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Facile Modification of Propiolated Castor Oil via Nucleophilic Thiol-Yne Click Reactions

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The combination of modern click protocols and bio-based building blocks is a great step toward energy-efficient, and sustainable polymer production. Herein, thiol-Michael addition (thiol-yne) reactions from the toolbox of click chemistry protocols are chosen and propiolated castor oil (PCO) is used, a vegetable oil derivative, as the bio-based building block for the facile functionalization of PCO with various thiols. In addition to the functionalization of PCO, hyperbranched and crosslinked polymers are also prepared. The thiol-yne click functionalization reactions of the PCO are conducted at room temperature within 5 min and in the presence of an organic catalyst. The yields are found to change between 80% and 99% depending on the type of the thiol compound. The effect of various organic catalysts is investigated, and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) is found to be the most effective catalyst for the thiol-yne modification reactions. The hyperbranched polymer reaches 23.8 kDa (M_w) within 5 min. The findings of this paper open up new horizons for polymer researchers who work in the field of sustainable polymers and click chemistry and the presented idea here is appealing because it offers a potential strategy for fast, reliable, modular, and functional macromolecule preparation from renewable vegetable oils.

1. Introduction

Owing to the high abundance and low cost of vegetable oils (VOs), they are considered ideal renewable resources for sustainable polymer production.[1] VOs bear various reactive groups, such as ester linkages, double bonds, and allylic positions, providing a variety of opportunities to design and synthesize novel materials.[1–6] However, the reactivity of the double bonds in VOs is not high and often these double bonds are converted to more reactive sites, such as epoxy or acrylate groups.[7] The introduction of more reactive sites on vegetable oils is of great importance in terms of modularity, ease of modification, and faster reaction rates.

One intriguing strategy to introduce more reactive groups on VOs is to benefit from click chemistry. The click chemistry concept was put forward by Sharpless and co-workers in 2001 and it refers to atom-economic reactions that are modular, give high yields, and are insensitive to various functional groups, oxygen, water, and solvents.[8] Several reactions such as thiol-ene, Diels Alder, and copper (I)-catalyzed azide-alkyne cycloaddition reactions are among the most widely studied click reactions.[9] In addition to the aforementioned advantages of click reactions, they also display highly desirable features, such as high conversion rates, low energy consumption, and low waste generation.[9,10] These benefits of click chemistry are in sync with the principles of Green Chemistry. The principles of Green Chemistry were introduced in the 1990s by Paul Anastas.[11] These principles include atom economy, energy efficiency, reducing derivatives, designing less hazardous chemical syntheses, using benign solvents and auxiliaries, and using renewable feedstocks, etc.[11,12] The mutual relationship between Green Chemistry and click chemistry has been demonstrated in many studies and several polymers have been produced from bio-based building blocks by utilizing click chemistry pathways in recent years.[13,14]

Our group has been intensively working on the design, synthesis, postmodifications, and applications of polymers via metal-free click reactions.[15–28] Our group focuses especially on the reactions of activated alkyne-bearing monomers and polymers. An activated alkyne is a type of alkyne that is coupled with electron-withdrawing groups such as carbonyl groups.[29] Due to their electron-deficient nature, activated alkynes display high reactivity and can undergo Michael addition reactions with a variety of nucleophiles under mild reaction conditions. Thiol-yne, amino-yne, and hydroxyl-yne are the most known nucleophilic Michael addition click reactions of activated alkynes.[30] The versatile nature of the Michael reactions allows to production of complicated macromolecular architectures and sophisticated topologies for a wide range of applications.[31]

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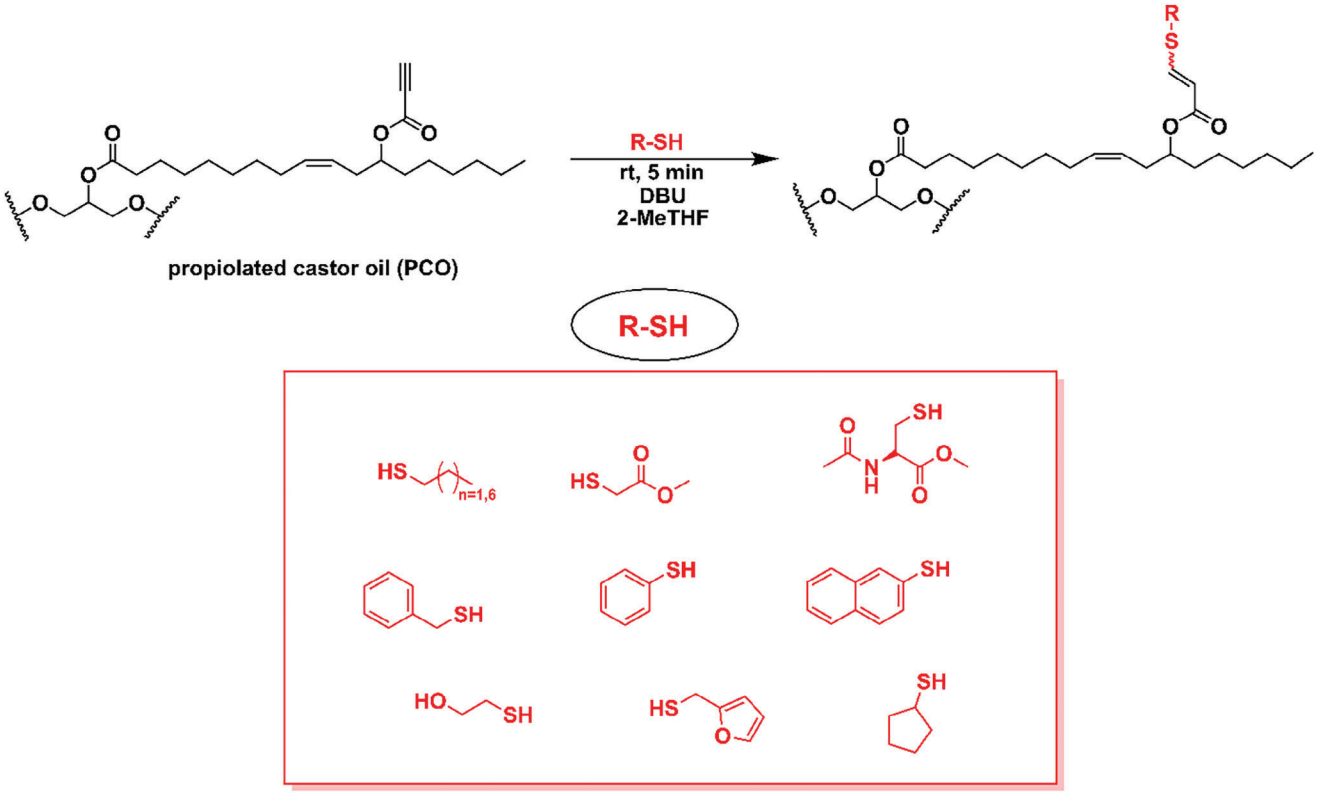


