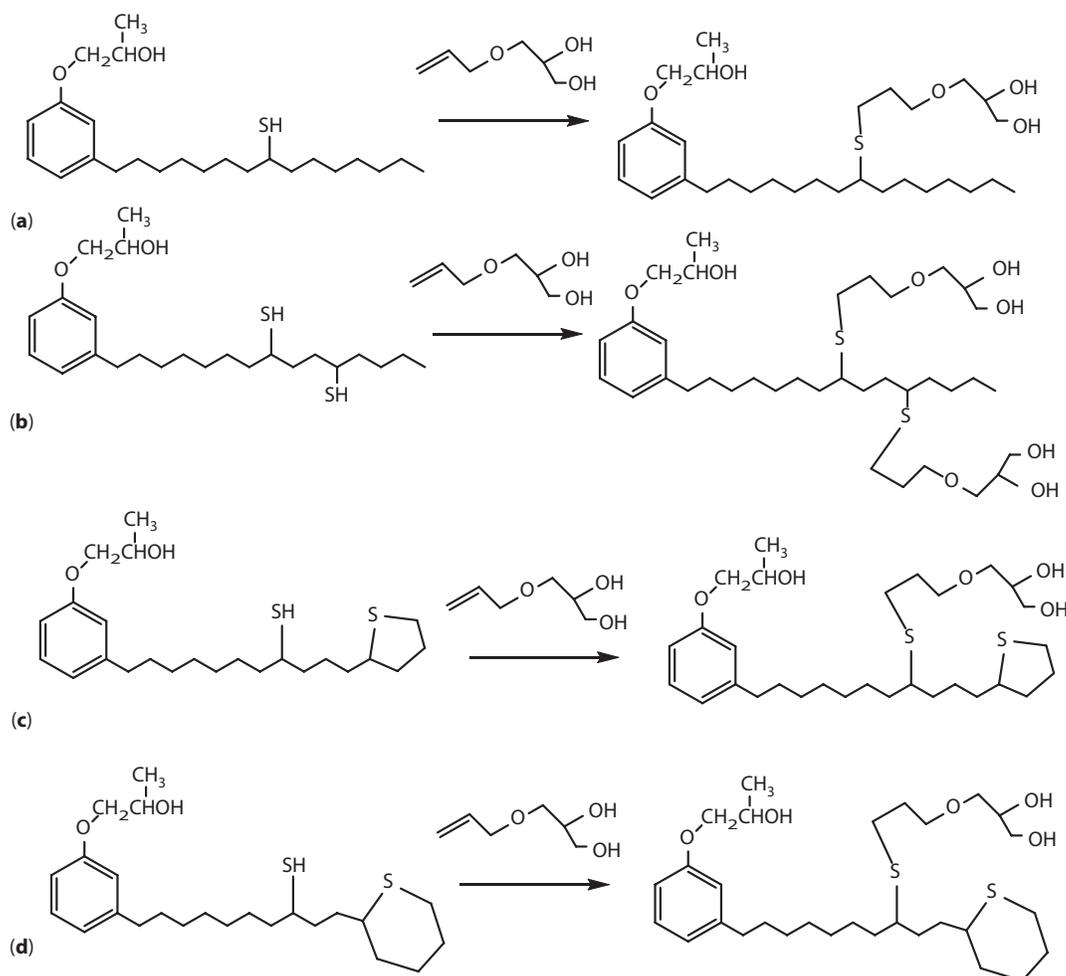
bonds, reacts first. Due to high mobility, intramolecular addition of the terminal thiol group to the neighboring double bonds is possible, forming cyclic thio-ethers containing 5- and 6-membered rings (Scheme 3). Thus, the intramolecular thiol-ene reaction may have been the reason for lower functionality of mercaptanized propoxylated cardanol (i.e., 1.26 thiol groups/mol instead of 2.1 thiol groups/mol).

As mentioned previously, the resulting polyols obtained from the reaction of MPO-Cardanol and allyl compounds (GAE, TMPAE and AA) are complex mixtures. The possible major products from the thiol-ene reaction with GAE are presented in Scheme 4 (compounds a, b, c and d). Nevertheless, the polyol with

5 OH groups/mol (compound b) would be the best polyol for preparation of rigid polyurethane foams due to its crosslink density.

In principle, a thiol group reacts with a C=C bond of GAE to form 2 hydroxyl groups. Considering 1.26 thiol groups/mol, the mercaptanized propoxylated cardanol must result in 2.52 hydroxyl groups after thiol-ene reaction with GAE. Therefore, average functionality of the polyol is calculated as $2.52 + 1 = 3.52$ hydroxyl groups/mol, which also includes the hydroxypropyl group of the polyols.

