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Alkene–azide chemistry: a facile, one-step, solvent- and catalyst-free approach for developing new functional monomers and polymers†

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In this study, a one-step Hüisgen 1,3-dipolar cycloaddition reaction, alkene–azide chemistry, was explored using a solvent and catalyst free method forming 1,2,3-triazoline ring-containing molecules. This facile method was utilized by synthesizing a mini library of small molecules, functional monomers, and polymers, which involved mixing a terminal alkene with a terminal azide at elevated temperature. Similar to traditional "click" chemistry, the proposed alkene–azide strategy uses solvent and heavy-metal catalyst free conditions and no further workup or purification steps are required. In our design, small molecule-based compounds, AB-type prepolymers and macromolecules are synthesized at 80–100 °C with more than 90% purity. Polymers made using this chemistry formed high molecular weight macromolecules (M_w = 59.1k, 34.9k, and 49.3k g mol^{-1}). The synthesized new small molecules, functional monomers and polymers were characterized using various chromatographic and spectroscopic methods. The results indicated that the molecular linking, orthogonal green chemistry reaction proceeds well under gentle conditions, forming products with high yields and reserving atom economy. This chemistry provides a facile approach by offering modular synthetic routes, being highly efficient when using equivalent stoichiometric ratios, and by being solvent and catalyst free, which will be of particular interest to the pharmaceutical and industrial settings.

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Introduction

Custom, designer molecules are the backbone of many chemical disciplines including materials science and pharmaceuticals, where molecular design provides the desired structure property relationships. Synthesizing these designer compounds in most cases requires complex, multi-step reactions,[1] heavy-metal catalysts,[2] and toxic solvents[3] to elucidate the desired compound or polymer. Residual catalysts and solvents left after purification pose a problem where they can lead to harmful or dangerous side effects in environmental and biological systems. Also, strict chemical and purity restrictions on pharmaceutical products while vital drive up the cost and chemical limits for researchers and industry. These limitations, among the environmental impact of harmful chemicals, stimulate a societal and environmental push for solvent and catalyst-free chemistries.[4–8] This push is happening in not only the pharmaceutical industry but also polymer chemistry, since everyday products we use today are likely made using polymers derived from ecologically unwholesome processes. With this in mind, scientists seek to develop better approaches for custom molecule design, bioconjugation, and polymer chemistry, opening the door to exciting, new solvent and catalyst-free compounds.

Solvent and catalyst-free approaches in molecular design involve the use of cost-effective, ecologically compatible processes in each step of ideal syntheses.[9] For example, designing bimodal compounds in such a way that two molecules that serve two different functions can be joined together without the use of solvent or a catalyst is an ideal synthesis; this plays an essential role in the design of prodrugs,[10] biologically active small molecules,[11] polymer synthesis,[12] and the post-functionalization of polymeric materials.[13] In the past, the Diels–Alder reaction,[14] the thiol–ene reaction,[15] and alkyne–azide "click" chemistry have been used for linking molecules together.[16] All these reactions have a high atom economy and all the atoms of the reactants are incorporated into the final product. The Diels–Alder (DA) reaction is an essential click reaction used in the efficient formation of complex cyclic molecules. Dienes with one set of substituents can undergo a DA cycloaddition with dienophiles having another set of substitu-