Scheme 1. Schematic representation for the modification of PCO with thiols via thiol-yne click reaction.

Recently, we decided to expand the scope of activated alkyne-based chemistries and started to apply them to bio-based building blocks. For instance; we reported the synthesis of propiolated castor oil (PCO) and its modification with primary or secondary amines via aza-Michael reactions.[32] The introduction of the propiolate group boosted the reactivity of castor oil. The modifications occurred at room temperature within 5 min and without any catalysts or solvents. We have also shown the preparation of thermosets by using the PCO and multifunctional amines. Since our previous findings displayed that the PCO was highly reactive toward amine groups,[32] we wanted to explore the organobase-catalyzed thiol-yne reactions with this bio-based novel building block. The organobase-catalyzed thiol-yne click route is considered a promising technique for the synthesis of sulfur-containing polymers due to its high efficiency, simplicity, and selectivity.[33]

The radical-induced thiol-ene functionalization of VOs via thiols is widely employed in the literature,[34–37] yet the steric hindrance of the double bonds of VOs often requires the use of large amounts of thiols and longer reaction times for high conversion percentages.[36–38] Besides, it was shown that side reactions, such as the oxidation of the VO or crosslinking reactions could occur in classical photoinitiated thiol-ene reactions of VOs.[39] On the other hand, the organobase-catalyzed thiol-yne reaction could be a good alternative for a fast, modular, tailorable, and side reaction-free functionalization of VOs compared to the radical-induced thiol-ene route. We must admit that we need green synthetic methods for the introduction of activated alkyne sites on VOs. Nevertheless, we believe the thiol-yne reactions conducted on VOs will open up new horizons in the future. Herein, we report the facile functionalization of PCO with various thiols under benign reaction conditions and the preparation of hyperbranched and crosslinked polymers via nucleophilic thiol-yne reactions (**Scheme 1**).

2. Results and Discussion

2.1. Modification of PCO with Different Thiols via Thiol-Yne Click Reaction

PCO was prepared according to our previous publication.[32] Similar to that study, the number of alkyne units per triglyceride of castor oil was found to be 2.28 from the integral ratio of ester methylene protons "b" (4H) to the propiolate alkyne proton "i" (**Figure 1A**). It is known that thiol-yne reactions require a catalyst to reach high conversions. Thus, after PCO was prepared, it was aimed to determine the appropriate catalyst required in this study. To this end, various organocatalysts (0.25 equiv. per PCO) were tested (see **Table 1**) in the reaction between PCO and a slight excess 1-propanethiol (1.2 equiv. per alkyne). Also, the reactions were performed for 5 min at room temperature using -2-methyltetrahydrofuran (2-MeTHF) as the solvent. It should be noted here that we did not investigate the effect of the solvent in this study and chose to use only 2-MeTHF, a bio-based green solvent. The thiol-yne reaction efficiencies were determined by comparing the integral areas of the aforementioned propiolate alkyne proton at 2.89 ppm and the ester methylene protons at 4.25–4.12 ppm. As can be seen from Table 1, DMAP, TEA, and TBD gave very low efficiencies, while MTBD and DBU gave