In a similar fashion, TMPAE also reacts with MPO-Cardanol. Despite the fact that these polyols have medium-range functionality, we expected to obtain



Scheme 4 Possible major polyols prepared from MPO-Cardanol and GAE.

Table 1 Characteristics of polyols from mercaptanized propoxylated cardanol.

MPO-cardanol polyols	OH#, (mg KOH/g)	Viscosity @ 25 oC (Pa.s)	Acid value (mg KOH/g)	Mn	Mw	Mw/Mn
MPO-cardanol-AA	299.9	0.77	2.21	343	583	1.69
MPO-cardanol-GAE	389.1	1.66	13.47	335	723	2.15
MPO-cardanol-TMPAE	413.4	2.10	0.79	355	671	1.88

rigid polyurethane foams with good physical-mechanical properties due to their structure containing aromatic rings (calculated 11–15% aromatic ring content). Furthermore, allyl alcohol, with only one hydroxyl group/mol leads to polyols with even lower functionality, i.e., 2.26 hydroxyl groups/mol, which need to be mixed with higher-functionality polyols based on sorbitol or sucrose to obtain rigid PU foams with properties useful in the polyurethanes' applications.

The characteristics of polyols prepared by thiol-ene reaction of MPO-Cardanol with GAE, TMPAE and

AA are presented in Table 1. These low-viscosity polyols have hydroxyl numbers in the range from 299–413 mg KOH/g.

The FTIR spectra of the polyols show a very weak absorbance at 2220 cm⁻¹, which could be due to the presence of some unreacted thiol groups (Figure 4). An absorbance at 3010 cm⁻¹ corresponding to C=C bonds is absent. These results suggest that the addition of thiol groups to the double bonds has occurred. A strong absorbance of hydroxyl groups at 3400 cm⁻¹ and absorbance for C15 hydrocarbon chains (-CH₂ and

-CH₃ groups) in the range of 1450 cm⁻¹ and 2920 cm⁻¹ are also observed.

Figure 5 shows the ¹H NMR spectra of the starting material cardanol, PO-Cardanol and MPO-Cardanol,

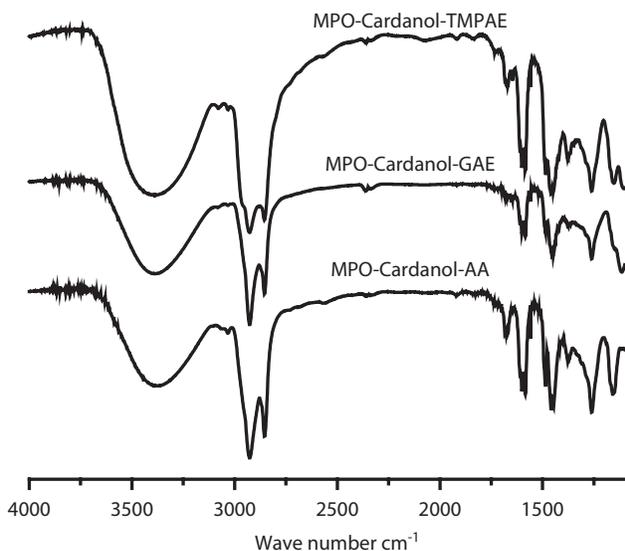


Figure 4 Overlay of FTIR spectra of polyols prepared from MPO-Cardanol.

respectively. As analyzed previously, cardanol is a complex mixture, which may contain one double bond, two double bonds, or three double bonds [10, 19–21]. A multiplet that is centered at 5.84 ppm and peaks at the range of 4.96–5.10 ppm correspond to terminal C=C bonds. Peaks centered at around 5.35 ppm suggest the presence of internal vinyl protons. ¹H NMR of PO-cardanol shows methine and methylene protons at 4.19 ppm and 3.83–3.94 ppm, respectively. Absence of the vinyl peaks in the ¹H NMR of mercaptanized propoxylated cardanol (MPO-Cardanol) suggests a successful thiol-ene reaction between C=C bonds of PO-Cardanol and hydrogen sulfide. However, a very weak peak at around 5.35 ppm is still observed, which may be due to traces of internal vinyl peaks. Furthermore, a methine proton at 2.77 and a triplet at around 1.45 ppm also suggest the presence of -SH group. A triplet centered at 2.57 ppm is assigned for methylene protons next to the aromatic ring, which can be observed in the ¹H NMR spectra of the starting materials cardanol and PO-cardanol. The peak may also be assigned for methylene protons associated with 5- or 6-membered cyclic thio-ethers (Scheme 3). Unfortunately, due to a possible overlap of methylene peaks possessing similar chemical shifts, we were not able to assign the peak clearly. However, the formation