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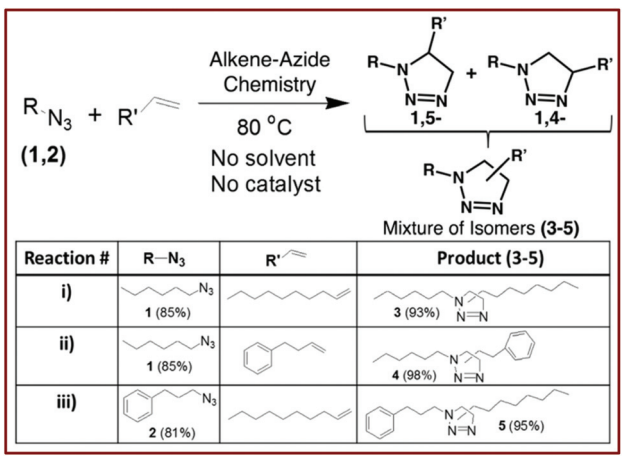
ents under various conditions (sometimes in the presence of a Lewis acid) to join together two molecules serving two different functions.[17–20] Applications of the DA cycloaddition also include those in the field of materials science. Various macromolecular architectures have been achieved using DA click style reactions including homopolymers, telechelic polymers, and block and graft copolymers.[21–23] Another significant linking reaction is the thiol–ene reaction, based on the hydrothiolation of a carbon–carbon double bond under free radical-mediated and Michael addition reaction (requiring a catalyst) pathways. This reaction is used heavily in polymer synthesis, polymer post-functionalization, and polymer conjugation and is also known to proceed in the presence of UV light without a catalyst.[24–28] Another vital molecular linking reaction is the well-established alkyne–azide "click" chemistry, which is used heavily for synthesizing biomolecules, drug delivery systems, monomer species, polymeric materials, and polymer surface modification and functionalization.[29–36] Traditionally this reaction involves the linking of a terminal alkyne and an azide *via* a Hüisgen [2 + 3] cycloaddition at elevated temperatures. This reaction is slow and produces multiple isomers; however, when a heavy-metal catalyst is used such as copper(I) or ruthenium(II), the reaction rates increase exponentially, and the production of a single isomer can be achieved at room temperature.[37] These molecular linking reactions are a vital component to the molecular design process and inherently use a green approach; however, these reactions are often criticized for the cytotoxicity associated with the heavy-metal catalysts and toxic solvents used for the reactions.[38] Recently, alkyne–azide click chemistry has been used to synthesize linear polymers and crosslinked gels under strained conditions, without the use of heavy-metal catalysts, forming high molecular weight polymers.[39,40]

Click chemistry faces some challenges in achieving a completely solvent and catalyst-free chemistry, and there have been some approaches to improve it.[41] In the past, many efforts have been made to reduce or remove catalysts from reactions completely, including modification of alkynyl moieties, highly strained cyclic or substituted alkynes including fluoro-substituted cyclooctynes, amides, alkynyl esters, and sulfones, and the use of activated alkynes that are able to perform cycloaddition with azides without a catalyst.[29,34] These methods have been proven to be "greener" through catalyst-free conditions, but they rely on more complicated building blocks and functional groups, which reduces the original simplicity of click chemistry. Herein, we propose a molecular linking chemistry dubbed one-step "Click-ene" chemistry as an efficient way to produce various materials in a catalyst and solvent-free manner. While the reaction between a carbon–carbon double bond and an azide group is known and has been used to make cyclic and linear compounds,[42–46] to the best of our knowledge and research, this chemistry has not been used to synthesize linear polymeric compounds. In this alkene–azide chemistry, commercially available alkenes and azides are allowed to react under catalyst and solvent-free conditions. The reaction forms a 1,2,3-triazoline ring which provides unique properties including metal-ion coordination, large dipole-moments, acid/base solubility, and hydrogen bonding similar to the traditional "click" chemistry.[47] To this end, we have synthesized a small library of various triazoline-containing small molecules, an AB functional monomer, and polymers. This catalog demonstrates the ease and potential that our alkene–azide chemistry provides. While the synthesized small molecules show the feasibility of this alkene–azide chemistry, the synthesized polymers represent an essential evolution of "click-ene" chemistry. The synthesized AB functional monomer was polymerized *via* transesterification, and the polymers were made from azide terminating and carbon–carbon double bond terminating monomers. This chemistry is advantageous over other linking reactions by being able to synthesize both petroleum and bio-based functional compounds and polymers in a highly economical way, which is an essential quality for commercial applications. Compounds are easily synthesized in one-step with high yields and no toxic by-products, the synthesis is low-cost and solvent and catalyst-free and requires no post-processing/workup or purification, and it can be easily applied to large scale industrial applications for commercial use. This work establishes the ability to design monomers, small molecules, and polymers using this alkene–azide chemistry.

Results and discussion

Traditional alkyne–azide "click" chemistry can be achieved with the use of heavy-metal catalysts and toxic solvents. To improve on this method by providing a solvent and catalyst-free approach to building small molecules and polymers, we utilized the double bond(s) of various linear alkenes and azide functionalized linear alkanes to synthesize small molecules, monomers, and polymers, using only heat to catalyze the reaction. Toward proving that this chemistry works, we first synthesized various triazoline-containing small molecules, whose syntheses are demonstrated in Scheme 1. First



Scheme 1 Proof-of-concept, small molecule reactions for the establishment of "click-ene" chemistry.