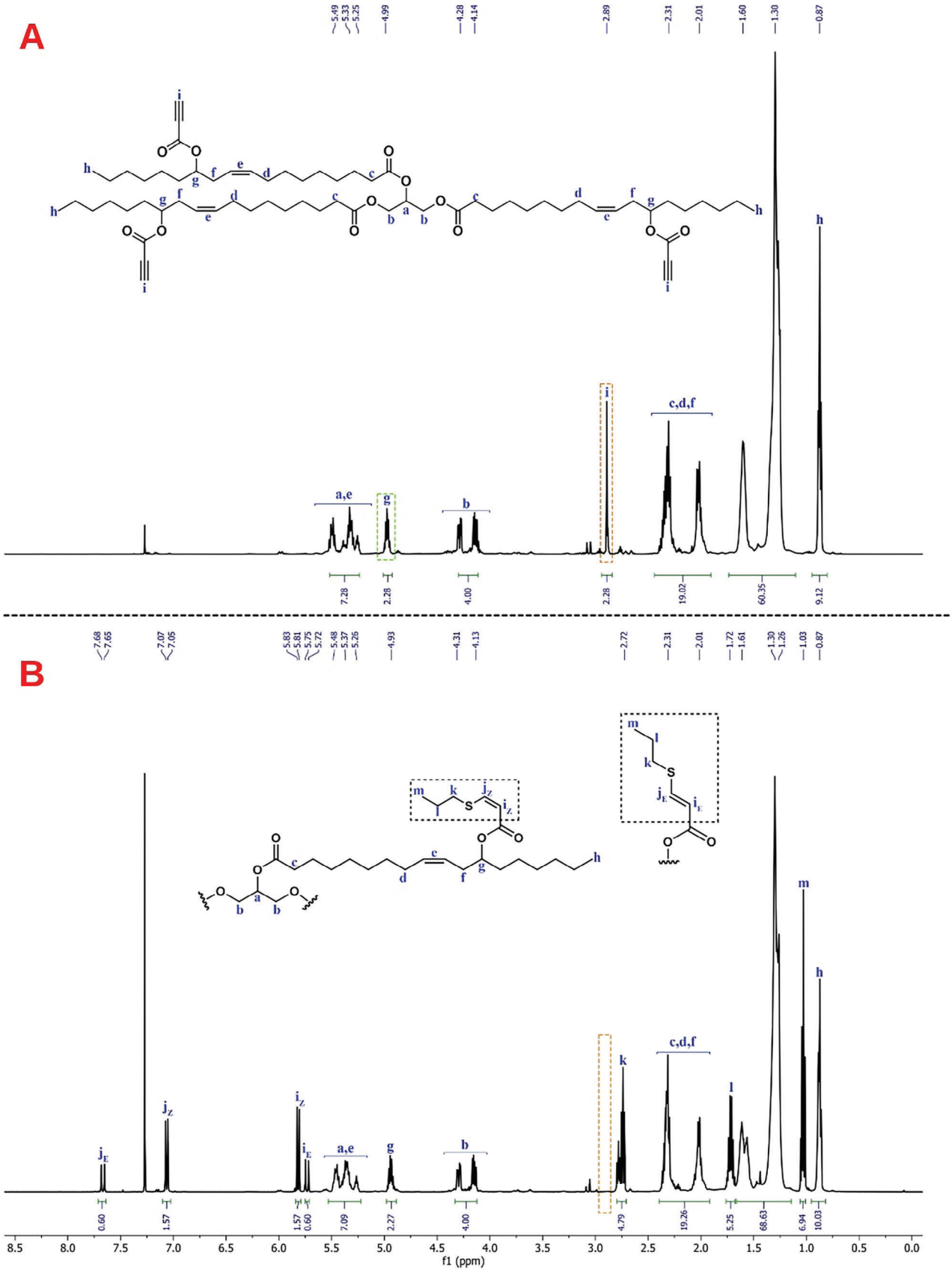
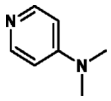
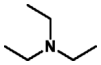
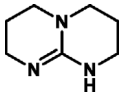
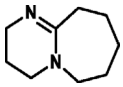
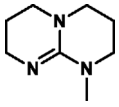


Figure 1. Stacked ^{1}H NMR spectra of PCO A) and 1 B).

Table 1. The effect of catalyst on the reaction of PCO and 1-propanethiol.

Entry[a]	Catalyst	Thiol-yne eff. [%][b]	E/Z ratio[b]	p*K*a (acetonitrile)
1	 (DMAP)	10	—	18.2[41]
2	 (TEA)	14	—	18.8[42]
3	 (TBD)	34	29/71	26[41]
4	 (DBU)	≥99	28/72	24.2[41]
5	 (MTBD)	96	27/73	25.4[41]
6	 (DABCO)	72	69/31	18.3[42]

[a] Conditions: PCO (1equiv.), 1-propanethiol (1.2 equiv. per alkyne), catalyst (0.25 equiv. per PCO), 2-MeTHF (500 µL) at room temperature for 5 min; [b] Determined by ^{1}H NMR.

excellent efficiencies. When the p*K*a values (in acetonitrile) of these amine catalysts are compared[40–42], it can be seen that catalysts having relatively lower basicity (TEA and DMAP) give lower efficiencies. Despite its high basicity TBD[40,43,44] (the most basic catalyst among the investigated ones) also displayed a lower efficiency, which might be attributed to its poor solubility in the reaction solvent (i.e., 2-MeTHF) used in this study. It is worth noting here that the thiol-yne reaction efficiencies are indeed promoted by TBD in halogenated solvents (e.g., chloroform)[40]; however, as emphasized above, we did not purposely select halogenated solvent in this study to preserve the green concept as much as possible. However, when TBD was replaced with MTBD, the efficiency was boosted and almost quantitative efficiency was obtained. Strikingly, quantitative efficiency was achieved when DBU was used as a catalyst, which might be attributed to its good compatibility with PCO and 2-MeTHF. Moreover, although it is less basic, a highly nucleophilic catalyst DABCO led to a moderate efficiency (72%). Collectively, based on the obtained results, we chose DBU to conduct the thiol-yne reactions on PCO.

