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Research Article

Propiolated Castor Oil: A Novel and Highly Versatile Bio-Based Platform for Extremely Fast, Catalyst-, and Solvent-Free Amino-yne Click Reactions

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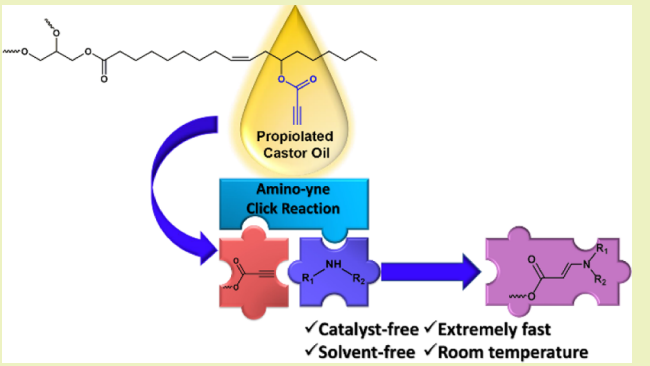
ABSTRACT: The quest for sustainable monomers and "green" synthetic pathways for the design, fabrication, and modification of various polymers is of great importance and attracts a great deal of attention. Here, a highly versatile and novel bio-based platform was developed by reacting castor oil with propiolic acid for performing amino-yne click reactions. Owing to the electron-deficient nature of the propiolic acid esters, amino-yne click reactions were conducted with ease at room temperature, in the absence of any catalyst and solvent (as long as the amines were low-viscosity liquids at room temperature), and within 5 min. Several primary and secondary amines were shown to react readily with the developed platform. Furthermore, thermosets were prepared by using the propiolated castor oil and multifunctional amines. The prepared thermosets displayed improved thermal properties and elastomer-like mechanical properties.



KEYWORDS: *green chemistry, aza-Michael, amino-yne click reactions, castor oil, propiolic acid, activated alkyne*

INTRODUCTION

Today, rapid population growth and consequent increasing energy and material consumption cause serious environmental pollution problems, affect the earth's climate, and threaten human health.[1−3] Environmental problems caused by the high dependence on petrochemicals in material goods and energy production are the driving force behind the development of the "green chemistry (GC)" concept which was introduced by Paul Anastas in 1990s.[4,5] The principles of GC which focus on atom economy use benign solvents, reactants, and chemicals, prevent waste, and encourage the use of bio-based building blocks for sustainable production of polymers, paving the pathway toward a circular economy and circular chemistry.[6]

Within the palette of bio-based building blocks for the synthesis of organic molecular architectures and polymers, vegetable oils (VOs) are far by the most widely preferred natural sources. Due to their high abundance, low cost, low toxicity, renewable nature, various functional groups, rich functionalization options, and ease of manipulation, VOs are regarded as the perfect renewable alternatives and most suitable candidates to replace petroleum-derived monomers and polymers.[7−16] VOs offer a wide range of chemical transformation routes; until now several reactions including epoxidation, acrylation, metathesis, acyclic diene metathesis, thiol−ene, multi-component reactions, azide−alkyne click reactions, etc.,[7−11] have been utilized for the functionalization of VOs as well as VO-derived fatty acids, and thermoset materials,[17,18] hydrophobic coatings,[19] phase change materials,[20] lubricants,[21] plasticizers,[22,23] surfactants,[24] etc., have been produced therefrom.

The aza-Michael reaction is one of the most explored fundamental organic reactions, which takes place between a primary or a secondary amine (nucleophile, Michael donor) and an electron-deficient alkene/alkyne (Michael acceptor).[25,26] The aza−Michael reaction is a powerful and versatile tool in organic chemistry as well as in polymer science to synthesize complex molecules, dendrimers, monomers, and networks for numerous applications such as coatings, adhesives, bio-medical/pharmaceutical, and specialty chemicals.[27] The aza−Michael reaction generates low or no waste, can be conducted in the absence of solvents, does not generate volatile organic compounds, is highly atom-economic, has superior features such as high conversion rates under mild

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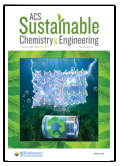
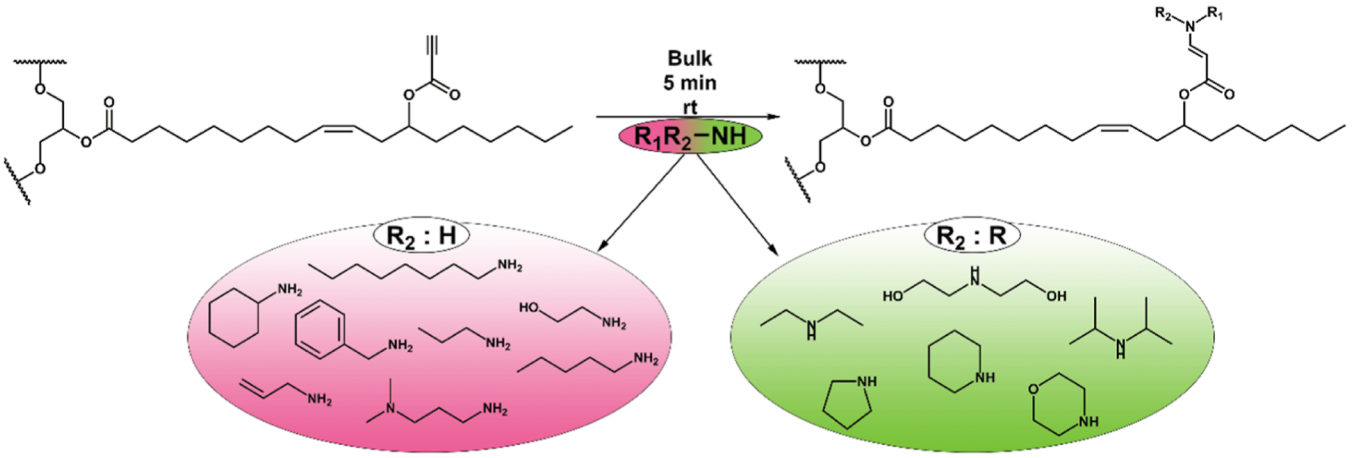


Scheme 1. Schematic Representation for the Modification of Propiolated Castor Oil with Different Amines via Amino-yne Click Reactions



reaction conditions and high functional group tolerance, and has the ability to react at ambient temperature.[27,28] Besides, several commercial Michael acceptors and donors which are readily available make this reaction quite suitable for industrial applications. With all these properties and unique advantages, aza-Michael reactions are not only consistent with the principles of GC but also fulfill most of the pre-requisites of "click-chemistry".[29] As Michael acceptors, olefins with electron-withdrawing groups (EWGs) such as acrylates are highly preferred, while alkynes are much less investigated. Nevertheless, it was previously shown that alkynes bearing EWGs (activated alkynes) are also suitable Michael acceptors. Indeed, the reaction between an amine and an activated alkyne is named as spontaneous amino-yne click reactions,[30] and these reactions have been successfully adopted for various applications and the synthesis of several polymers known as poly(enamine)s.[30−39] As the name suggests, spontaneous amino-yne click reactions are straightforward, fast, and occur spontaneously at room temperature.