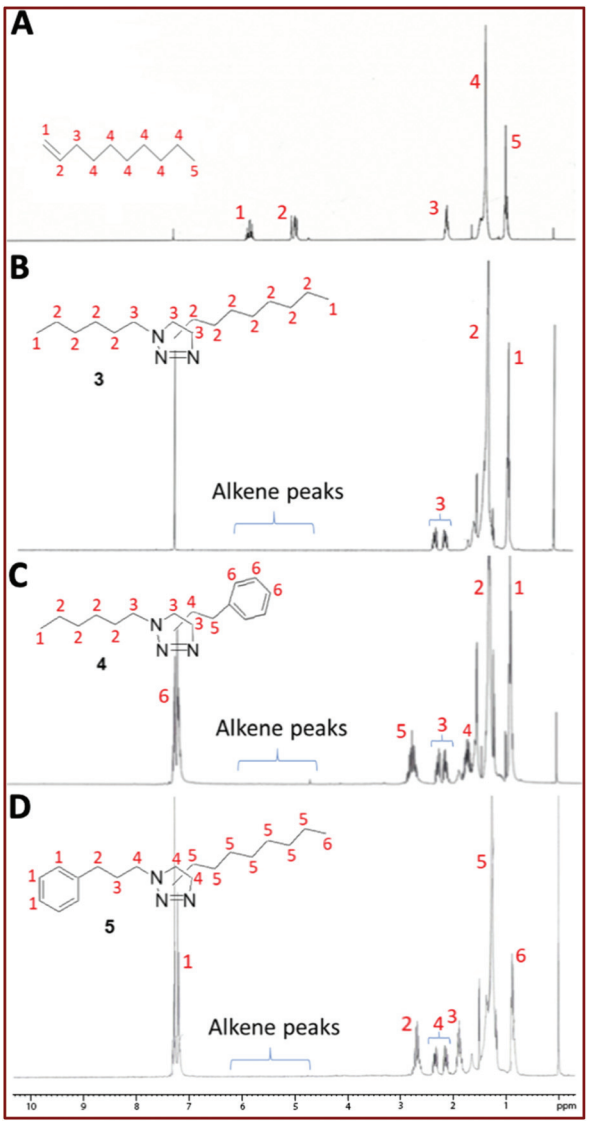


Fig. 1 ^{1}H NMR spectra of (A) the dec-1-ene starting material, (B) small molecule **3**, (C) small molecule **4**, and (D) small molecule **5** with the synthesized small molecules showing a disappearance of alkene peaks. All samples were taken in $CDCl_3$ (7.26 ppm).