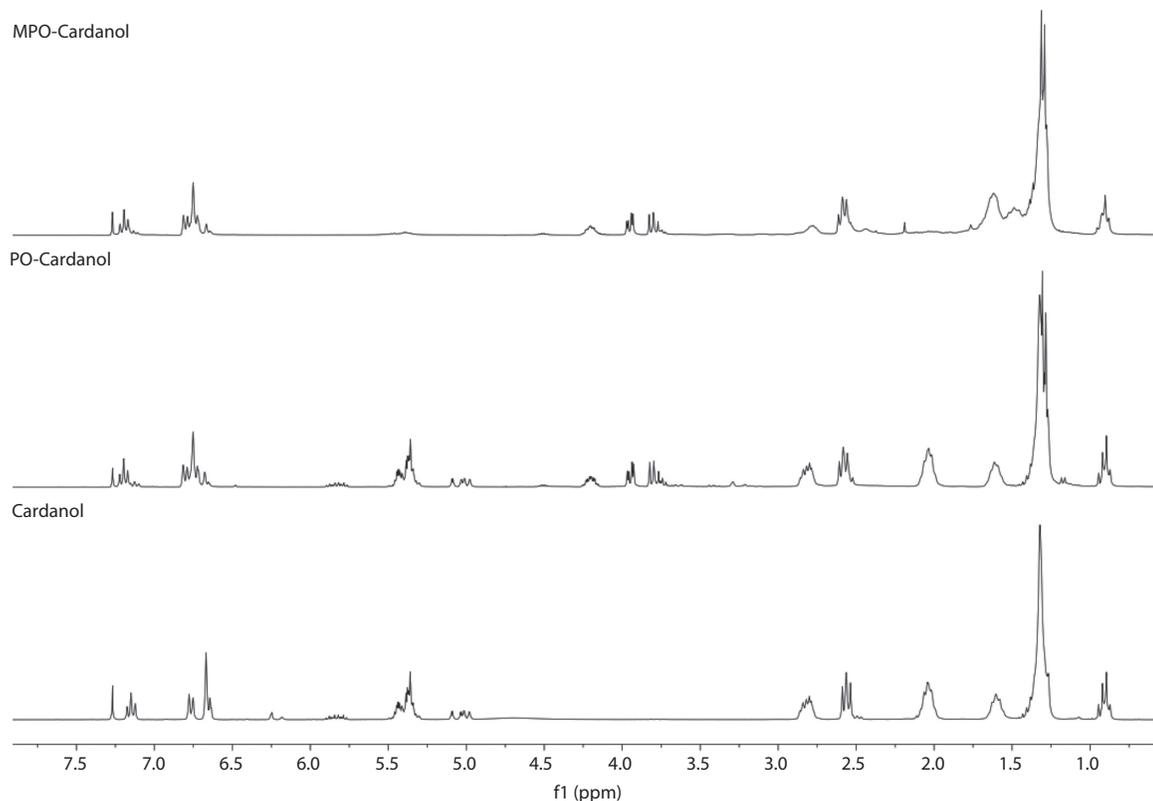


Figure 5 ¹H NMR spectra overlay of cardanol, Cardanol-PO and MPO-Cardanol.

of these cyclic thio-ethers better explains why the sulfur content of MPO-Cardanol of 1.26 thiol groups/mol is lower than the theoretical value of 2.1 groups/mol.

The following ^1H NMR spectra were obtained from polyols prepared by photochemical thiol-ene reactions of MPO-Cardanol with AA, GAE and TMPAE (Figure 6). A characteristic $-\text{SH}$ peak is absent in all the spectra, suggesting that the thiol-ene reaction occurred successfully. However, some unreacted starting materials containing $\text{C}=\text{C}$ bonds (AA, GAE and TMPAE) were still found in these spectra, which are consistent with SEC results. The chemical shifts at 5.25 ppm and 6.0 ppm correspond to the protons linked to allyl double bonds of the starting materials.