Recently, our group has been interested in the metal-free click reactions, modifications, and polymerization of electron-deficient triple bond-containing monomers such as acetylene dicarboxylic acid and its derivatives.[40−50] We have shown that polyesters containing acetylene dicarboxylate on their backbone can be easily modified with aza-Michael and thiol-Michael reactions under benign conditions, in the absence of metal catalysts, and in high yields.[42−49] We have demonstrated that diallyl esters of acetylene dicarboxylic acid can be functionalized similarly.[49,50] In light of the studies in the literature and foresights that we have gained with our studies on electron-deficient triple bond-containing monomers, we speculated that the activated triple bond-containing castor oil could be a versatile platform for the synthesis of bio-based functional materials and thermoset polymers. Here, we present the synthesis of propiolated castor oil and demonstrate its subsequent functionalization with a series of primary and secondary amines (Scheme 1). Furthermore, thermoset materials were also synthesized by using multifunctional amines and the propiolated castor oil.

EXPERIMENTAL SECTION

Materials. Castor oil was retrieved from a local company. Propiolic acid (95.0%, Sigma-Aldrich), methanesulfonic acid (≥99.0%, Sigma-Aldrich), propylamine (≥99.0%, Sigma-Aldrich), pentylamine (≥99.5%, Sigma-Aldrich), octylamine (99%, Sigma-Aldrich), cyclohexylamine (≥99.9%, Sigma-Aldrich), benzylamine (99.0%, Sigma-Aldrich), 3-(dimethylamino)-1-propylamine (99.0%, Sigma-Aldrich), ethanolamine (≥98.0%, Sigma-Aldrich), allylamine (98.0%, Sigma-Aldrich), diethylamine (≥99.5%, Sigma-Aldrich), diethanolamine (≥98.0%, Sigma-Aldrich), morpholine (≥99.0%, Sigma-Aldrich), diisopropylamine (≥99.5%, Sigma-Aldrich), pyrrolidine (99.0%, Sigma-Aldrich), piperidine (99.0%, Sigma-Aldrich), piperazine (PZ, 99.0%, Sigma-Aldrich), triethylenetetramine (TETA, 97.0%, Sigma-Aldrich), *m*-xylylenediamine (MXDA, 99.0%, Sigma-Aldrich), and sodium sulfate anhydrous (Na_2SO_4, ≥99.0%, Aldrich) were used as received. Solvents: toluene (99.8%, Sigma-Aldrich), 2-methyltetrahydrofuran (2-MeTHF, ≥99.5%, Sigma-Aldrich), ethyl acetate (EtOAc, 99.8%, Sigma-Aldrich), hexane (95%, Sigma-Aldrich), and diethyl ether (≥99.7% Sigma-Aldrich) were anhydrous or of HPLC quality and used without further purification. Dimer diamine [DD, PRIAMINE 1071 by Croda, M_n (theoretical) = 547 g/mol, amine number = 205 mg KOH/g] was obtained as a gift from MCT chemicals (Turkey).

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}. Thermogravimetric analyses (TGAs) of the photocured films were performed by using a PerkinElmer thermogravimetric analyzer (Pyris 1 TGA model). Samples were run from 30 to 600 °C with a heating rate of 10 °C/min under a nitrogen atmosphere. Gel contents were determined by immersing the pre-weighted 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 PerkinElmer Pyris Diamond DSC apparatus. The mechanical properties of the thermosets were measured at room temperature on a Materials Testing Machine Z010/TN2S using a crosshead speed of 2 mm/min on rectangular specimens.

Synthesis of Propiolated Castor Oil (1). To a 250 mL round-bottom flask equipped with a Dean−Stark apparatus, castor oil (5 g, 5.36 mmol) was added and dissolved in 100 mL of toluene. Then, propiolic acid (2.97 mL, 48.24 mmol) and methanesulfonic acid (122 μL, 1.88 mmol) were added to this solution, respectively. The mixture was gradually heated to 110 °C and stirred overnight. After that, toluene was removed under reduced pressure, and the residue was dissolved in 100 mL of diethyl ether and extracted with water (3 × 30 mL). The collected organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with EtOAc/hexane (1:4, v/v) to give the product as a yellow liquid (yield = 4.15 g, 74%). The synthesis of **1** is shown in Scheme 2.

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Scheme 2. Synthetic Pathway for the Propiolated Castor Oil (1)

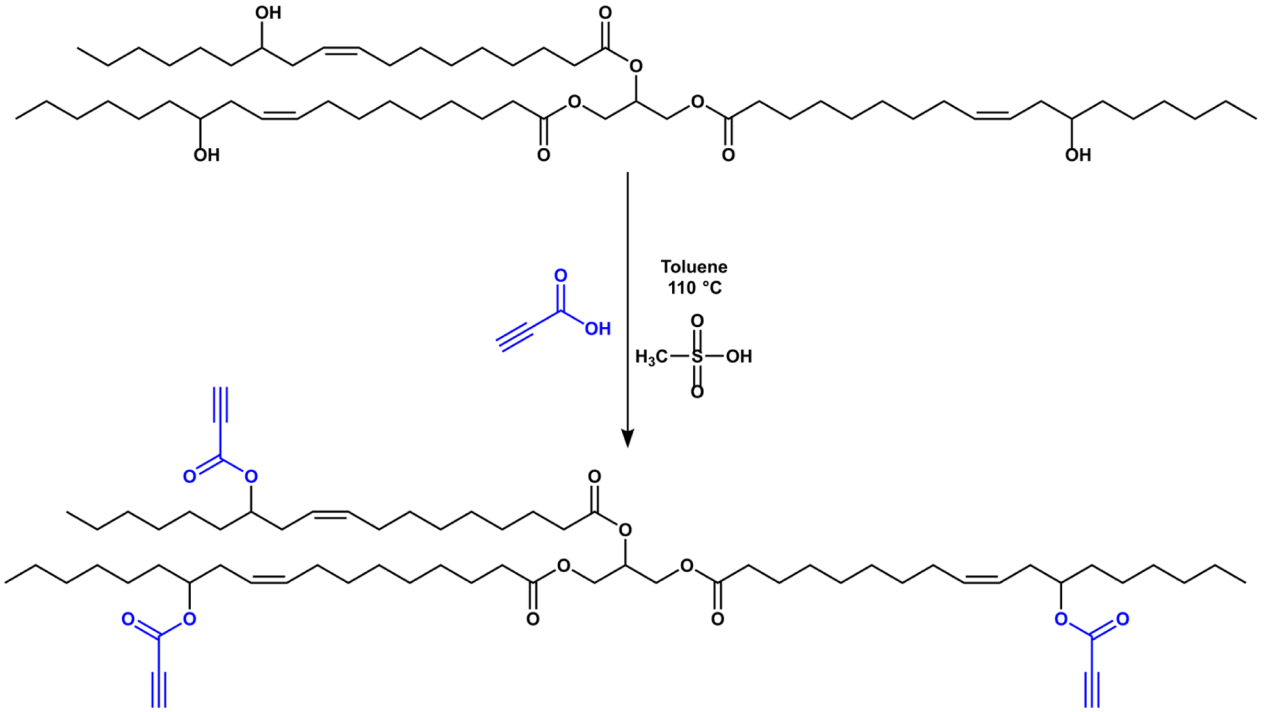

Table 1. Results of the Amine Scope[a]

