

ONE STEP SYNTHESIS OF HIGHLY FUNCTIONAL POLYOLS BY PHOTOCHEMICAL THIOL-ENE “CLICK” CHEMISTRY

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Abstract

One step photochemical thiol-ene reaction was utilized successfully for preparation of highly functional polyols. Various commercially available mercaptopropionates, trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate and dipentaerythritol hexakis(3-mercaptopropionate) were reacted with the C=C bond of allyl hydroxyl compounds under UV irradiation in the presence of 2-hydroxy-2-methylpropiophenone, a photoinitiator. Allyl hydroxyl compounds utilized in these reactions were allyl alcohol, glycerol-1-allyl ether and 2-hydroxy-2-methyl propiophenone. All these reactions provided quantitative yields within 1 to 3 hours. These polyols were also characterized by standard analytical techniques

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Introduction

Commercially available polythiols¹⁻⁵, such as trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate) and dipentaerythritol hexakis(3-mercaptopropionate), are interesting precursors that can be utilized in preparation of highly functional polyols. Thiol-ene “Click” chemistry is a very efficient pathway for reaction of thiols containing starting materials with terminal C=C bonds.^{3, 6-11} This reaction delivers quantitative yields in a short period of time providing predominantly anti-Markovnikov product. In addition, the reaction does not require solvent, which further supports the novelty of thiol-ene reaction. The reaction can be initiated thermally using a radical initiator, or photochemically using a photoinitiator.¹² Another important feature of thiol-ene reaction is that it inhibits oxidation of the resulting compound.^{1, 13-15} Consequently, there is increasing interest in the use of the thiol-ene reaction to generate multifunctional polyols.¹⁶⁻¹⁷

Thiols containing mercaptopropionates can simply react with the C=C bond of hydroxyl compounds in the presence of 2-hydroxy 2-methylpropiophenone, a photoinitiator, to deliver a wide range of polyfunctional hydroxy compounds.^{10, 18-22} This approach can be employed for synthesis of polyols that can be beneficial for production of rigid polyurethanes. It is a known fact that polyols with 4-8 hydroxyl groups are considered optimum for preparation of rigid polyurethane foams.²³ The best rigid polyurethane properties can be achieved using polyols in this range. Herein we report the synthesis of highly functional polyols directly from commercially available starting materials by following this simple procedure. Trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate) and dipentaerythritol hexakis(3-mercaptopropionate) were utilized as thiol counterparts for this purpose. Likewise, allyl alcohol (AA), glycerol-1-allyl ether (GAE) and trimethylolpropane allyl ether (TMPAE) were used as the reactants containing ene functional group. Highly functional polyols were thus successfully prepared from thiol-ene “Click” chemistry with very high yields. These polyols were also analyzed by various standard techniques that includes Size Exclusion Chromatography (SEC), Fourier Transform Infrared Spec-

troscopy (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy.

Experimental

Materials

Trimethylolpropane tris(3-mercaptopropionate) ($\geq 95.0\%$) and pentaerythritol tetrakis(3-mercaptopropionate) ($> 95.0\%$) were obtained from Aldrich, while dipentaerythritol hexakis(3-mercaptopropionate) ($> 93.0\%$) was purchased from TCI America. Glycerol-1-allyl ether ($> 99.0\%$) and 2-hydroxy 2-methyl propiophenone (98.0%) were also supplied from TCI America. Allyl alcohol (98.0+ %) was obtained from Alfa Aesar, and trimethylolpropane allyl ether (98.0%) was supplied by Aldrich.

Synthesis of Polyols

General procedure of the polyol synthesis included photochemical thiol-ene reaction that used an equimolar mixture (1:1) of thiols and the C=C bond of compounds containing hydroxyl groups with the addition of about 1.0 wt % of 2-hydroxy 2-methyl propiophenone. The reaction mixture was stirred under UV irradiation (20 W UV lamp) for 1-3 hours. For example, the polyol TMP-3MPA-AA was prepared by mixing 39.85 g (0.1 mol) of trimethylolpropane tris(3-mercaptopropionate) with 17.4 g (0.3 mol) of allyl alcohol in a 120 mL glass jar. 0.57 g (1 %) of 2-hydroxy 2-methyl propiophenone was also added to the mixture. Then the reaction mixture was stirred under the UV lamp for 3 hours. All other polyols were obtained by following the general procedure unless mentioned otherwise.