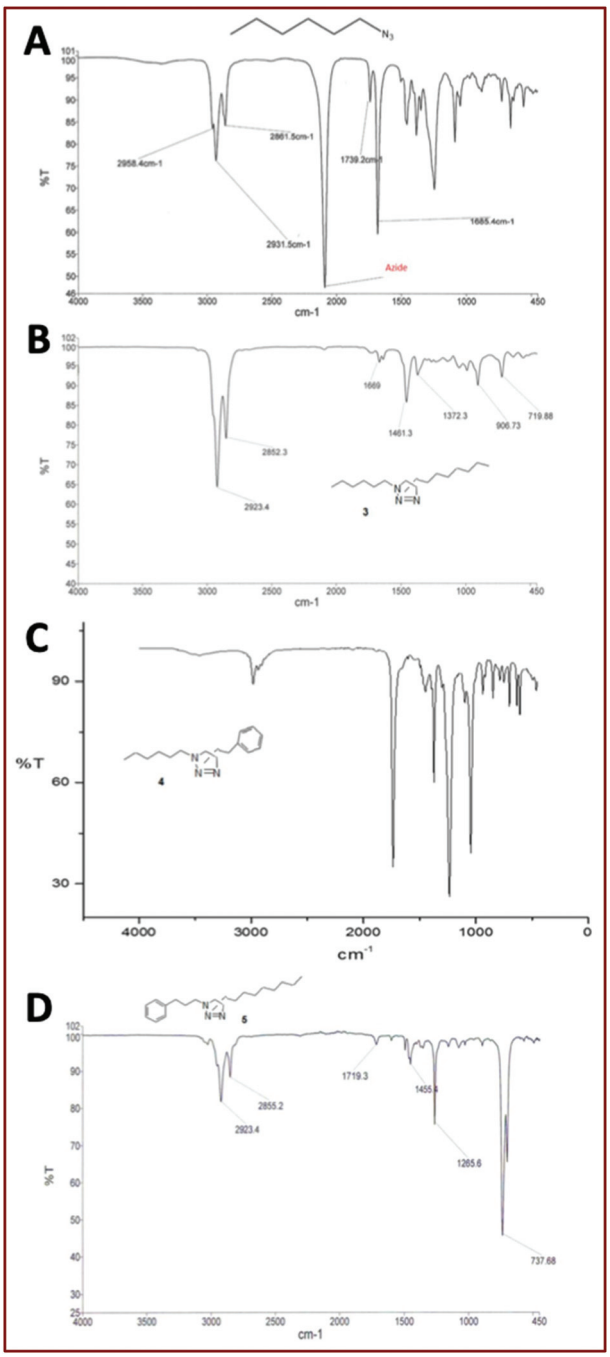


Fig. 2 FT-IR spectra of (A) the hexyl azide starting material, (B) small molecule **3**, (C) small molecule **4**, and (D) small molecule **5** with the latter three showing azide peak disappearance.

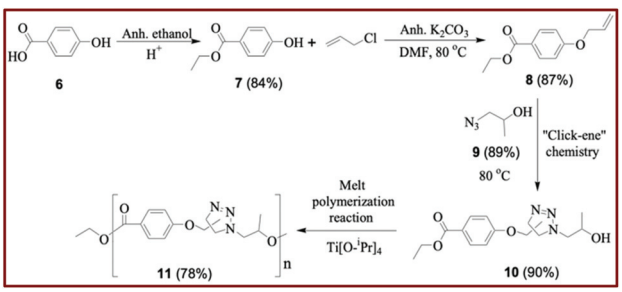
we synthesized azide derivatives **1** and **2** from commercially available 1-bromohexane and (3-bromopropyl)benzene respectively, confirmed by both ^{1}H NMR and FT-IR spectroscopy (Fig. 1 and ESI, Fig. S1†). Then, a series of reactions (**i–iii**) were carried out in an effort to prove the proposed "click-ene" chemistry, resulting in the 1,2,3-triazoline ring-based molecules (**3–5**). Briefly, the corresponding synthesized azides 1-azidohexane (**1**) and (3-azidopropyl)benzene (**2**) undergo a Hüisgen 1,3-dipolar cycloaddition with commercial alkenes dec-1-ene and but-3-en-1-ylbenzene, only by heating at 80 °C for 12 hours without the use of toxic solvents or heavy-metal catalysts (Scheme 1). The triazoline ring containing molecules (**3–5**) were characterized by ^{1}H NMR and FT-IR spectroscopic methods without any workup or further purification (Fig. 1 and 2).

^{1}H NMR spectra of dec-1-ene and the triazoline ring containing products (**3–5**) are shown in Fig. 1. The representative peaks for the carbon–carbon bonds of an azole ring in compounds **3** (peaks 3 and 4 at 2.1 and 2.29 ppm, respectively), **4** (peaks 3 and 4 at 2.13 and 2.26 ppm, respectively), and **5** (peaks 4 and 5 at 2.16 and 2.32 ppm, respectively) confirm the successful formation of a 1,2,3-triazoline ring between the vinyl terminated and azide terminated starting materials. In

addition, peaks corresponding to vinyl protons (5–6 ppm range) present in the starting material are absent in the product as seen in Fig. 1, confirming reaction completion and validating the previous conclusion.

An analysis of the FT-IR spectra of compounds **3–5** compared to the starting material 1-azidohexane (**1**) shows a new band at 1637 cm^{-1}, indicative of the nitrogen–nitrogen double bond of a 1,2,3-triazoline ring configuration (Fig. 2). Additionally, the absence of an azide band at 2100 cm^{-1} in the spectra of the products shows the successful conversion of an azide functional group. Taken together, characterization data show not only that our proposed alkene–azide chemistry works, but also that it works without the use of toxic solvents or heavy-metal catalysts and has huge applications in the pharmaceutical industry and for the formation of biological compounds, which prompted further investigation into the capabilities of this chemistry.