structure	amine	Amino-yne eff. (%)[b]	E/Z ratio	yield (%)[c]
1				74
2	Propylamine	≥99	24/76	96
3	Pentylamine	≥99	38/62	99
4	Octylamine	≥99	28/72	98
5	Cyclohexylamine	≥99	19/81	99
6	Benzylamine	≥99	37/63	97
7	3-(dimethylamino)-1-propylamine	≥99	38/62	99
8	Ethanolamine	≥99	29/71	95
9	Allyl amine	≥99	25/75	97
10	Diethylamine	≥99	100/-	99
11[d]	Diethanolamine	≥99	100/-	99
12[e]	Diisopropylamine	≥99	100/-	95
13	Pyrrolidine	≥99	100/-	98
14	Piperidine	≥99	100/-	99
15	Morpholine	≥99	100/-	97

[a]All reactions were carried out at room temperature for 5 min using 2 equiv of amine per alkyne in bulk unless stated otherwise. [b]Determined by ^{1}H NMR spectroscopy. [c]Isolated yields after purification. [d]The reaction was performed in 0.5 mL of 2-MeTHF for 15 min. [e]The reaction was performed for 8 h.

^{1}H NMR ($CDCl_3$, δ): 5.49−5.26 (m, $(OCH_2)_2CHOC{=}O$ and $CH{=}CH$), 4.98 (m, $CHOC{=}OC{\equiv}CH$), 4.27−4.15 (m, $(OCH_2)_2CHOC{=}O$), 2.89 (s, $CHOC{=}OC{\equiv}CH$), 2.31−2.02 (m, $OC{=}OCH_2$, $CH_2CH{=}CHCH_2$, and $CH_2CH{=}CHCH_2$), 1.60−1.30 (m, $OC{=}OCH_2(CH_2)_5CH_2CH{=}CH$ and $CH{=}CHCH_2CHO(CH_2)_5CH_3$), 0.88 (m, CH_2CH_3). ^{13}C NMR ($CDCl_3$, δ): 179.54, 152.53, 133.29, 123.47, 75.01, 74.32, 68.89, 62.09, 33.96, 33.40, 31.66, 29.04, 27.30, 25.25, 24.65, 22.55, 14.05.

General Procedure for the Amino-yne Reactions. Excess amounts of liquid primary or secondary liquid amines (2 equiv per alkyne) were mixed directly with **1** in a round-bottom flask and stirred for 5 min (except diethanolamine and diisopropyl amine, see Table 1 for details) at room temperature. In the case of diethanolamine, which is a highly viscous liquid amine at room temperature, around 0.5 mL of 2-MeTHF was added. 2-MeTHF is derived from renewable sources such as xylose and glucose and is considered environmentally friendly, greener alternative to tetrahydrofuran.[51] 2-MeTHF is a suitable solvent choice in terms of GC principles. After 5 min, the reaction mixture was dissolved in diethyl ether and washed with water to remove unreacted amines. In the case of secondary amines, the organic phase was washed with a 10% HCl solution, followed by water extraction. Then, the organic phase was separated and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Notably, modified castor oil derivatives were obtained in high yields (>90%) in all cases (see Table 1). The detailed experimental procedures are given in the Supporting Information.

Preparation of the Thermosets via Amino-yne Reactions (Synthesis of 1DD, 1PZ, 1TETA, and 1MXDA). Liquid multifunctional amines, DD, MXDA, and TETA, were mixed directly with **1**, whereas piperazine (PZ) was added after dissolving in a minimum amount of 2-MeTHF. Each $-NH_2$ group was taken as one functional group, and therefore, DD and MXDA were treated as they are di-

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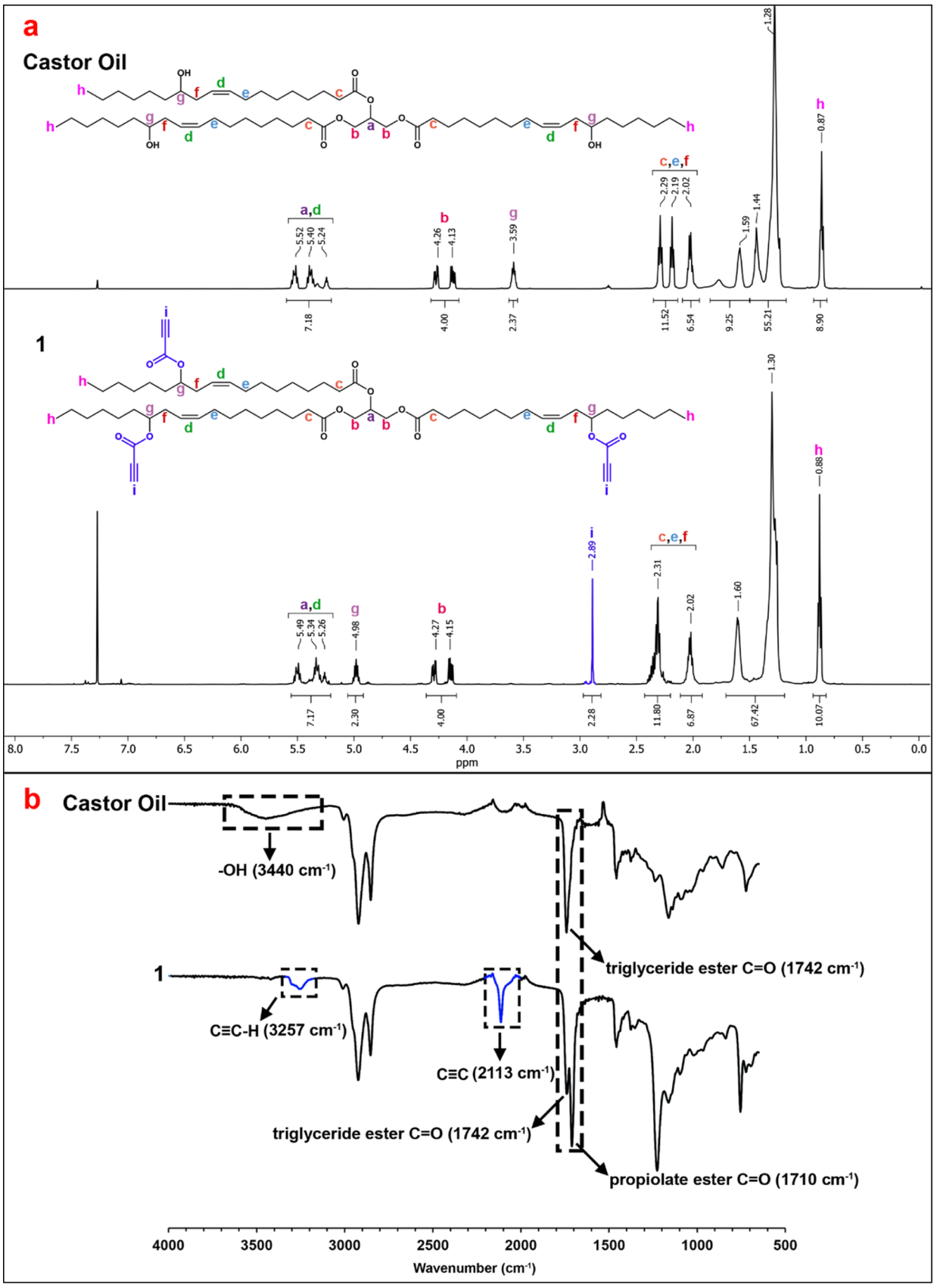