Before examining other thiol compounds, PCO modified with 1-propanethiol was characterized in detail by NMR and FTIR, respectively. As can be seen from the ^{1}H NMR of 1 the terminal alkyne (≡C*H*) signals completely disappeared (Figure 1B). As a result of the thiol-yne reaction, new signals appeared due to the formation of alkene groups. Depending on the stereochemistry (*E*/*Z*) of the newly formed alkene, the hydrogens of the alkene were detected between 8.0–7.0 and 6.0 and 5.5 ppm. The signals for the aliphatic hydrogens in the propyl groups were observed at 2.72 ($SCH_2CH_2CH_3$), 1.72 ($SCH_2CH_2CH_3$), and 1.03 ($SCH_2CH_2CH_3$) ppm. All these findings proved that 1-propanethiol was added to the PCO. Moreover, the ^{13}C NMR of 1 is also in good accordance with the expected product as marked in Figure S2 (Supporting Information).

Finally, the FTIR spectrum of 1 was recorded and it can be seen that the alkyne vibration bands at 3257 and 2113 cm^{-1} disappeared (see Figure S3, Supporting Information) indicating that the thiol-yne click reactions took place. Moreover, a new band at around 1615 cm^{-1} appeared in the FTIR spectrum of 1 which belongs to the newly formed carbon—carbon double bond.

It should be noted here that the nucleophilic thiol-yne reactions are thought to occur via two different mechanisms.[30,40,45] According to the first mechanism, the organobase catalyst removes the —SH proton, and the resulting deprotonated thiol attacks the activated alkyne. The other route involves the nucleophilic attack of the organobase to the activated alkyne to generate allene enolate that subsequently removes the proton of the thiol compound. Depending on the reaction conditions the intermediates formed in these mechanisms lead to *syn*- or *anti*-additions. In most cases, nucleophilic thiol-yne additions lead to *β*-sulfido- *α*,*β*-unsaturated esters which exhibit stereospecificity. These *syn*- or

Table 2. Results obtained from the reaction between PCO and various thiols via thiol-yne click reactions.

Product code[a)]	Thiol	Yield [%][b)]	*E*/*Z* ratio[c)]
1	1-Propanethiol	90	28/72
2	1-Octanethiol	93	28/72
3	2-Mercaptoethanol	96	36/64
4	*N*-acetyl-L-cysteine methyl ester	80	55/45
5	Methyl thioglycolate	98	43/57
6	Benzyl mercaptan	82	31/69
7	2-Furanmethanethiol	90	32/68
8	Cyclopentanethiol	88	26/74
9	2-Naphthalenethiol	99	29/71
10	Thiophenol	92	31/69

[a)] Conditions: PCO (1 equiv.), thiol (1.2 equiv. per alkyne), DBU (0.25 equiv. per PCO), 2-MeTHF (500 µL) at room temperature for 5 min; [b)] Isolated yield; measured gravimetrically; [c)] Determined by ^{1}H NMR.

anti-additions generate *E*- and *Z*- stereoisomers which is a well-known feature of the nucleophilic thiol-yne conjugate addition reactions.[30,45,46] The nucleophilic thiol-yne reactions often generate products with mixed stereochemistries.[45] The product distribution is affected by several variables such as the structure of the thiols, solvents, pH, catalyst, temperature, etc. All the catalysts used herein produce almost similar *E*/*Z* ratios (≈30/70) except for DABCO which displayed an *E*/*Z* ratio of 69/31.

Various thiol compounds were then reacted with PCO using the same conditions described for 1-propanethiol. The names of the thiols and the product codes are collected in **Table 2**. Regardless of the thiol used, similar to 1-propanethiol, all thiols tested afforded quantitative efficiency in 5 min and high isolated yields ranging from 80% to 99%. The corresponding ^{1}H NMR, ^{13}C NMR, and FTIR spectra of all the products (1–10) are presented in the Supporting Information (Figures S4–S30, Supporting Information). Notably, the above-mentioned 30/70 *E*/*Z* ratio is preserved for almost all the thiol compounds used in this work (see Table 2). Only *N*-acetyl-L-cysteine methyl ester displayed large deviations from this ≈30/70 *E*/*Z* ratio, instead, it produced *E*- and *Z*-isomers at a ratio of 55/45. Randive et al. investigated the effect of various organobase catalysts on the stereochemistry of the nucleophilic thiol-yne reaction of ethyl propiolate with dodecanethiol and found that DBU is a highly efficient catalyst producing 100% conversion and a 34:66 *E*/*Z* ratio within 10 min at a low loading (1 mol%).[47] On the other hand, TEA produced an 85% yield and a 97:3 *E*/*Z* ratio after 60 min at 10 mol% loading.