Since our alkene–azide chemistry is able to link two small molecules together to form new compounds, we thought to apply this chemistry in the field of materials science to synthesize new monomers and polymers. Accordingly, we used a vinyl and an azide terminated compound to synthesize an AB-type monomer capable of polymerization with a traditional transesterification catalyst, demonstrated in Scheme 2. In order to obtain the aryl difunctional vinyl–ethyl ester (**8**), readily available 4-hydroxybenzoic acid (**6**) is subjected to acid-catalyzed esterification to obtain the protected ethyl ester (**7**). From here, the secondary hydroxyl group of compound **7** is alkylated with allyl chloride using a weak base in a polar aprotic solvent resulting in the aryl difunctional vinyl–ethyl ester (**8**). To synthesize the azide functionalized glycol (**9**), propylene oxide is subjected to a ring-opening nucleophilic substitution reaction with sodium azide in a polar protic solvent. Now that we have our alkene–azide precursors **8** and **9**, we react them together without the use of a solvent or heavy-metal catalyst *via* a Hüisgen 1,3-dipolar cycloaddition, forming our AB-type alkene–azide-derived monomer (**10**). The alkene–azide-derived polyester polymer (**11**) was obtained through a transesterification of the AB-type alkene–azide-derived monomer (**10**) under the melt conditions, using a catalytic amount of titanium(IV) isopropoxide. We then characterized the "click-ene"-derived polyester (**10**) by NMR and FT-IR spectroscopic methods (Fig. 3 and ESI, Fig. S2 and S3†).



Scheme 2 Synthesis of "click-ene" AB monomer **10** and the resulting polyester **11**.

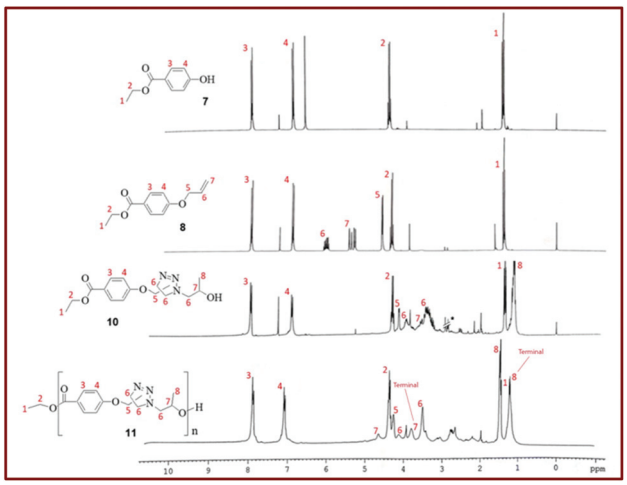
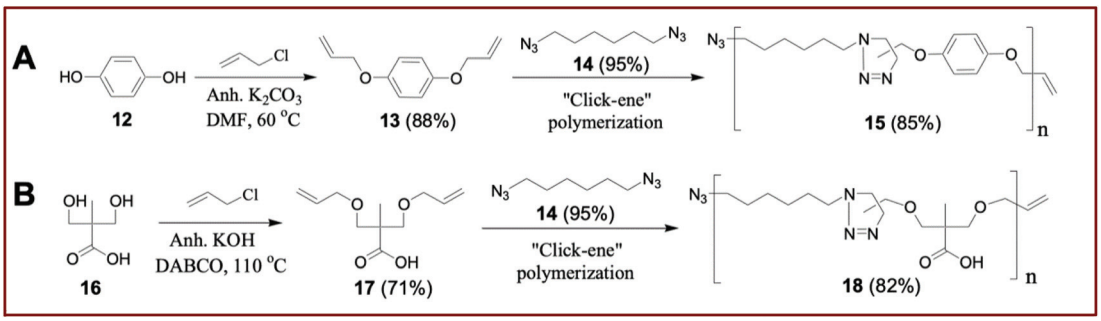


Fig. 3 ^{1}H NMR of the "click-ene" constructed AB monomer (**10**) and resulting polyester (**11**). All samples were taken in $CDCl_3$ (7.26 ppm). Residual solvent peaks can be seen from 2.75 to 3.0 ppm. *Residual solvent peaks were reduced to improve the clarity of the spectrum.

^{1}H NMR spectra of compounds **7**, **8**, **10**, and the resulting polymer **11** are shown in Fig. 3. The absence of alkene peaks in the 5.2–6.1 ppm range for the AB-type monomer **10** shows that the alkene in compound **8** was successfully converted by the azide group in compound **9** to a 1,2,3-triazoline ring. Subsequent transesterification of the AB-type "click-ene" monomer (**10**) yielded the polyester polymer **11** through the shift of peak 8 in compound **10**, confirming new ester bond formation. FT-IR spectroscopy of compound **8** reveals its successful formation by the removal of the hydroxyl functionality (broad peak at 3350 cm^{-1}) present in compound **7** (ESI, Fig. S2†). Additionally, FT-IR shows a reduction in the alcohol functionality for polymer **11** compared to the monomer species **10**, again confirming polymer formation. These syntheses represent an important application of "alkene–azide" chemistry in the field of materials science where this chemistry can be applied to synthesize bio-friendly monomers to make new polymeric materials.