Figure 1. Overlaid ^{1}H NMR (a) and FT-IR spectra (b) of castor oil and **1**.

functional monomers. If the amines have −NH (secondary amine), they were counted as a functional group, and as a result, TETA and PZ were regarded as tetra- (two $-NH_2$s and two −NHs) and di-functional monomers, respectively. Briefly, 0.5 g of **1** (0.45 mmol) was

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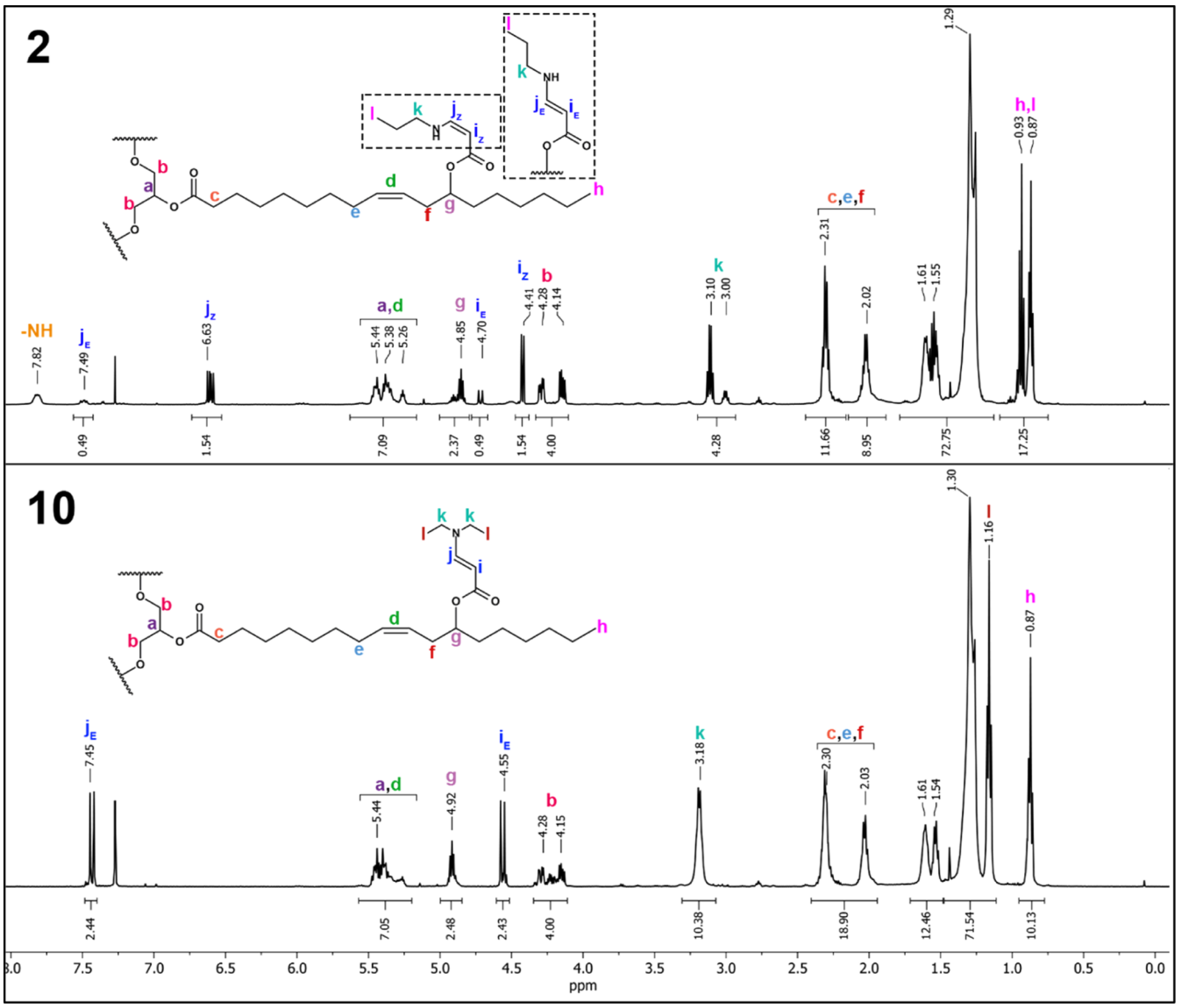

Figure 2. Overlaid ^{1}H NMR spectra of **2** and **10**.

mixed with 0.27 g of DD. As the reaction progresses, the viscosity of the mixture increased and the liquid mixture turned into a gel. For the other gels, 0.068 g of MXDA, 0.043 g of PZ, and 0.037 g of TETA were used per 0.5 g of **1**, respectively. All the samples were left to further react at room temperature for a week before testing. The thermosets were named 1DD, 1PZ, 1TETA, and 1MXDA.

RESULTS AND DISCUSSION

Characterization of Propiolated Castor Oil (1). The activated alkyne-functionalized castor oil was synthesized via esterification of the hydroxyl groups of castor oil with propiolic acid in the presence of methanesulfonic acid as the acid catalyst (Scheme 2). A large excess of propiolic acid was used in this reaction to shift the equilibrium toward the product side. **1** was purified via column chromatography and obtained in good yields. The ^{1}H NMR spectra of castor oil and **1** are shown in Figure 1a. The ester methylene protons (b) of the triglyceride unit in castor oil were observed at 4.26−4.13 ppm while the −CH proton (a) at 5.24 ppm and the alkene double bond protons (d) at 5.6−5.4 ppm. In addition, the characteristic signal of the methine proton (g) adjacent to the −OH group was detected at 3.59 ppm.[17,52] After esterification, the signal at 3.59 ppm completely disappeared and shifted to 4.98 ppm. Furthermore, a new peak (i) appeared at 2.89 ppm in the spectrum of **1**, indicating the formation of alkyne (≡C*H*) units. Notably, the number of alkyne units per triglyceride of castor oil was found to be 2.28 from the integral ratio of "*b*" (4H) to "*i*".