2.2. Characterization of the Hyperbranched Polymer

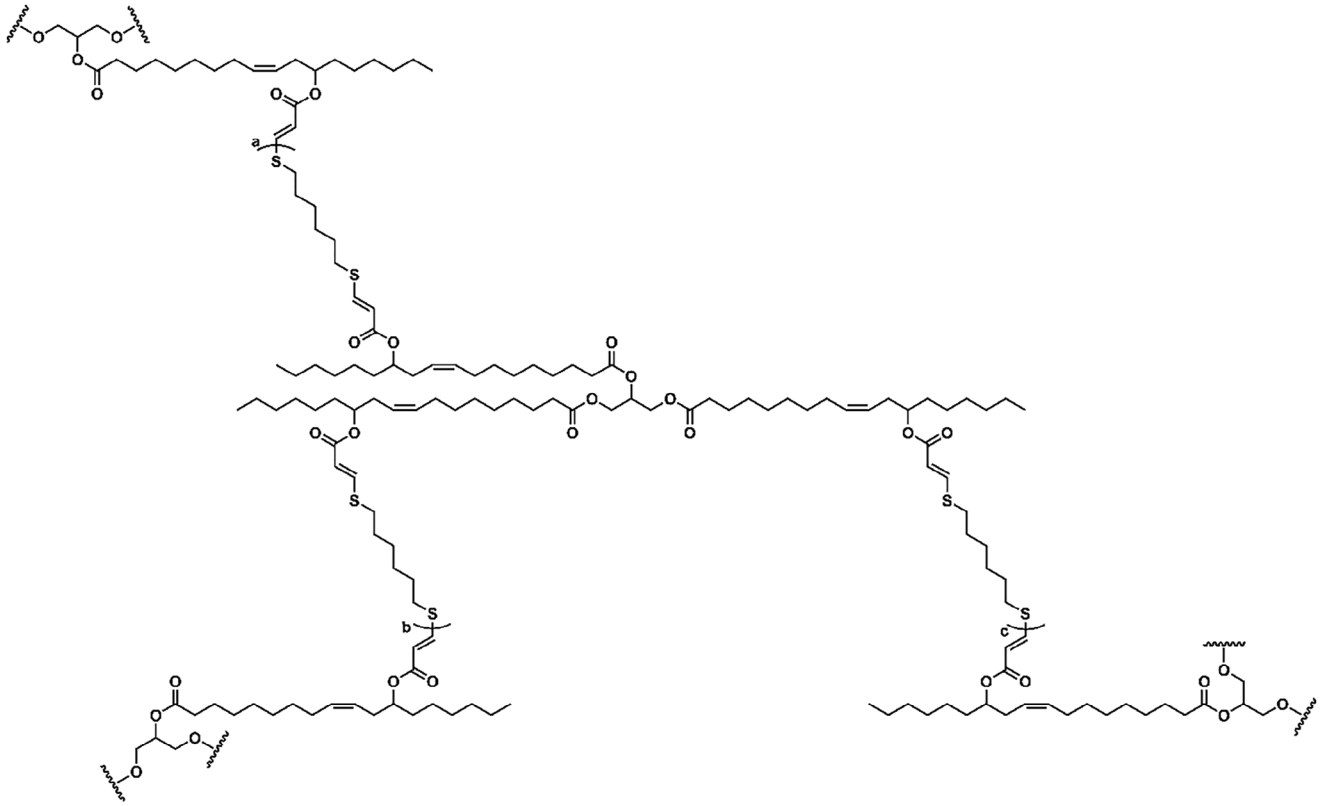
Hyperbranched polymers are an attractive class of macromolecules due to their unique 3D and highly branched structure and have found extensive applications for applications ranging from drug delivery to nanotechnology.[48,49] Highly efficient and robust character of the proposed thiol-yne click reaction on PCO prompted us to investigate this chemistry to synthesize oil-based hyperbranched polymer (HBP), as described in **Scheme 2**. To this end, PCO was reacted with 1,6-hexanedithiol (HDT), at a 1:1 alkyne to thiol molar ratio. The reaction was conducted in 2-MeTHF and DBU was used as the catalyst. The progress of polymerization was monitored by GPC for up to 6 h, during which aliquots of 30 µL were withdrawn from the reaction medium at different time intervals and precipitated in 1 mL of acidified methanol and analyzed by GPC. The GPC traces of HBP concerning the reaction time are shown in **Figure 2**. According to the GPC results, the HBP reached a high molecular weight (M_w = 23.8 kDa) only within 5 min and 31.2 kDa after 15 min. After that, the molecular weight increased gradually, yet the increase was not so significant and reached 36.0 kDa after 6 h.

The resulting HBP was characterized by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopy. The ^{1}H NMR spectrum of HBP (Figure S31, Supporting Information) displays the expected alkene proton signals and the alkyne (≡C*H*) proton signal has disappeared. The structure of HBP was further confirmed via ^{13}C NMR (Figure S32, Supporting Information). The unassigned peaks in the ^{1}H NMR and ^{13}C NMR spectra stem from the complex architecture of the HBP. The FTIR spectrum of HBP (Figure S33, Supporting Information) displays the complete disappearance of the alkyne vibration bands and the formation of the carbon—carbon double bond vibration band at 1615 cm^{-1}.