Analysis

Viscosity of the resulting polyols was measured at 25 °C using AR 2000 EX Rheometer (TA Instruments). Acid values and hydroxyl numbers were determined by titration method (ASTM D4662) and phthalic anhydride pyridine method (ASTM D4274) respectively.

Size exclusion chromatography (SEC), using a pump (Waters 515 pump from Water Corporation, Milford, MA) and a set of 5 columns (Phenogel™ columns from Phenomenex®, Torrance,

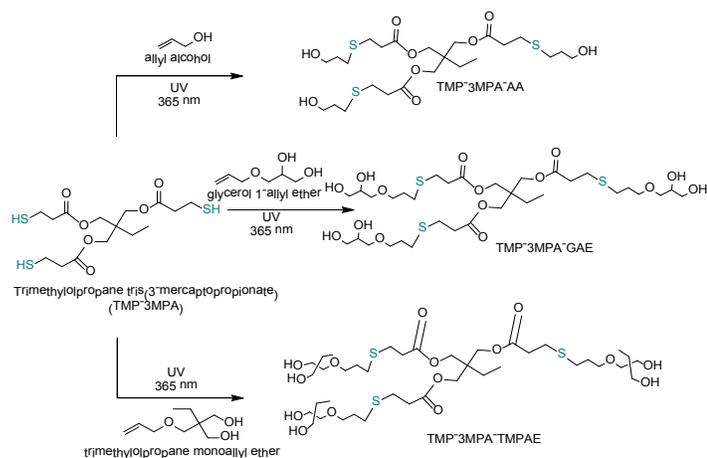
CA), was employed to determine number average, weight average and polydispersity of the polyols. Tetrahydrofuran was used as an eluent.

Fourier transform infrared (FTIR) spectroscopy (IRAffinity-1, Shimadzu) was used to determine functional group/s of the polyols, and detail structure of the polyols was examined using a 300 MHz Bruker Avance DPX-300 Nuclear Magnetic Resonance (NMR) Spectroscopy.

Results and discussion

The photochemical thiol ene reaction was utilized for the synthesis of various polyols from the reaction of commercially available thiol containing mercaptopropionate and C=C bond containing hydroxy compounds. Various commercially available mercaptopropionates derived from trimethylolpropane and pentaerythritol were chosen for this purpose. At first, trimethylolpropane tris(3-mercaptopropionate) (TMP-3MPA) was reacted with allyl alcohol to produce trifunctional polyols. The progress of the reaction was monitored using Size Exclusion Chromatogram (SEC), which showed the disappearance of the starting material and formation of a new peak at lower retention time corresponding to higher molecular weight polyols with higher functionality. Similar outcomes were observed when a 3-hour reaction was compared with results from a 5-hour reaction. These results suggested that a maximum 3-hour reaction time was sufficient to obtain a high conversion. Following the first reaction, two other highly functional polyols were also prepared from the same mercaptopropionate, reacting with glycerol-1-allyl ether (GAE) and trimethylolpropane monoallyl ether (TMPAE). Viscosity measurement using AR 2000 EX Rheometer confirmed the later polyols, TMP-3MPA-GAE and TMP-3MPA-TMPAE were more viscous compared to the trifunctional TMP-3MPA-AA polyol, 11.08 Pa.s. and 33.76 Pa.s. vs 1.78 Pa.s., which was expected given their higher functionality (Scheme 1 and Table 1).

Similarly, pentaerythritol tris(3-mercaptopropionate) was reacted with allyl alcohol (AA), glycerol-1-allyl ether (GAE) and trimethylolpropane monoallyl ether (TMPAE) respectively for preparation of 3 new highly functional polyols. The polyol PeT-3MPA-AA was tetrafunctional whereas the polyols PeT-3MPA-GAE and PeT-3MPA-TMPAE were octafunctional (Scheme 2).