^{13}C NMR spectra of castor oil and **1** are shown in Figure S1. Although the carbon attached to the hydroxyl group of castor oil resonated at around 71 ppm, it slightly shifted downfield and appeared at 74 ppm after esterification. Besides, a new peak appeared at around 152 ppm belonging to the carbonyl carbon of the propiolate unit, and it was observed that the carbons of the triple bond resonated at 75 ppm. The structure of **1** was further characterized by FT-IR spectroscopy. The FT-IR spectrum (Figure 1b) of castor oil displays its characteristic ester carbonyl bond vibration band at 1742 cm^{-1}. and the wide band at around 3440 cm^{-1} belongs to the hydroxyl stretching. After the esterification reaction, the hydroxyl band disappeared and an additional carbonyl band was observed at 1710 cm^{-1}. Furthermore, the characteristic ≡CH and −C≡C− vibrations were detected in the spectrum of **1** at 3257 and 2113 cm^{-1},

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respectively. All the spectral findings clearly indicate that the triglyceride structure of the neat oil was intact during the esterification reaction and **1** was synthesized successfully.

Modification of 1 with Various Amines via Amino-yne Click Reactions. **1** was reacted with various primary and secondary amines at room temperature in bulk. After some preliminary trials (results are not shown), we determined that the optimum amine equivalent per alkyne unit of **1** is 2. The results of the reactions with different amines are listed in Table 1. Regardless of the structure of the amines, the amino-yne click reactions were completed within 5 min for almost all studied amines, with quantitative efficiency and with over 95% isolated yields. Among them, solvent (2-MeTHF) was used only in the case of diethanolamine for proper mixing, and the quantitative efficiency for this amine was obtained in 15 min. Moreover, a prolonged reaction time (8 h) was required to achieve the quantitative efficiency when diisopropylamine was used, which might be attributed to the reduced nucleophilicity of this molecule due to its sterically hindered character.

The spectra of all the amino-yne reaction products (2−15) listed in Table 1 are given in the Supporting Information. The ^{1}H NMR spectra of **2** and **10** are given in Figure 2 and discussed in detail as examples of the amino-yne click reaction performed on **1**.

For instance, reaction product **2** was obtained from the amino-yne click reaction between propylamine and **1**. As can be seen in the ^{1}H NMR spectrum of **2** (Figure 2), the terminal alkyne hydrogen (i) completely disappeared and new peaks appeared, indicating that the activated triple bonds fully reacted with propylamine to produce an enamine structure. Moreover, the −NH hydrogen in this enamine structure was detected at around 7.82 ppm, and the protons in the newly formed enamine double bonds resulted in four different peaks in the ^{1}H NMR spectrum depending on the structure of the produced isomers. It was previously reported that the addition of primary amines to activated alkynes is a stereoselective reaction, producing *E*- and *Z*-isomers, and it was shown that the ratio of *E*- or *Z*-isomers depends on the polarity of the solvent.[30,38,42,53−55] Similar to the findings in the literature, we detected *E*/*Z* isomerism in this study (see Table 1). For instance, in the case of propylamine, the *E*/*Z* ratio was found to be 24/76. Previously when activated alkyne-bearing polyesters were functionalized with primary amines in the presence of a non-polar solvent such as chloroform, *E*-isomers were found to be the major products.[42] On the other hand, when this type of reaction was carried out in polar protic solvent, *Z*-isomers were the main products.[53] It is worth noting that in the case of a primary amine, the hydrogen bonding effect comes into play and favors the *Z*-isomer geometry. The geometry of the *Z*-isomer favors the formation of an intramolecular hydrogen bond between the carbonyl oxygen and the −NH hydrogen, and the polar protic solvent also promotes the formation of the *Z*-isomer, leading to energetically favorable structures.[53,54] Here, the reactions were carried out in the absence of any solvent, and the results revealed that the *Z*-isomers were the prevailing products. Nevertheless, a mixture of *E*- and *Z*-isomers was produced with primary amines in this study.

Additionally, the hydrogen neighboring the NH group (NHC*H*═CHCO) was observed at 7.49 and 6.63 ppm for *E*- and *Z*-isomers, respectively. The other hydrogen in the enamine double bond neighboring the carbonyl group (NHCH═C*H*CO) was observed at 4.70 ppm for the *E*-isomer and at 4.41 for the *Z*-isomer. The structure of **2** was further characterized by ^{13}C NMR spectroscopy. The peak that appeared at 75.0 ppm (alkyne carbons) disappeared after the click reaction, and new peaks were detected in the ^{13}C NMR spectrum of **2**. The carbons of the enamine group displayed two peaks at 82 ppm (NHCH═*C*HCO) and 152 ppm (NHCH═CHCO), respectively. Moreover, the carbonyl carbon of the propiolate group, which resonated at 152 ppm, shifted downfield and appeared at 170 ppm (Figure S2).

Finally, the structure of **2** was also confirmed with FT-IR spectroscopy. As can be seen from Figure S3, the vibration bands of the alkyne units at 3257 and 2113 cm^{-1} completely disappeared after the efficient click reaction. The band at 3330 cm^{-1} in the FT-IR spectrum of **2** is attributed to the −NH stretching vibrations. The amino-yne reaction leads to the formation of an enamine carbon−carbon double bond. In the FT-IR spectrum of **2**, the vibration band of the enamine double bond was detected at around 1612 cm^{-1}. The FT-IR spectrum of **1** exhibited two carbonyl bands: one belongs to the characteristic triglyceride ester units at 1742 cm^{-1} and the other band at 1710 cm^{-1} belongs to the propiolate group. After the amino-yne click reaction, the latter carbonyl was shifted to 1664 cm^{-1}. The spectra of the reaction products of the other primary amines (3−9, Table 1) which are given in the Supporting Information were found to be similar to **2**. The explanations and discussions made for **2** are also valid for other primary amines utilized here.