Now that we established the successful synthesis of AB-type monomers using alkene–azide chemistry, we thought of further demonstrating the capabilities of this methodology through the one-step synthesis of aromatic (**15**) and aliphatic (**18**) polymers (Scheme 3).

To synthesize the aromatic polymer **15**, we used an $A_2 + B_2$ approach by preparing a divinyl monomer (**13**) and a diazide monomer (**14**). Briefly, the secondary hydroxyl groups of a commercially available hydroquinone (**12**) are alkylated with allyl chloride using a weak base in a polar aprotic solvent, resulting in our divinyl monomer (**13**). The diazide monomer (**14**) was prepared *via* a nucleophilic substitution of commercially available 1,6-dibromohexane with sodium azide in a polar aprotic solvent. Alkene–azide polymerization was carried out *via* a Hüisgen 1,3-dipolar cycloaddition using equimolar amounts of the divinyl (**13**) and diazide (**14**) monomers using heat without a solvent or heavy-metal catalyst, resulting in our



Scheme 3 (A) Synthesis of aryl (**15**) and (B) aliphatic (**16**) "click-ene" polymers.

aromatic polymer (**15**). The functional aliphatic polymer (**18**) is prepared in a similar way. To synthesize the aliphatic divinyl monomer (**17**), the primary hydroxyl groups of commercially available dimethylolpropionic acid (**16**) are alkylated with allyl chloride using a strong base in a non-polar organic solvent, catalyzed by DABCO. For alkene–azide polymerization of the aliphatic divinyl monomer (**17**) and the prepared diazide monomer (**14**), equimolar ratios of each are reacted together in the absence of solvents and heavy-metal catalysts, resulting in our functional aliphatic polymer (**18**). The synthesized "click-ene" polymers (**15** and **18**) were characterized by NMR and FT-IR spectroscopic methods (Fig. 4; ESI, Fig. S4–S8†).

^{1}H NMR spectra of compound **13** and the resulting aromatic polymer **15** are shown in Fig. 4. Reduction of the representative alkene peaks in the 5.2–6.1 ppm range for compound **13** confirms a successful conversion of the carbon–carbon double bond, with the residual peaks in compound **15** assigned to terminal vinyl groups. Formation of a 1,2,3-triazoline ring is confirmed by the peaks representing CH_2 and CH protons in the 2.1–2.6 ppm range and at 3.9 ppm, respectively. FT-IR spectra of the constructed aliphatic polymer (**15**) and the starting materials (**13** and **14**) show a reduction in the azide functionality (2093 cm^{-1}) and an increase in nitrogen–nitrogen double bonds (1667 cm^{-1}), further confirming the conversion to a 1,2,3-triazoline ring (ESI, Fig. S4†). ^{1}H NMR spectra of compound **17** and the resulting aliphatic polymer **18** confirm polymer formation exhibited by broad polymer peaks and CH_2 and CH protons in the 2.5–3.0 ppm range and at 3.9 ppm, respectively (ESI, Fig. S5†). The FT-IR spectrum of the aliphatic "Click-ene" polymer **18** shows a terminal azide functionality (2092 cm^{-1}) and nitrogen–nitrogen double bonds (1665 cm^{-1}) (ESI, Fig. S6†). Next, we took the three polymers (**11**, **15**, and **18**) and determined their molecular weights.

All the "click-ene" chemistry derived polymers (**11**, **15**, and **18**) were further characterized by size exclusion chromatography (SEC), matrix assisted laser desorption/ionization-time of flight (MALDI-TOF), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) spectroscopic methods (Fig. 5; ESI, Fig. S9–S11†). As shown in Fig. S9,† SEC chromatograms of the three polymers (**11**, **15**, and **18**) showed the formation of high molecular weight macromolecules with M_w values (g mol^{-1}) calculated at 59.1k (Polydispersity Index, $Đ$ = 2.4), 34.9k ($Đ$ = 2.3), and 49.3k ($Đ$ = 2.9), respectively, against a polystyrene standard. The formation of high molecular weight polymers was further confirmed by MALDI-TOF spectroscopy which revealed polymers **11**, **15**, and **18** with weights (g mol^{-1}) of 27.7k, 21.9k, and 26.8k, respectively (Fig. 5). DSC chromatograms revealed glass transition temperatures at −3.3 °C, 5.9 °C, and −23.5 °C for polymers **11**, **15**, and