Thus, the synthesized polyols were utilized in the preparation of two different groups of rigid polyurethane foams. The first group is based on a mixture of 25% MPO-Cardanol polyols and 75% sucrose-glycerol based polyol Jeffol SG-360 (Formulation 1). The second group was prepared from 100% MPO-Cardanol polyols (Formulation 2). The formulations used for preparation of foams are as follows:

Formulation 1:

1. Cardanol polyol	5.0
2. Jeffol SG-360	15.0
3. Silicon B 8404	0.4
4. Amine Niax A-1	0.12
5. Tin catalyst T-12	0.04
6. Water	0.8
<u>Total A</u>	<u>21.4</u>
7. Rubinate M	(index 105)

Formulation 2:

1. Cardanol polyol	20.0
2. Silicon B 8404	0.4
3. Amine Niax A-1	0.12
4. Tin catalyst T-12	0.04
5. Water	0.8
<u>Total A</u>	<u>21.4</u>
6. Rubinate M	(index 105)

Rubinate M, a polymeric MDI (methylene diphenyl isocyanate), with functionality 2.7 isocyanate groups/mol, was selected to increase crosslink density of rigid polyurethanes. The amount of isocyanate for each

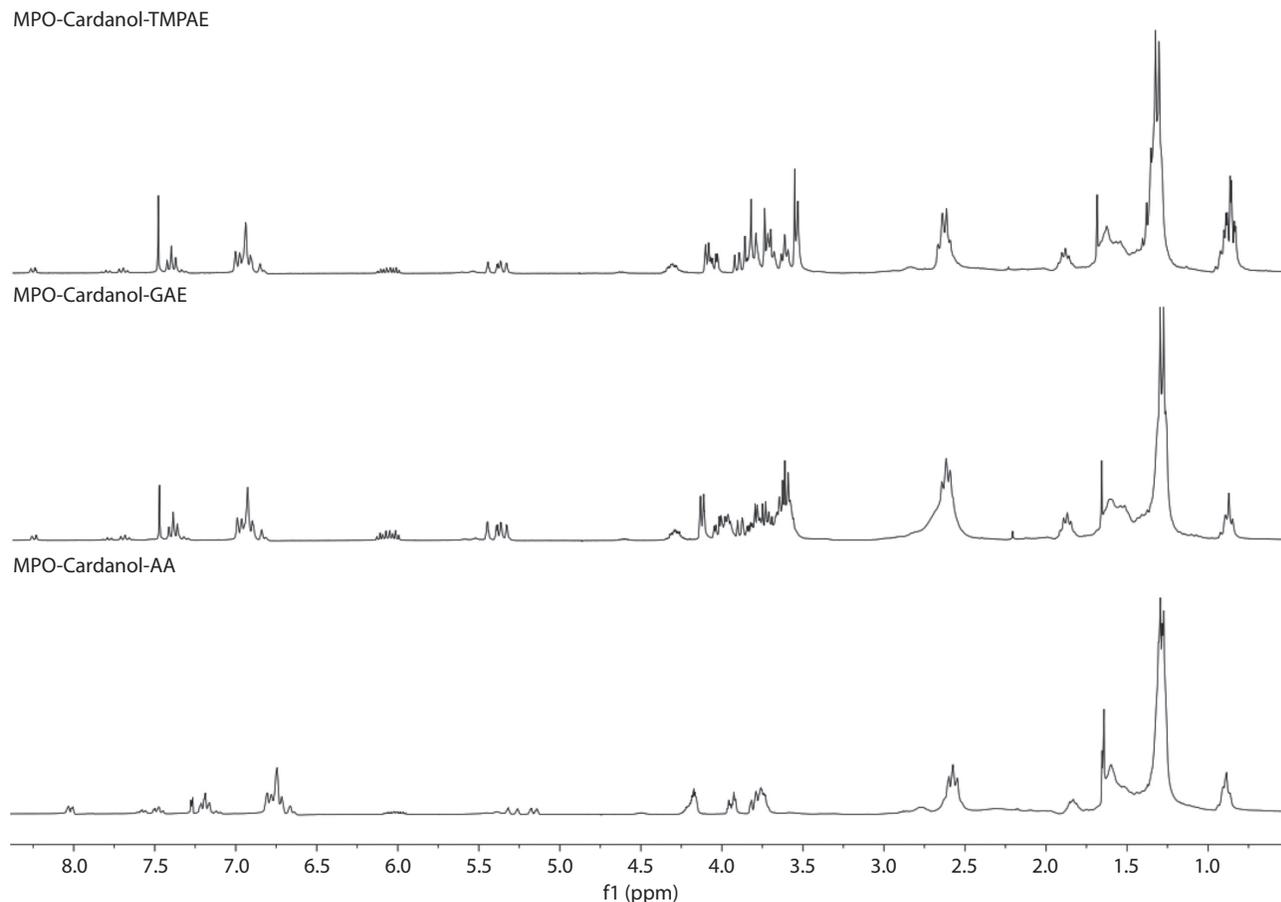


Figure 6 ^1H NMR spectra overlay of MPO-Cardanol-AA, MPO-Cardanol-GAE and MPO-Cardanol-TMPAE.

formulation was calculated as a function of hydroxyl number of polyols and water used.