As for the secondary amines, diethylamine was selected as the representative. The product (**10**) obtained from the amino-yne click reaction between **1** and diethylamine was characterized by ^{1}H NMR (Figure 2). Similar to the primary amines, the alkyne signal at 2.89 ppm completely disappeared after the click reaction. The most striking difference between secondary amines and primary amines is that in the case of secondary amines, the amino-yne reactions led to pure *E*-isomers rather than a mixture of *E*- and *Z*-isomers. Similar results were also obtained in the literature.[42,55] For instance, Thorwirth and Stolle investigated the reaction of primary and secondary amines with alkyl esters of propiolic or but-2-yne dicarboxylic acid in a ball mill.[55] When they reacted secondary amines with methyl propiolate, solely *E*-isomers were obtained. It was previously shown that the Gibbs free energy for the *E*-isomer is lower than that of the *Z*-isomer in the case of secondary amines, making them thermodynamically stable and facilitating the formation of a single isomer.[30,38,55]

In the ^{1}H NMR spectrum of **10**, two distinct signals resonated at 4.55 and 7.45 ppm are assignable to the structure of the resulting *E*-isomer. The former signal belongs to the enamine double bond near the carbonyl (NCH═C*H*C═O). The other hydrogen close to the tertiary amine unit (NC*H*═CHC═O) becomes much more deshielded, and therefore, its signal is pushed further in the downfield region. The structure of **10** was further analyzed by ^{13}C NMR spectroscopy. Similar to **2**, the ^{13}C NMR signal of alkyne carbons at 75.0 ppm disappeared, and the carbonyl peak of the propiolate group observed at 152 ppm shifted to 170 ppm due to the transformation of the triple bond (Figure S25). Also, similar findings observed in the FT-IR spectrum of **2** were also found in the FT-IR spectrum of **10** (Figure S26).

All these findings clearly prove that the amino-yne click reactions proceed smoothly with both primary and secondary amines with the newly developed bio-based substrate.

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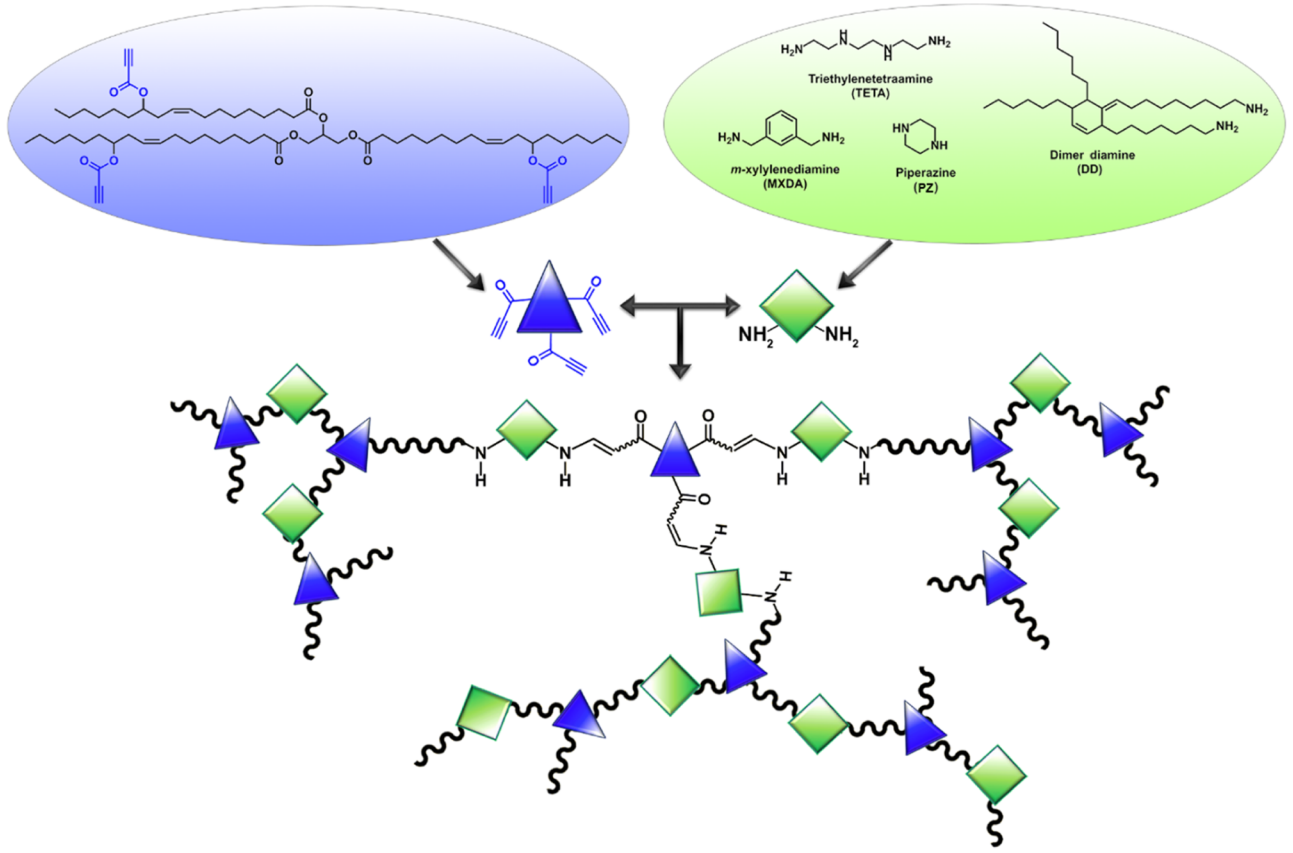
Scheme 3. Schematic Representation of Thermosets Prepared via Amino-yne Click Reactions



Properties of the Thermosets Prepared via Amino-yne Click Reactions. As noted in the Introduction, aza-Michael reaction was performed previously with acrylate group-containing monomers to prepare various polymeric materials such as coatings. However, these reactions are rather slow and require long reaction times, catalysts, solvents, and high temperatures.[56−59] For instance, Chen et al. reacted acrylated epoxidized soybean oil with methylaziridine in dichloromethane for 18 h for a quantitative aza-Michael reaction.[56] In another work, macromers were prepared by using diacrylates and different amines, and the reactions were carried out in the absence of solvent, yet long reaction times (48−120 h) and heating (90 °C) were applied.[57] Ecochard et al. prepared thermosets by aza-Michael polymerization from acrylated epoxidized linseed oil.[58] They investigated the effect of different amines on the reaction and gelation rates and found that most of the amines required high-temperature processing. Thus, they post-cured their aza-Michael reaction mixtures at 100−150 °C for 1−2 h. Dean Webster's group showed that the thermosets could be prepared at ambient temperature via aza-Michael reactions by using acrylated epoxidized sucrose soyate and amine crosslinkers in the presence of solvent and p-toluene sulfonic acid catalyst.[27]

Recently, Peyrton and Avérous performed model reactions with simple acrylates and amines to provide an in-depth analysis of the aza-Michael reactions of vegetable oil-derived acrylates and amines.[59] They reacted 2-hydroxyethyl acrylate with a sterically hindered amine, methylethylenediamine, at room temperature; the conversion percentage reached a plateau after 6 h and only 66% of the acrylate double bonds were reacted. They also reacted multifunctional amines with acrylated vegetable oil derivatives and found that the gel times changed between 300 and 165,000 s depending on the temperature and the type of the amines.