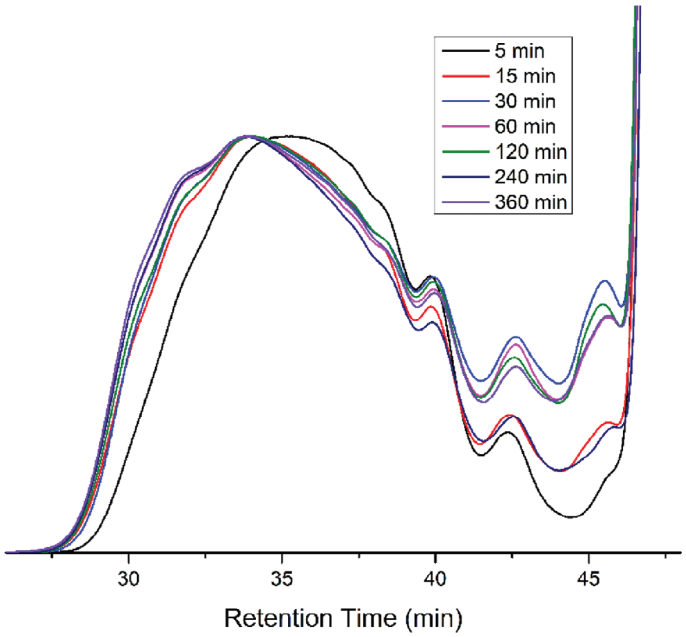
Previously, linear,[50] crosslinked,[51–53] and hyperbranched polymers[54–56] were prepared by using radical-induced thiol-ene/yne reactions. Postpolymerization functionalizations were also performed via these radical-induced thiol-ene/yne routes.[57,58] For instance; Konkolewicz et al. synthesized an AB_2 type monomer having a thiol and an alkyne end groups, and then photopolymerization of this compound in the presence of a photoinitiator and DMF produced 69% conversion within 10 min of UV irradiation time and a hyperbranched polymer with a molecular weight of 2.4 kDa (M_w).[56] After 90 min the conversion was 99% and the molecular weight increased to 17.8 kDa (M_w) with a polydispersity (*Đ*) of 11.94. Higher molecular weights were obtained with similar AB_2 monomers when long reaction times (4–5 h) and thermal polymerization were utilized[59]; however, PDI values were found between 13.0 and 17.5. When these hyperbranched polymers synthesized via radical routes are compared to this work (regardless of the structures of the thiols and alkyne species), it can be said that the nucleophilic thiol-yne route has prominent advantages; it produces high molecular weight at shorter durations and is operationally simple. Collectively, the proposed strategy promises milder conditions to prepare complex macromolecular architectures compared to radical-based strategies, particularly on a bio-based system, and thus holds a potential to be utilized in bio-relevant systems.

2.3. Characterization of the Bio-Based Thermosets

The network polymers were prepared similarly to the modification reactions or HBP synthesis but instead of DBU, TEA was used as a catalyst. The preparation of the thermosets is illustrated in **Scheme 3** and the recipe for the preparation of thermosets is given in Table S1 (Supporting Information). When DBU was used, a very fast gelation occurred as soon as the catalyst was added, leading to heterogeneous films. By using DBU as a catalyst we could not be able to synthesize self-standing films without defects. The digital images of the films are given in Figure S34 (Supporting Information). Among the images of the films,