Cream time, rise time and tack-free time of the rigid polyurethane foams were 8–10 s, 42–90 s and 44–92 s respectively. Cream time is in the normal range; however, the rise time of the foams prepared from 100% MPO-Cardanol polyols was higher, i.e., 90 s, which may probably be due to the presence of unreacted thiol group. Thiol group is acidic in nature, which may block tertiary amine used as a catalyst in foam preparation, resulting in longer rise time.

Foaming process begins with a reaction between isocyanate and water, which generates carbon dioxide, resulting in cellular structure. Gas-liquid foam is formed initially, which is stabilized by silicone surfactant. It is then transformed into gas-solid foam as a result of crosslinking between isocyanate and polyols; hence, the cellular structure is conserved. Thus, prepared foams were characterized after maturation for a week. Images of rigid polyurethane foams based on MPO-Cardanol polyols show the normal appearance of conventional rigid polyurethane foams (Figure 7).

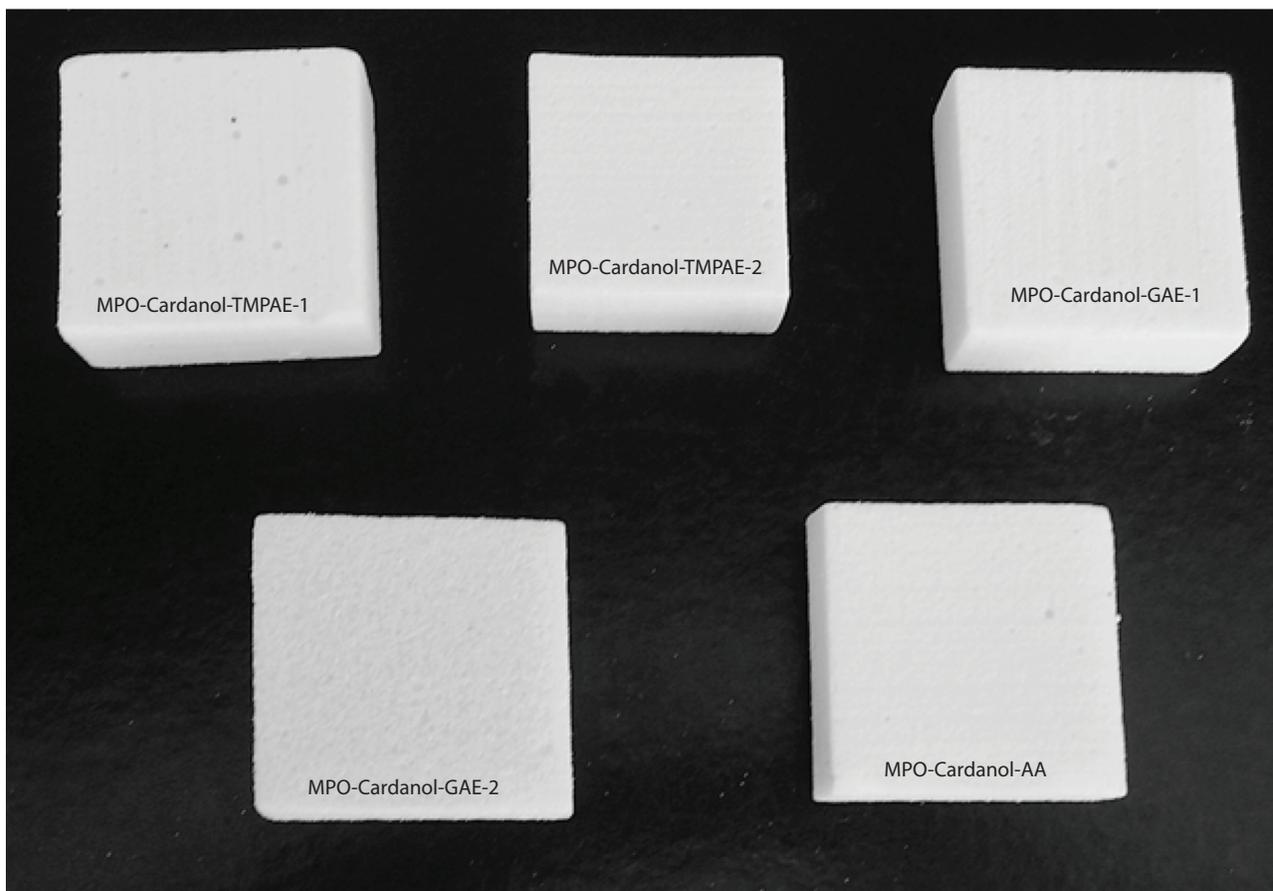


Figure 7 Images of rigid polyurethane foams based on MPO-Cardanol polyols.