It is also worth noting that when compared to the amino-acrylate-based networks, the amino-yne networks offer a unique feature, reprocessability. This property arises from the presence of enamine-one groups which are reversible dynamic covalent bonds. Thermosetting materials having this feature are known as vitrimers and amino-yne click reactions are powerful chemical tools for preparing such networks.[60−62] It is believed that the propiolated castor oil introduced in this study could be a good candidate to prepare bio-based vitrimers and is currently our ongoing project.

Here, we reacted **1** with four different diamines, DD, PZ, TETA, and MXDA. Scheme 3a depicts the formation of networks via amino-yne click reactions. Similar to the amino-yne model reactions described above, the reactions between **1** and the multifunctional amines occurred rapidly and led to gelation in 5 min. The gel formation increased the viscosity of the mixtures, and the fluidity of the mixtures was lost. In all cases, the thermosets turned into sticky substances.

The FT-IR spectra of all the obtained thermosets (via amino-yne reactions) are given in Figure 3a. As can be seen in all FT-IR spectra, the related bands of alkyne groups at 3257 and 2113 cm^{-1} completely disappeared. Thus, it can be concluded that based on the FT-IR results, 100% triple bond conversion was obtained. Similar to the previous model reactions, enamine double bond vibrations were detected at 1600 cm^{-1}. The triglyceride's characteristic ester carbonyl was not affected by the amino-yne reaction, and its vibration band was observed at 1735 cm^{-1}. The carbonyl group of the

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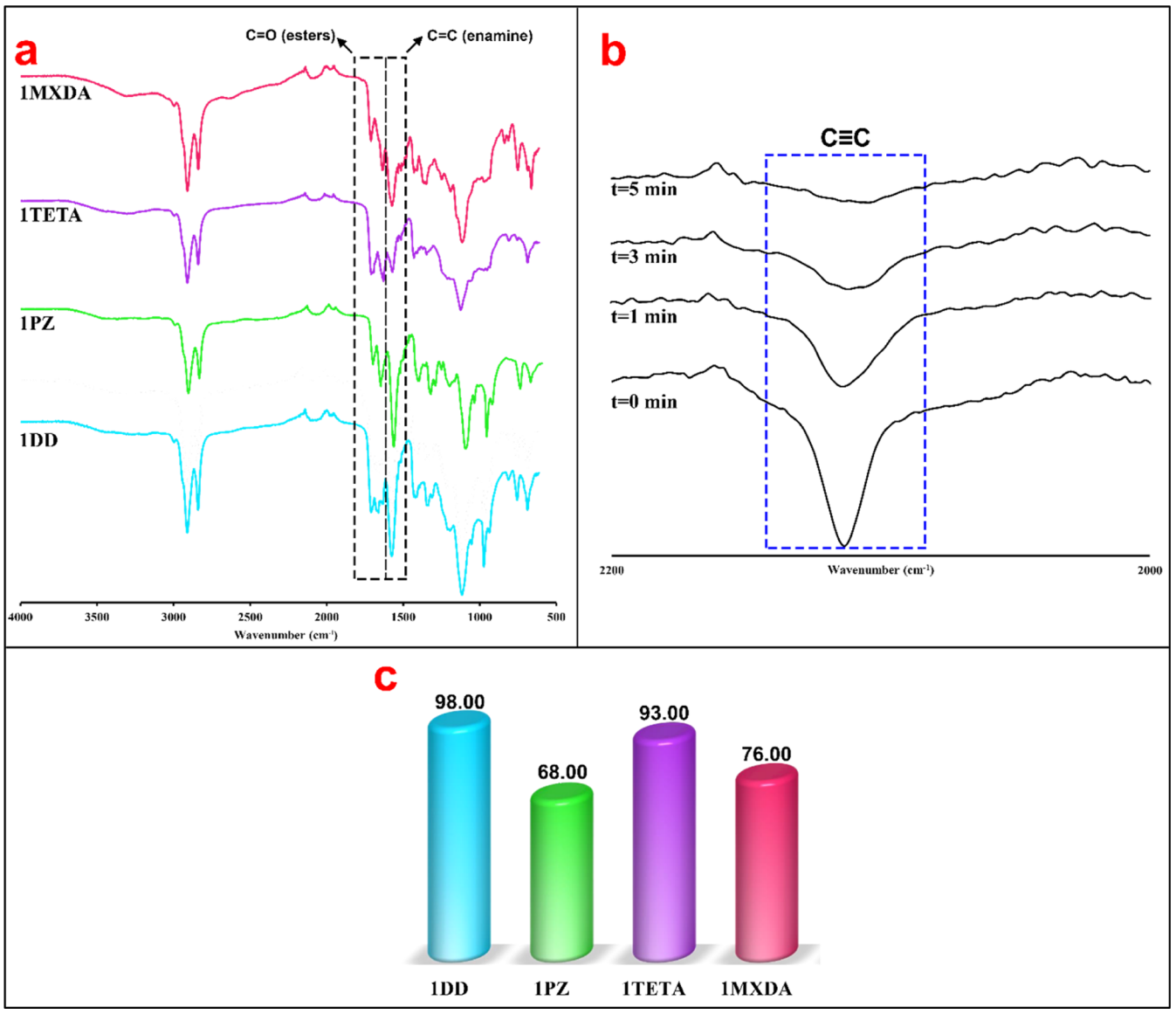

Figure 3. Overlaid FT-IR spectra of 1DD, 1PZ, 1TETA, and 1MXDA (a), FT-IR spectra of 1DD at different time intervals in the range of the 2200−2000 cm^{-1} region (b), and gel contents (as a percentage) (c).

propiolate was shifted to 1690−1650 cm^{-1} upon amino-yne click reaction.

The gelation was monitored via FT-IR analysis by recording the FT-IR spectrum at 1, 3, and 5 min. Figure 3b displays the evolution of the FT-IR bands for 1DD, and it can be seen that the intensity of the propargyl band at 2100 cm^{-1} declines rapidly. After 5 min, the −C≡C-band completely disappeared, indicating a fast gelation feature.