Scheme 1: Synthesis of trimethylolpropane tris(3-mercaptopropionate) derived polyols from photochemical thiol-ene reaction

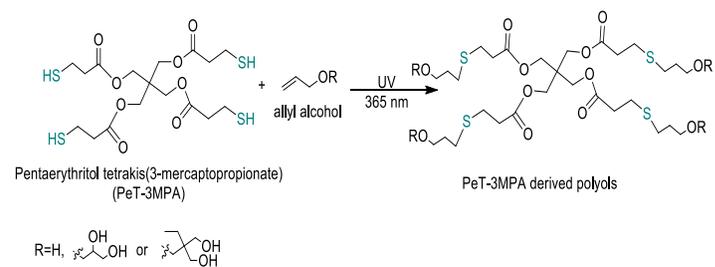
Further, dipentaerythritol hexakis(3-mercaptopropionate) was utilized in the photochemical thiol-ene reactions that delivered even higher functional polyols containing up to 12 hydroxy groups/molecule. All these polyols, DiPeT-3MPA-AA, DiPeT-3MPA-GAE and DiPeT-3MPA-TMPAE were very viscous (Scheme 3, Table 1).

The acid values of all the polyols prepared from mercaptopropionates were in the acceptable range, 0.6-1.81 mg KOH/g. The hydroxyl number of the polyols were variable, 263 mg KOH/g being the lowest and 438 mg KOH/g, the highest. The hydroxyl value increased with the functionality of the starting materials used, i.e. Glycerol-1-allyl ether (GAE) > trimethylolpropane allyl ether (TMP) > allyl alcohol (AA), as anticipated.

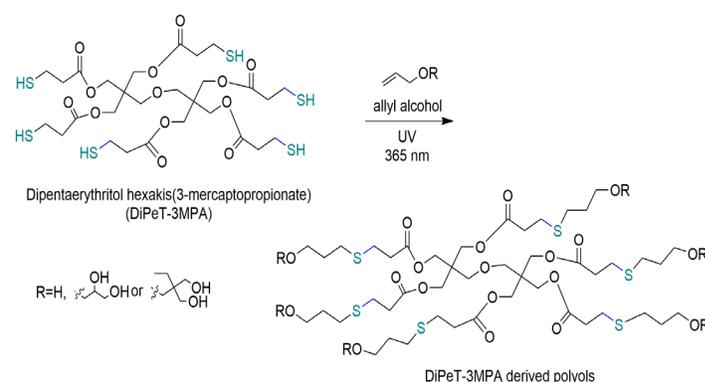
SEC overlay of the polyols prepared from trimethylolpropane tris(3-mercaptopropionate) with that of the starting material reveals that the reaction occurred successfully without any residual starting materials (Figure 1). A small shoulder peak at around 32.5 mins could be a result of oligomerization²⁴ which is possible due to formation of reactive thiols in photochemical thiol-ene reaction resulting disulfides.²⁵ Decreasing retention time with increasing

Table 1: Characteristics of the polyols derived from various mercaptopropionates using photochemical thiol-ene reaction

Polyols	Viscosity (Pa.s) @ 25 °C	Acid value (mg KOH/g)	OH # (PAP) mg KOH/g	M _n	M _w	Polydispersity
TMP-3MPA-AA	1.755	1.78	272.11	427.20	458.56	1.07
TMP-3MPA-GAE	11.08	0.98	412.80	628.88	652.65	1.04
TMP-3MPA-TMPAE	33.76	0.67	363.97	797.75	867.81	1.08
PeT-3MPA-AA	4.247	1.81	290.80	561.19	597.14	1.06
PeT-3MPA-GAE	25.17	0.83	438.78	831.51	867.62	1.04
PeT-3MPA-TMPAE	72.52	0.74	375.55	1064.09	1189.82	1.12
DiPeT-3MPA-AA	16.06	1.58	263.62	849.21	944.86	1.11
DiPeT-3MPA-GAE	48.79	0.98	423.73	1089.71	1155.03	1.06
DiPeT-3MPA-TMPAE	152.60	1.09	357.29	1510.21	1782.69	1.18



Scheme 2: Synthesis of pentaerythritol tetrakis(3-mercaptopropionate) derived polyols from Photochemical Thiol-ene reaction



Scheme 3: Synthesis of dipentaerythritol hexakis(3-mercaptopropionate) derived polyols from photochemical thiol-ene reaction