Table 2 Properties of rigid PU foams prepared with MPO-Cardanol polyols.

PU foam sample	Density, Kg/m ³	Closed cell content, %	Compression strength, Stress@10 %, kPa	T _g (°C)
PU-MPO-Cardanol-TMPAE-1*	43.0	93	215	58.87
PU-MPO-Cardanol-TMPAE-2**	32.0	92	138	66.84
PU-MPO-Cardanol-GAE-1*	37.0	81	193	41.71
PU-MPO-Cardanol-GAE-2**	31.0	80	112	54.00
PU-MPO-Cardanol-AA**	32.0	91	119	61.40

*PU foam based exclusively on MPO-Cardanol polyol.

**PU foam based on 25% MPO-Cardanol polyol and 75% sucrose polyol Jeffol SG-360.

The characteristics of rigid PU foams based on MPO-Cardanol polyols are presented in Table 2. Compression strengths of the foams based exclusively on MPO-Cardanol polyols are higher than that of mixture of MPO-Cardanol polyols (25%) and sucrose-glycerol polyol Jeffol SG-360 (75%). This effect is probably due to the aromatic content of MPO-Cardanol polyols, since the presence of aromatic rings in polyols leads to rigid PU foams with superior physical-mechanical properties [18]. Generally, compression strength higher than 120 kPa is acceptable

for rigid polyurethane foams with densities of 30–45 Kg/m³. PU-MPO-Cardanol-TMPAE-1 and PU-MPO-Cardanol-GAE-1 comprise much higher compression strengths, 215 kPa and 193 kPa respectively. Closed-cell contents of the rigid PU foams based on MPO-Cardanol polyols are also slightly higher (Table 2).

Figure 8 presents TGA curves of the selected rigid polyurethane foams; a) PU-MPO-Cardanol-AA (based on 25% cardanol polyol and 75% sucrose polyol Jeffol SG-360), b) PU-MPO-Cardanol-GAE-1 and c) PU-MPO-Cardanol-TMPAE-1 (based exclusively

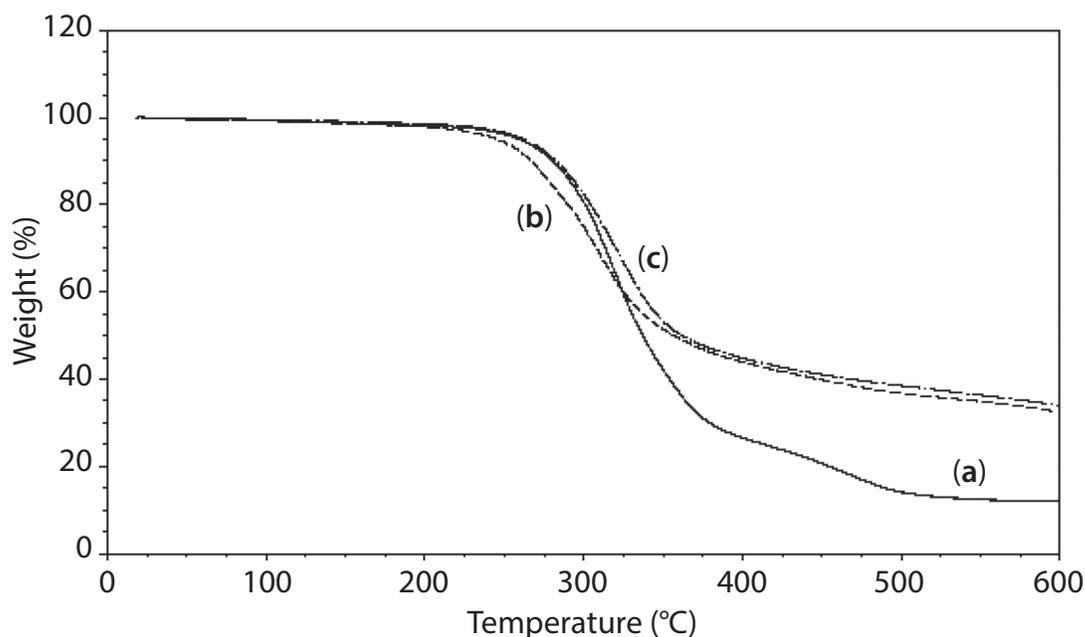


Figure 8 TGA curves of rigid PU foams: (a) PU-MPO-Cardanol-AA, (b) PU-MPO-Cardanol-GAE-1 and (c) PU-MPO-Cardanol-TMPAE-1.