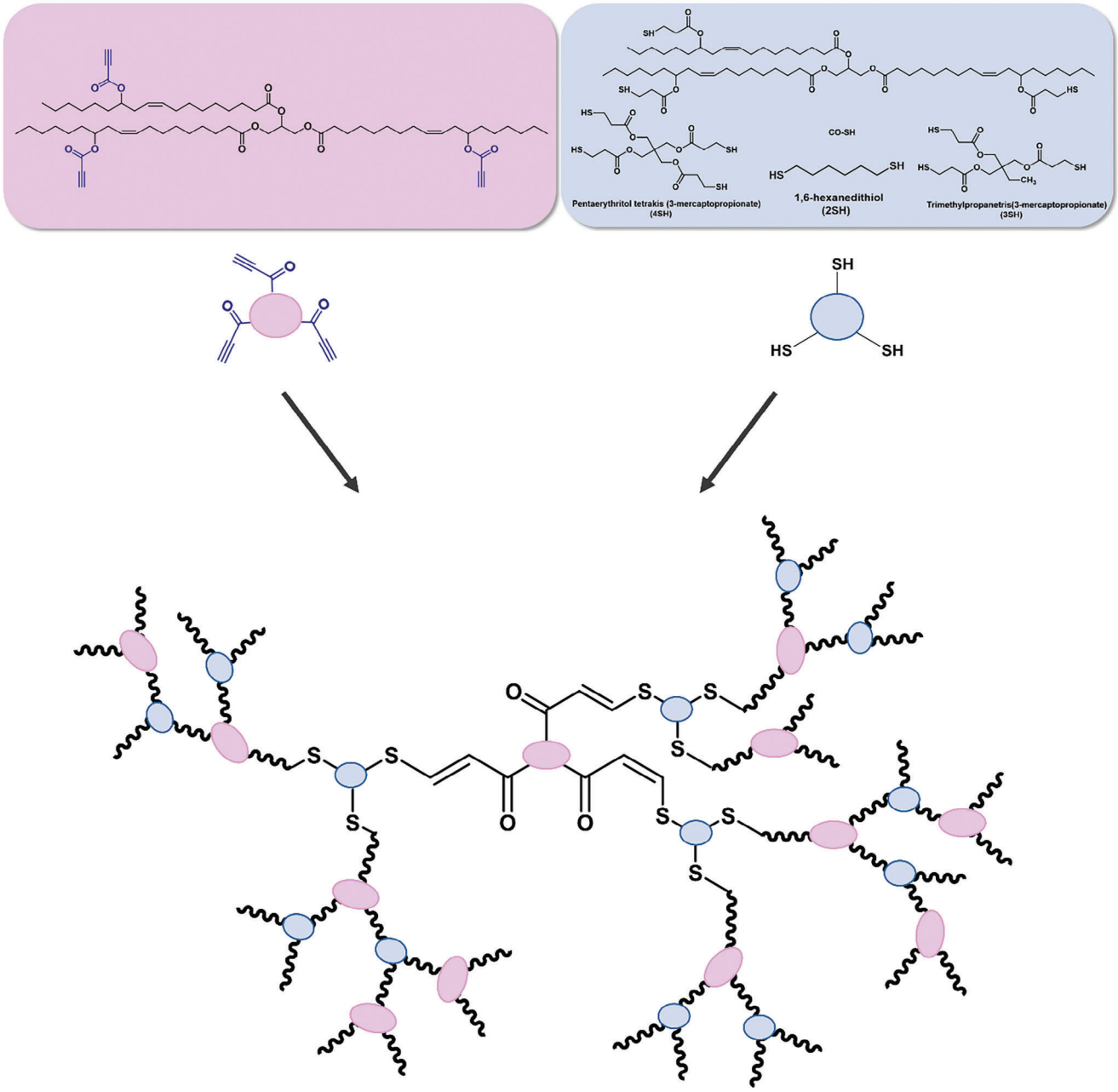


Scheme 2. Schematic representation for the synthesis of bio-based hyperbranched polymer (HBP) via thiol-yne click reaction.



t (min)	M_w (kDa)	$Đ$
5	23.8	3.13
15	31.2	3.35
30	32.1	3.45
60	34.9	3.54
120	33.8	3.22
240	35.0	3.46
360	36.0	3.24

Figure 2. GPC traces of HBPs in THF at 30 °C.



Scheme 3. Schematic representation for the preparation of crosslinked materials through the reaction between PCO and multifunctional thiols.

one example of a DBU-catalyzed film (PCO-CO-SH/DBU) is also presented, displaying heterogeneity, dark spots, and bubbles. We therefore utilized a mild catalyst to prepare the thermoset films. The films were soft and exhibited low mechanical properties (not measured).

The crosslinked films were structurally characterized via FTIR spectroscopy. The FTIR spectra of all the prepared films are presented in Figures S35–S38 (Supporting Information). All films exhibited similar spectra. In all spectra, it can be seen that the bands at around 2570 cm^{-1} (—SH vibration band) and around 2100 cm^{-1} (—C≡C—) either disappeared or their intensities were reduced. These findings prove that the thiol-yne reactions successfully occurred to a high extent.

Furthermore, we measured the gel contents of the films to determine the extent of crosslinking. As can be seen from Table S1 (Supporting Information), PCO-3SH and PCO-4SH display high gel content values (91%–94%), indicating highly crosslinked networks. PCO-2SH and PCO-CO-SH displayed relatively lower gel content values compared to PCO-3SH and PCO-4SH. The lower gel content value in the case of PCO-CO-SH films was attributed to the low conversion values arising from the steric hindrance of both PCO and CO-SH oligomers. The low gelation percentage

Table 3. Thermal properties of the crosslinked films.

Thermosets	T_5[a] [°C]	T_{10}[a] [°C]	T_1[a] [°C]	T_2[a] [°C]	T_g [°C]
PCO-2SH	325	350	378	439	−46
PCO-3SH	325	347	399	498	−28
PCO-4SH	328	352	399	500	−26
PCO-CO-SH	303	332	364	434	−44

[a] T_5 and T_{10} are the 5% and 10% weight loss temperatures. T_1 and T_2 are the maximum weight loss temperatures, which were determined from the maximum of the corresponding derivative curves.

for PCO-2SH can be attributed to lower crosslinking density due to the lower functionality of 2SH.

The thermal stability of the PCO-based films was determined via TGA under a nitrogen atmosphere. The TGA thermograms of the films are given in Figures S39–S42 (Supporting Information) and the results are listed in **Table 3**. T_5 and T_{10} are the 5% and 10% weight loss temperatures. T_1 and T_2 are the maximum weight loss temperatures obtained from the corresponding derivative weight curves. All samples displayed T_5 temperatures at around 300–330 °C and almost similar T_1 temperature values corresponding to the decomposition of the castor oil backbone. T_2 temperatures were attributed to the decomposition of the thioether linkages. Here, PCO-3SH and PCO-4SH displayed higher T_1 and T_2 temperatures compared to PCO-2SH and PCO-CO-SH, which can be attributed to the higher crosslinking density in PCO-3SH and PCO-4SH due to higher functionality of 3SH and 4SH monomers.

The glass transition temperatures (T_g) of the crosslinked films were determined via DSC measurements. The DSC spectra of the thermosets are given in Figures S43–S46 (Supporting Information). The T_gs of the thermosets are listed in Table 3. The T_g of the PCO-2SH was found as −46 °C which indicates a flexible network with high mobility and free-volume. This is related to the long flexible hexamethylene groups between crosslinking points in PCO-2SH. Similarly, PCO-CO-SH displayed a low T_g value. The T_g values of the PCO-3SH and PCO-4SH were found to be higher than PCO-2SH and PCO-CO-SH samples, and this could be attributed to the increased crosslinking density and relatively shorter chains between crosslinking points leading to tighter networks. The T_g values of the thermosets prepared via thiol-yne routes were found to be significantly lower than the ones prepared via amino-yne click reactions.[32] This could be ascribed to the presence of H-bonding interactions in the case of amino-yne routes, which bring additional physical crosslinking sites to the polymer network. Overall, the thiol-yne route produces flexible thioether linkages, increases chain mobility, and leads to low-T_g materials.[60,61]

3. Conclusion

Herein, we offered a bio-based building block for efficient modification and polymer synthesis via thiol-yne click reactions. The thiol-yne reactions were conducted at room temperature and within 5 min due to the high reactivity of the electron-deficient propiolate esters. Among the several catalysts, DBU displayed the best yields. We have also demonstrated that hyperbranched polymers and network polymers could be prepared with ease by using PCO and thiol-yne reactions. A high molecular weight (M_w = 23.8 kDa) HBP was obtained within 5 min. We also showed that crosslinked materials could also be prepared by using PCO. For the preparation of the thermosets, we replaced the DBU catalyst with a mild catalyst; TEA. The thermosets displayed moderate to high gel content values and low T_g values.