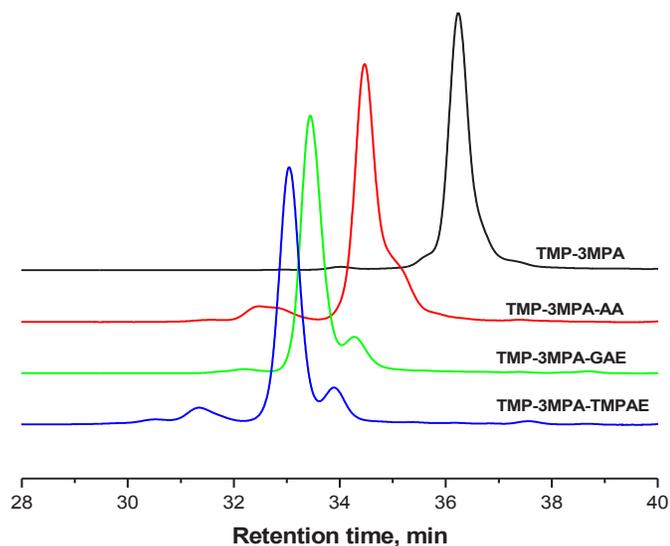


Figure 1: SEC overlay of TMP-3MPA-AA and polyols

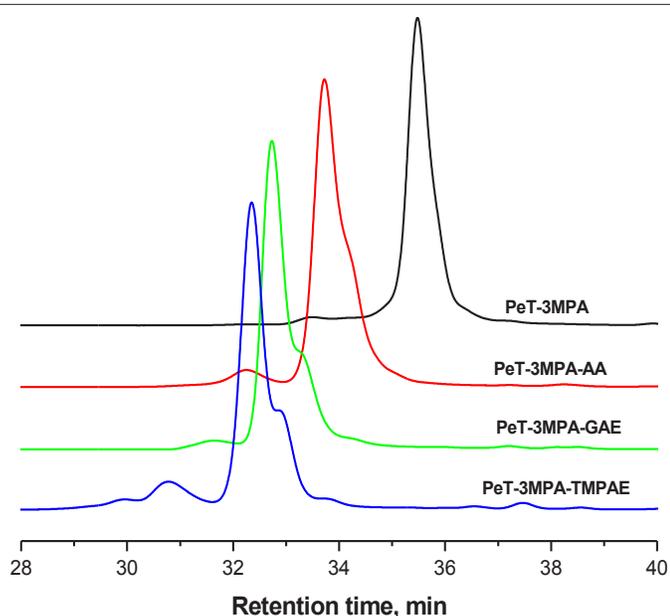


Figure 2: SEC overlay of PeT-3MPA and polyols

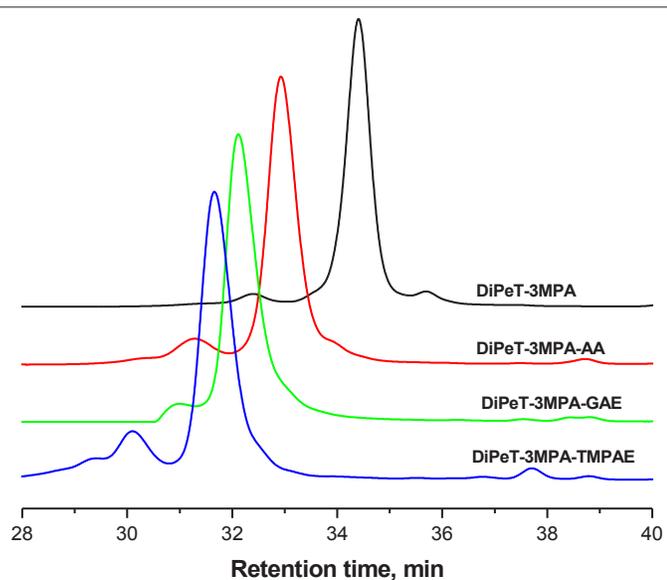


Figure 3: SEC overlay of DiPeT-3MPA and polyols

molecular weights of the polyols was also observed, as expected. Further, the molecular weights of the polyols (M_n and M_w) also increased with increase in the functionality, as determined by SEC. Polydispersity index of all the polyols were about 1 that indicated the narrow distribution of molecular weights.

Similar patterns of the SEC of the other 8 polyols also supports that the photochemical thiol-ene reaction was successfully employed to prepare a variety of polyols having a wide range of functionality (Figure 2 and Figure 3).