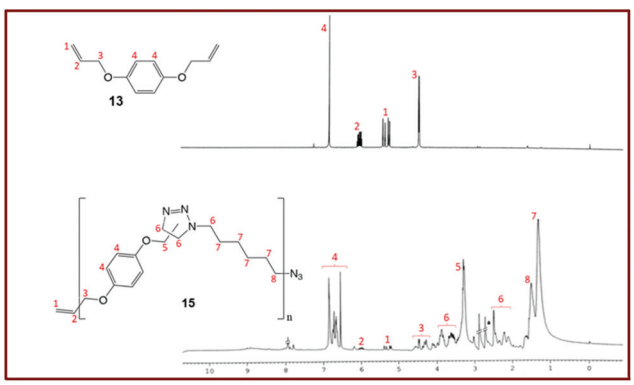


Fig. 4 ^{1}H NMR of aryl alkene (**13**) and the resulting constructed "click-ene" polymer (**15**). All samples were taken in $CDCl_3$ (7.26 ppm). Residual solvent can be seen in polymer **15** from 2.75 to 3.0 ppm and 8.0 ppm. *Residual solvent peaks were reduced to improve the clarity of the spectrum.

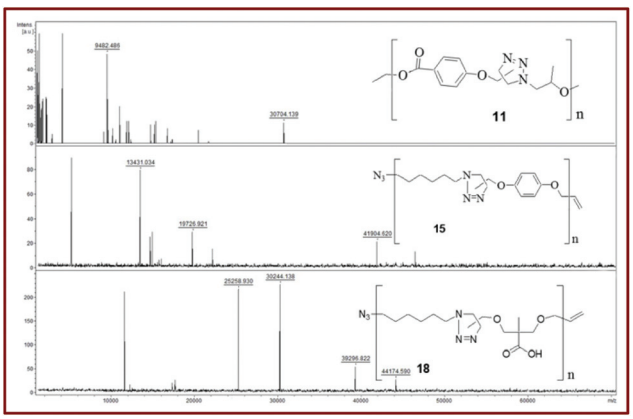


Fig. 5 MALDI-TOF of "click-ene" polymers showing polymers formed with high molecular weights.

18, respectively (Fig. S10†). TGA showed 10% weight loss at 127 °C, 150 °C, and 226 °C for polymers **11**, **15**, and **18**, respectively (Fig. S11†). These results indicated that our alkene–azide chemistry is highly efficient for the one-step synthesis of functional monomers, as well as high molecular weight polymers without the use of toxic solvents or heavy-metal catalysts.

Experimental

Materials and methods

Sodium azide, dimethylformamide (DMF), allyl chloride, 4-hydroxybenzoic acid, propylene oxide, titanium(IV) isopropoxide, decene, 4-phenylbutene, 3-phenylpropylbromide, dibromohexane, dimethylsulfoxide (DMSO), deuterated chloroform ($CDCl_3$) and DMSO were purchased from Acros Organic and used without further purification. Potassium carbonate (K_2CO_3), sulfuric acid, anhydrous ethanol, hexane, ethyl acetate, methylene chloride, and acetonitrile were purchased from Fisher Scientific and used as received.

Infrared spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer using TMS as an internal reference. Gel Permeation Chromatography (GPC) results were obtained using a JASCO MD 2010 Plus instrument with a PD 2020 light scattering detector with THF as the eluent. Thermal Gravimetric Analysis (TGA) was performed on a TA Instruments TGA 550 Discovery series, with sample sizes of 7–10 mg under a dry nitrogen atmosphere. Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) results were obtained on a Bruker Microflex spectrometer. Analytical Thin Layer Chromatography (TLC) was performed on aluminum backed silica gel GF 254 and the results were visualized under iodine vapor. Flash column chromatography was carried out using silica gel.