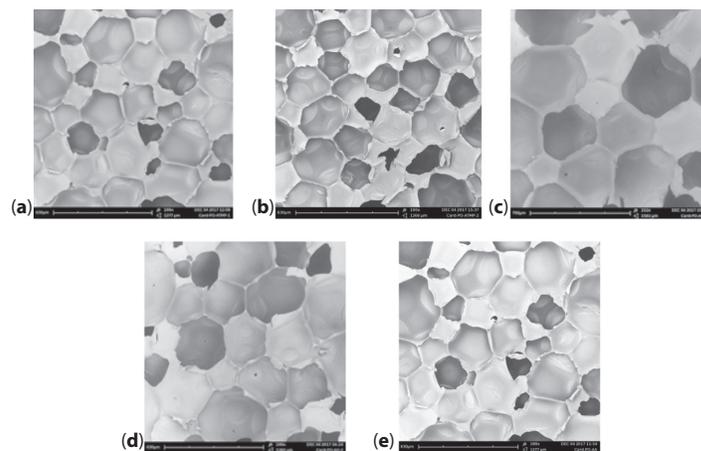


Figure 9 Images of rigid polyurethane foams prepared from MPO-Cardanol-based polyols: (a) PU-MPO-Cardanol-TMPAE-1 (average cell diameter: 253 μm); (b) PU-MPO-Cardanol-TMPAE-2 (average cell diameter: 245 μm); (c) PU-MPO-Cardanol-GAE-1 (average cell diameter: 483 μm); (d) PU-MPO-Cardanol-GAE-2 (average cell diameter: 225 μm); (e) PU-MPO-Cardanol-AA (average cell diameter: 257 μm).

on MPO-Cardanol polyols). As observed in the figure, thermal degradation of rigid polyurethane foams based on the mentioned MPO-Cardanol polyols starts at 220–250 °C, suggesting good thermal stability.

Figure 9 presents X-ray images of the rigid polyurethane foams prepared from MPO-Cardanol polyols. Average dimensions of cells are in the range of 225–257 μm, which is usual for conventional rigid polyurethane foams.

4 CONCLUSIONS

Successful preparation of biobased aromatic-aliphatic polyols by thermal or photochemical thiol-ene addition of hydroxyalkyl mercaptans to alkoxyated cardanol were described previously [10]. The present work was focused on a variant of synthesis of cardanol-based polyols by using photochemical thiol-ene reactions, in three steps. The first step consists of alkoxylation of the phenolic group of cardanol with propylene oxide. The second step is the addition of hydrogen sulfide to C=C bonds of propoxyated cardanol by UV-initiated photochemical thiol-ene reaction. The final step is the thiol-ene addition of thiol groups of mercaptanized propoxyated cardanol to the C=C bonds of glycerol-1-allyl ether, trimethylolpropane allyl ether, and allyl alcohol. The functionality of the resultant polyols are not very high (i.e. 2.26 to 3.52 OH groups/mol), possibly due to reaction of SH groups with internal double bond forming 5 or 6-membered cyclic sulfides. However, due to aromatic content (11-15%), the rigid polyurethane foams prepared from these polyols provided good physical and mechanical properties. The rigid polyurethane foams are useful for thermo-insulation (of freezers, storage tanks and pipes), wood substitutes and flotation materials.