FTIR spectra of the polyol, TMP-3MPA-AA shows the presence of hydroxyl and carbonyl groups at around 3400 cm^{-1} and 1730 cm^{-1} respectively. Hydrocarbon peaks were observed at

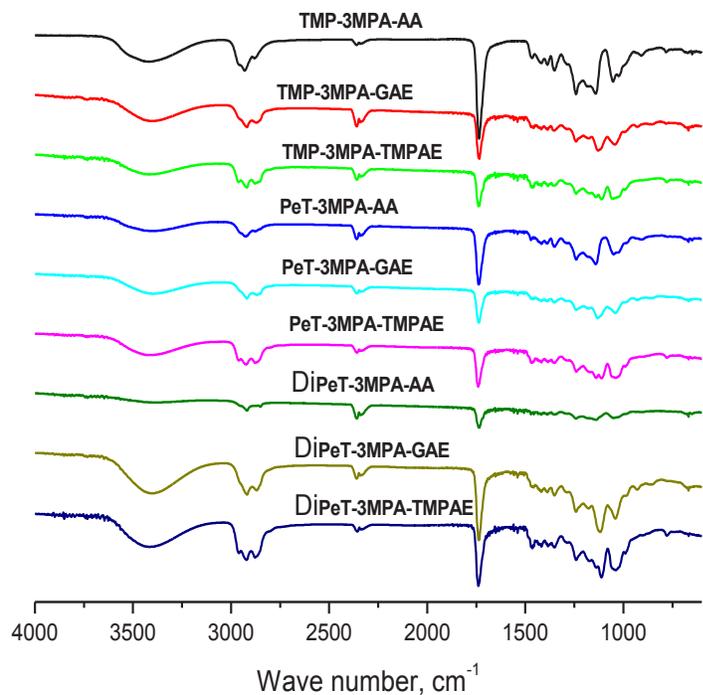
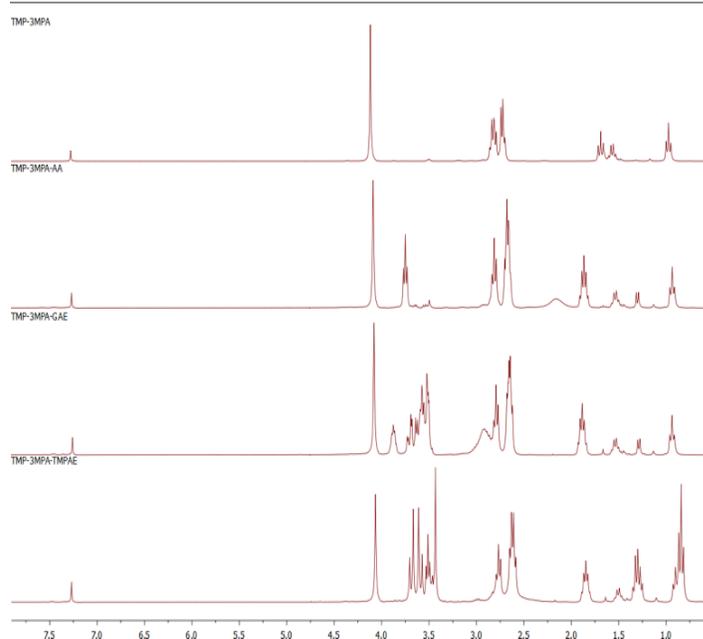


Figure 4: FTIR overlay of the Polyols prepared from Thiol-ene reaction

Figure 5: ^1H NMR overlay of TMP-3MPA and the resulting polyols

around 2900 cm^{-1} and 1450 cm^{-1} . Characteristic absorbance of C=C bond at 3010 cm^{-1} and -SH at 2220 cm^{-1} were absent, which suggests that the thiol-ene reaction between trimethylolpropane tris(3-mercaptopropionate) and the C=C bond of hydroxyl compounds occurred. Similar peaks were observed in FTIR of all other polyols reported in our current study.

^1H NMR spectrum of the starting material trimethylolpropane tris(3-mercaptopropionate) shows the presence of a methyl group and methylene group, a triplet centered at 0.90 ppm, and quartet centered at about 1.50 ppm respectively. A characteristic -SH peak was observed at around 1.62 ppm. Methylene peaks next to the carbonyl and thiol groups were found at around 2.68 ppm and 2.78 ppm, while the methylene peak adjacent to quaternary carbon was observed as a singlet at around 4.08 ppm. Similarly, another starting material, allyl alcohol was characterized by presence of methine peak, a multiplet centered at 5.99 ppm and methylene peak, doublet of doublet ranges 5.10-5.29 ppm. Further, a