The gel content of the thermosets was determined via acetone extraction (Figure 3c). DD and TETA were found to produce very high gel content values. Similar results were also obtained in the literature.[58] The high reactivity of DD and TETA is attributed to their compatibility, aliphatic nature, and high functionality. On the other hand, PZ and MXDA produced relatively low gel content values. This situation can be attributed to the low reactivity of the secondary amines in PZ and to the reduced basicity and steric hindrance of the aromatic ring-bearing MXDA.[59]

The thermal degradation behavior of the thermosets was investigated by TGA under a N_2 atmosphere. The TGA thermograms of the thermosets are presented in Figure 4a,b. All investigated thermosets started to decompose slowly after 200 °C and displayed maximum weight loss temperatures in the range of 300−400 °C. While the structure of the amines did not result in a significant change in these degradation temperatures, the char yields (Figure 4c) were found to depend on the structure of the amines used. The flexible and thermally weak DD led to the lowest obtained char values. While 1PZ resulted in relatively higher char yields than 1DD, the highest char yields were obtained in the case of 1TETA and 1MXDA. For the former case, the obtained relatively higher char yield might be attributed to the higher nitrogen percentage of TETA and the increased crosslinking density due to the increased functionality (f = 4). As for the 1MXDA, the aromatic groups improved the thermal stability and char yields. When compared to the literature, it can be seen that the thermosets prepared herein have improved thermal stability. For instance, in the study of Ecochard et al., the char yields for the thermosets composed of acrylated linseed oil and MXDA or DD were reported to be 0% at 550 °C.[58]

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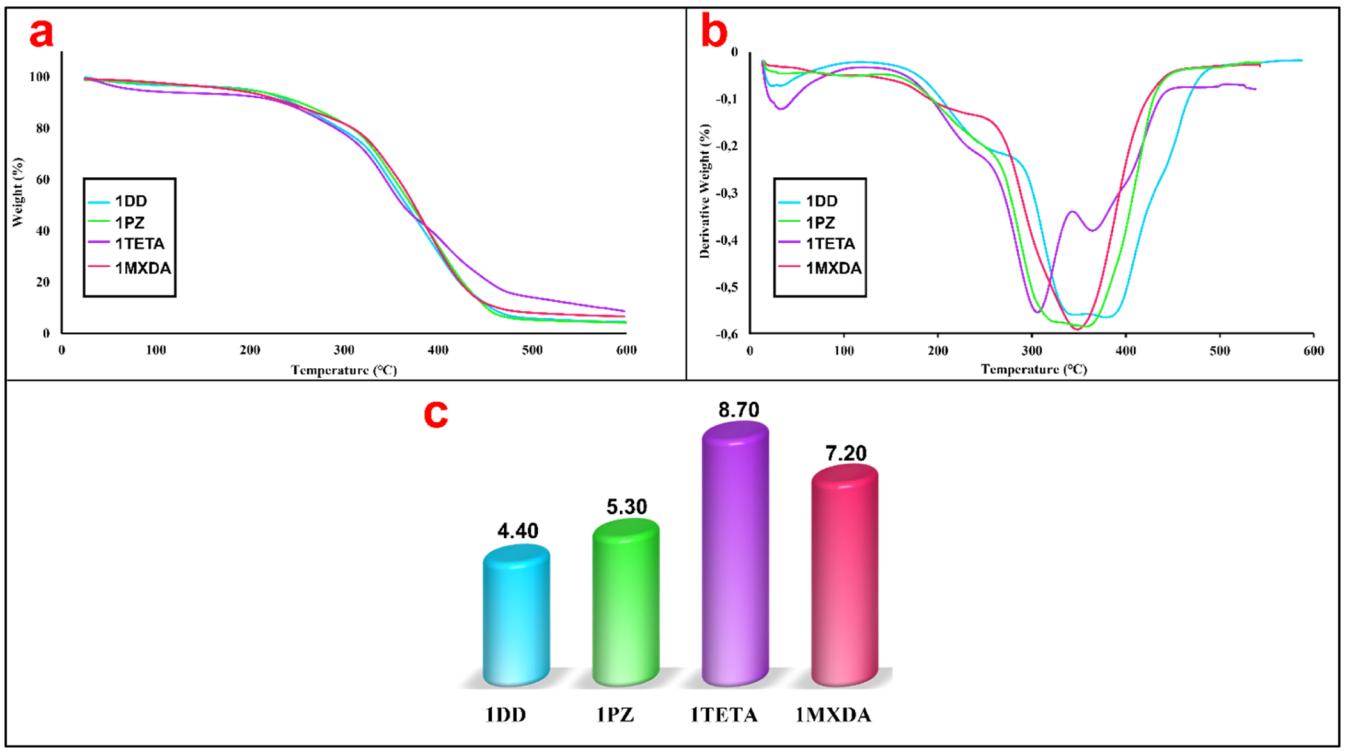

Figure 4. TGA thermograms (a), corresponding derivative weight curves (b), and char yields (as a percentage) (c) at 600 °C according to the TGA results of 1DD, 1PZ, 1TETA, and 1MXDA.

The glass transition temperatures (T_g) of the thermosets were determined via DSC measurements. The DSC spectra of the thermosets are given in Figures S42−S45. The T_gs of the thermosets were found as 13, 26, and 32 °C for 1DD, 1PZ, and 1MXDA, respectively. The DSC spectrum of 1TETA displayed two endothermic peaks at 8 and 36 °C, indicating an inhomogeneous network. The relatively higher T_gs measured for 1MXDA and 1PZ with respect to 1DD stem from the increased stiffness due to the presence of rigid aromatic rings or cycloaliphatic rings. In the case of 1TETA, the improved T_g can be explained by the increased crosslinking density. The obtained T_gs are in good accordance with literature. Ecochard et al. measured the T_g of the thermoset composed of acrylated linseed oil and MXDA as 31 °C and the T_g of the thermoset composed of acrylated linseed oil and DD as 13 °C.[58]

Finally, we investigated the mechanical properties of the prepared thermosets via standard tensile stress−strain tests. The representative stress−strain curves of the thermosets are presented in Figure S46 along with the images of the prepared films for tensile testing. We could not be able to test the 1PZ- and 1MXDA-encoded films since they did not give self-standing free films. According to the gel content test results, these two formulations (1PZ and 1MXDA) had relatively higher soluble fractions (i.e., low gel content values), and this situation led to poor film-forming properties.

The tensile test results for the other two thermosets (1DD and 1TETA) indicated that these materials are elastomers characterized by their low tensile strengths and high elongation at break values. Similar elastomeric behavior for vegetable oil-based thermosets was previously reported.[17,63] The tensile strength of 1DD and 1TETA was determined as 0.07 ± 0.02 and 0.1 ± 0.03 MPa, respectively. The elongation at break value for 1DD was found to be 32% ± 4, and it was determined to be 14% ± 2.

CONCLUSIONS

In summary, we have developed a bio-based platform that can be efficiently modified via amino-yne click reactions. Owing to the electron-deficient nature of the propiolic acid esters, amino-yne click reactions were conducted with ease at room temperature, in the absence of any catalyst and solvent, and within 5 min. When primary amines were used, a mixture of *E*- and *Z*-isomers was produced where predominately *Z*-isomers were present. In the case of secondary amines, the amino-yne reactions led to pure *E*-isomers. Also, we successfully prepared thermosets by using propiolated castor oil and multifunctional amines. The obtained thermoset materials exhibited improved thermal properties but poor mechanical properties.

We believe the versatile bio-based platform described in this study promises rapid and straightforward modification for vegetable oils as well as achieves various polymer architectures through vegetable oils in a practical way. We also believe that the activated alkyne-bearing vegetable oils will be used in various applications in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c06912.

Full experimental section, ^{1}H NMR, ^{13}C NMR, FT-IR, and DSC spectra (PDF)

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Notes

The authors declare no competing financial interest.

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