REFERENCES

1. C.E. Hoyle and N. Bowman, Thiol-ene click chemistry. *Angew. Chem. Int. Ed.* **49**, 1540–1473 (2010).
2. A.B. Lowe, Thiol-ene “click” reactions and recent applications in polymer and material synthesis. *Polym. Chem.* **1**, 17–35 (2010).
3. N.B. Cramer, S.K. Reddy, A.K. O’Brien, and C.N. Bowman, Thiol-ene photopolymerization mechanism and rate limiting step changes for various vinyl functional group chemistries. *Macromol.* **36**, 7964–7969 (2003).
4. M. Uygun, M.A. Tasdelen, and Y. Yagci, Influence of type of initiation on thiol-ene “click” chemistry. *Macromol. Chem. Phys.* **211**, 103–110 (2010).
5. M. Ionescu, D. Radojčić, X. Wan, Z.S. Petrović, and T.A. Upshaw, Functionalized vegetable oils as precursors for polymers by thiol-ene reaction. *Eur. Polym. J.* **67**, 439–448 (2015).
6. M. Ionescu, D. Radojčić, X. Wan, M.L. Shrestha, Z.S. Petrović, and T.A. Upshaw, Highly functional polyols from castor oil for rigid polyurethanes. *Eur. Polym. J.* **84**, 736–749 (2016).
7. Cardolite Corporation, Cardanol, <http://www.cardolite.com> (2017).
8. M.L. Shrestha, M. Ionescu, X. Wan, N. Bilić, and Z.S. Petrović, Biobased aromatic-aliphatic polyols from cardanol by thermal thiol-ene reaction. *J. Renew. Mater.* Available online (2017). DOI: 10.7569/JRM.2017.634187
9. M. Desroches, S. Cailol, V. Lapinte, R. Auvergne, and B. Boutevin, Synthesis of biobased polyols by thiol-ene coupling from vegetable oils. *Macromol.* **44**, 2489–2500 (2011).
10. S. Cailol, B. Boutevin, and M. Desroches, Method for functionalizing natural fatty substances, WO Patent 2012001315, assigned to Centre Nationale de Recherche Scientifique and Université Montpellier II (2012).
11. J.H.P. Tyman, D. Wilczynski, and M.A. Kashani, Compositional study on technical cashew nut shell liquid (CNSL) by chromatography and mass spectroscopy. *J. Am. Oil Chem. Soc.* **55**, 663–668 (1978).
12. V. Pauland and L.M. Yeddapanali, On the olefinic nature of anacardic acid from Indian cashew nut shell liquid. *J. Am. Chem. Soc.* **78**, 5675–5678 (1956).
13. C.H.V. Subbarao, Review on application, extraction, isolation and analysis of cashew nut shell liquid (CNSL). *The Pharm. Res.* **6**, 21–41 (2011).
14. K.I. Suresh and V.S. Kishanprasad, Synthesis, structure and properties of novel polyols from cardanol and developed polyurethanes. *Ind. Eng. Chem. Res.* **44**, 4504–4512 (2005).
15. M. Ionescu and Z.S. Petrović, From cashew nut shell liquid to polyols for polyurethanes. *INFORM* **24**, 6 (2013).
16. M. Ionescu, *Chemistry and Technology of Polyols for Polyurethanes*, vol. 2, pp. 79–88 and pp. 267–273, Rapra Technology Ltd., Shawbury, Shrewsbury, Shropshire, UK (2016).
17. M. Ionescu, X. Wan, N. Bilic, and Z.S. Petrovic, Polyols and rigid polyurethane foams from cashew nut shell liquid. *J. Polym. Environ.* **20**, 647–658 (2012).
18. F. Jailliet, E. Darromon, A. Ratsimithety, B. Boutevin, and S. Caillol, Synthesis of cardanol oil building blocks for polymer synthesis. *Green Mat.* **3**, 59–70 (2015).
19. K.I. Suresh, Rigid polyurethane foams from cardanol: Synthesis, structural characterization, and evaluation of polyol and foam properties. *ACS Sus. Chem. Eng.* **1**, 232–242 (2013).
20. K.I. Suresh and V. S. Kishanprasad, Process for preparing polyurethane polyol and rigid foams therefrom, US Patent 7244772, assigned to Council of Scientific and Industrial Research (India).
21. F. Jailliet, E. Darroman, B. Boutevin, and S. Caillol, A chemical platform approach on cardanol oil: From synthesis of building block to polymer synthesis. *OCL* **23**, D511 (2016). DOI: 10.1051/ocl/2016022
22. C. Voirin, S. Caillol, N. Sadavarte, B.V. Tawade, B. Boutevin, and P.P. Wadgaokar, Functionalization of cardanol: Towards biobased polymers and additives. *Polym. Chem.* **5**, 3142–3162 (2014).

23. K.I. Suresh and V.S. Kishanprasad, Synthesis, structure and properties of novel polyols from cardanol and developed polyurethanes. *Ind. Eng. Chem. Res.* **44**, 4504–4512 (2005).
24. F. Changqing, L. Jiancheng, X. Hongying, and S. Liang, Effect of structure on the properties of polyurethanes based on aromatic cardanol-based polyols prepared by thiol-ene coupling. *Prog. Org. Coat.* **83**, 19–25 (2015).
25. R.K. Gupta, M. Ionescu, D. Radojčić, X. Wan, and Z.S. Petrović, Novel renewable polyols based on limonene for rigid polyurethane foams. *J. Polym. Environ.* **22**, 304–309 (2014).
26. T. Upshaw, W.S. Young, and E.J. Netemeyer, Chevron Phillips Chemical Co. LP, Natural oil polythiols: A life cycle comparison. *World Adhesive Conf. & Expo* (2008).
27. T. Upshaw and M.S. Matson, Polythiols with carbamate groups, US Patent 20160257647, assigned to Chevron Phillips Chemical Co. LLP (2016).