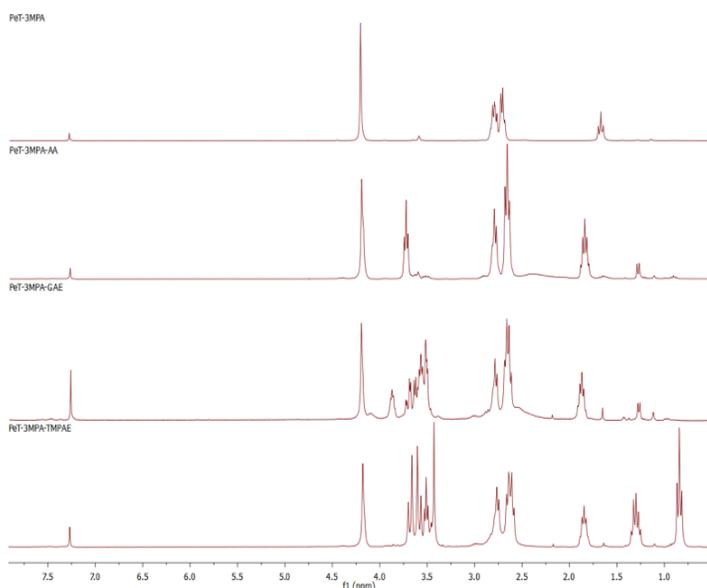


Figure 6: ^1H NMR overlay of PeT-3MPA and the resulting polyols

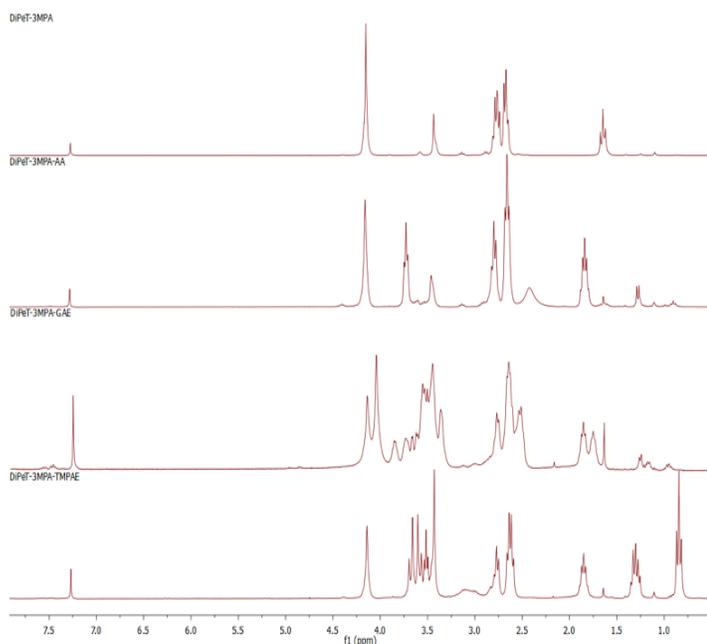


Figure 7: ^1H NMR overlay of DiPeT-3MPA and the resulting polyols

methylene peak adjacent to -OH was observed at 4.15 ppm. Absence of characteristic -SH peak and C=C bond bearing methine and methylene peaks in the ^1H NMR spectrum of the resulting trifunctional polyols, TMP-3MPA-AA NMR, clearly suggest that the photochemical thiol-ene reaction between trimethylolpropane (3-mercaptopropionate) and allyl alcohol occurred successfully.^{16, 26} Evolution of a new methyl peak, a doublet at 1.25 ppm and a methylene peak, a triplet at 1.83 ppm also supports the formation of thiol-ene products. Integral estimation of these peaks suggests the product containing a mixture ratio of ~1:7, in which major product resulted from anti-Markovnikov's addition. Proton NMR analysis of all other polyols also shows similar results, i.e. disappearance of characteristic peaks, -SH of mercaptopropionates and vinylic protons of C=C bond. Evolution of new methylene peaks was also observed consistently in the newly synthesized polyols. Furthermore, these NMR results are very consistent with the SEC results, which also supports that the new polyfunctional polyols were synthesized in a single step, simply by reacting commercially available starting materials.

Conclusions

A group of new polyols were prepared from a single step photochemical thiol-ene reaction utilizing commercially available starting materials. Various mercaptopropionates containing thiol groups and C=C bond/s containing hydroxyl compounds were reacted in the presence of a photoinitiator under UV light. The reaction provided a variety of new polyols with a wide range of functionality, ranging from 3 hydroxy groups/molecule to 12 hydroxy groups/molecule.

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