Along with our previous study[32] and this work, we have demonstrated that PCO is a versatile platform for functional macromolecule synthesis, hyperbranched polymer synthesis, and preparation of thermosets. The modularity of the straightforward nucleophilic thiol-yne conjugate addition allows to design and synthesis of complex architectures on biobased PCO precursor. We believe this study is another good example demonstrating the intriguing combination of modern click routes and Green Chemistry.

4. Experimental Section

Materials: Castor oil was obtained from a local store. Propiolic acid, methanesulfonic acid, 1-propanethiol, 1-octanethiol, 2-mercaptoethanol, *N*-acetyl-L-cysteine methyl ester, methyl thioglycolate, benzyl mercaptan, 2-furanmethanethiol, cyclopentanethiol, 2-naphthalenthiol, thiophenol, 4-dimethylaminopyridine (DMAP), triethylamine (TEA), triazabicyclodecene (TBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), 7-Methyl-1,5,7-triazabicyclo(4.4.0)dec-5-ene (MTBD), 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), anhydrous sodium sulfate (Na_2SO_4), toluene, 2-methyltetrahydrofuran (2-MeTHF), diethyl ether, 1,6-hexanedithiol (HDT, 2SH), trimethylolpropane tris(3-mercaptopropionate) (3SH), and pentaerythritol tetrakis(3-mercaptopropionate) (4SH) were purchased from Sigma-Aldrich and used as received. Propiolated castor oil (PCO) was prepared according to the previous publication.[32] Castor oil-based thiol compound (CO-SH) was prepared according to the literature.[62]

Characterization Methods: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using an Agilent VNMRS 500 instrument in $CDCl_3$. FT-IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR instrument over the range of 4000–400 cm^{-1}. Gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (model 1100) with a pump, refractive index, UV detectors, and four Waters Styragel columns. THF was used as an eluent at a flow rate of 0.3 mL min^{-1} at 30 °C, and 2,6-ditert-butyl-4-methylphenol (BHT) was used as an internal standard. The weight-average molecular weights (M_w) and dispersities ($Đ$) of the polymers were calculated based on linear polystyrene (PS) standards (Polymer Laboratories). Thermogravimetric analyses (TGA) of the photocured films were performed by using a PerkinElmer thermogravimetric analyzer (Pyris 1 TGA model). Samples were run from 30 to 750 °C with a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. Gel contents were determined by immersing the preweighted samples in acetone for 24 h. The insoluble gel fraction was dried in a vacuum oven at 40 °C to constant weight and the gel percentage was calculated. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere on the TA instruments Q1000 series DSC apparatus. Samples were heated from −70 to 100 °C with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere, followed by cooling to −70 °C with rate of 10 °C min^{-1}. Finally, samples were reheated to 100 °C at the same rate.

General Procedure for Modification of PCO via Thiol-Yne Click Reaction: PCO (100 mg, 0.095 mmol) was added to a 10 mL round-bottom flask and dissolved in 500 µL of 2-MeTHF. Then, the thiol compound (1.2 equiv. per alkyne, 0.260 mmol) and DBU (4 µL, 0.024 mmol, 0.25 equiv. per PCO) were added to the flask in the given order and the mixture was allowed to stir for 5 min at room temperature. After the specified time, the reaction mixture was diluted with 20 mL of EtOAc and extracted with 10 mL of 1 M HCl and 10 mL of water, respectively. The collected organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced

pressure to give the final product. Experimental procedure and characterization details for all thiols used are provided in the Supporting Information.

General Procedure for Hyperbranched Polymer via Thiol-Yne Click Reaction: PCO (350 mg, 0.333 mmol) was added to a 10 mL round-bottom flask and dissolved in 2 mL of 2-MeTHF. Then, HDT (2SH) (59 µL, 0.383 mmol), and DBU (12 µL, 0.08 mmol) were added to the flask in the given order and the mixture was allowed to stir at room temperature. The evolution of the polymer was monitored by taking samples from the reaction medium at regular intervals. After the reaction was completed, the polymerization mixture was precipitated in 20 mL of acidified methanol and the solvent was removed by decantation. The dissolution-precipitation ($CHCl_3$-acidified methanol) procedure was repeated two times. The final polymer was obtained as a yellow viscous liquid (yield: 0.335 g).

Preparation of the Thermosets via Thiol-Yne Click Reactions: Thermoset films were prepared by using a 1:1 thiol to alkyne ratio. 0.25 equiv. of TEA per PCO was used as the catalyst. Here, 2SH, 3SH, 4SH, and CO-SH were used as thiol compounds. PCO and the thiol were mixed in a beaker and then poured into molds followed by the addition of the catalyst. The molds were then placed in an oven at 80 °C and kept for 24 h for complete curing. The samples were named PCO-2SH, PCO-3SH, PCO-4SH, and PCO-CO-SH.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

activated alkyne, castor oil, hyperbranched polymers, thiol-michael click reactions

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