Synthetic methods

Synthesis of alkyl azide. To a 50 mL round-bottom flask, 1-bromoalkane (0.1 mol) and sodium azide (0.5 mol) were added with 20 mL of DMF. The mixture was heated to 75 °C and allowed to react for 24 h. The reaction mixture was washed with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The resulting product was concentrated *via* rotary evaporation until neat, characterized, and stored at 4 °C for further use. Yield (**1**): 0.54 g (71%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.90 (m, 3H), 1.32 (m, 2H), 1.60 (m, 2H), 3.25 (m, 2H). FT-IR: 2958, 2931, 2861, 2109, 1739, 1685 cm^{-1}.

Synthesis of 1-hexyl-4-octyl-4,5-dihydro-1*H*-1,2,3-triazoline (3). To a 25 mL round-bottom flask, commercially available dec-1-ene (1.0 mol) and 1-azidohexane (**1**) (1.0 mol) were added and mixed. The flask was heated to 80 °C with continuous stirring overnight. The reaction mixture was then cooled to room temperature, characterized, then stored at 4 °C for further use. Yield: 1.87 g (93%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.88 (m, 6H), 1.27 (m, 22H), 2.1 (m, 2H), 2.29 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.12, 14.12, 22.71, 22.71, 25.84, 26.73, 28.9, 29.46, 29.46, 29.46, 31.6, 31.6, 32.8, 54.45, 63.3, 69.82. FT-IR: 2923, 2852, 1669, 1461, 1372, 907, 720 cm^{-1}.

Synthesis of 1-hexyl-4-phenylethyl-4,5-dihydro-1*H*-1,2,3-triazoline (4). To a 25 mL round-bottom flask, commercially available but-3-en-1-ylbenzene (1.0 mol) and 1-azidohexane (**1**) (1.0 mol) were added and mixed, and the reaction, characterization, and storage were carried out as reported for compound **3**. Yield: 1.92 g (98%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.90 (m, 3H), 1.32 (m, 8H), 1.58 (m, 2H), 2.13 (m, 2H), 2.26 (m, 1H), 2.77 (m, 2H), 7.21 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.04, 21.94, 27.32, 28.84, 30.9, 31.26, 33.6, 54.5, 63.78, 70.24, 125.75, 128.2, 128.2, 128.6, 128.6, 142.97. FT-IR: 3188, 2980, 1749, 1497, 1316, 1243, 1070 cm^{-1}.

Synthesis of 4-octyl-1-(3-phenylpropyl)-4,5-dihydro-1*H*-1,2,3-triazoline (5). To a 25 mL round-bottom flask, commercially available dec-1-ene (1.0 mol) and (3-azidopropyl)benzene (**2**) (1.0 mol) were added and mixed, and the reaction, characterization, and storage were carried out as reported for compound **3**. Yield: 2.14 g (95%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.89 (m, 3H), 1.29 (m, 14H), 1.90 (m, 2H), 2.16 (m, 2H), 2.32 (m, 1H), 2.70 (m, 2H), 7.26 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.3, 22.64, 25.7, 29.13, 29.54, 29.54, 30.1, 30.9, 31.8, 32.36, 54.1, 63.78, 70.1, 126.3, 128.9, 128.9, 128.9, 128.9, 143.2. FT-IR: 2923, 2855, 1719, 1455, 1265, 738 cm^{-1}.

Synthesis of ethyl 4-hydroxybenzoate (7). To a 250 mL round-bottom flask, 4-hydroxybenzoic acid (**6**, 0.0724 mol), anhydrous ethanol (2.556 mol, 150 mL), and concentrated sulfuric acid (0.0552 mol, 3 mL of 18.4 M) as a catalyst were added and subsequently refluxed at 80 °C for 6 h. The reaction mixture was neutralized using solid $NaHCO_3$, diluted with water, and extracted using ethyl acetate. The product was recrystallized in water with methanol, characterized, and stored at 4 °C for further use. Yield: 10.11 g (84%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.38 (m, 3H), 4.35 (m, 2H), 6.88 (m, 2H), 7.95 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 13.64, 61.04, 116.32, 118.30, 123.1, 130.9, 132.1, 162.26, 171.1. FT-IR: 3188, 2980, 1557, 1589, 1516, 1443, 1370 cm^{-1}.

Synthesis of ethyl-4-(allyloxy)benzoate (8). To a 50 mL round-bottomed flask, the synthesized ethyl 4-hydroxybenzoate (**7**, 0.0015 mol), commercially available allyl chloride (0.00225 mol), oven dried K_2CO_3 (0.0045 mol) as a catalyst, and 10 mL of DMF were added and the mixture was stirred at 80 °C for 24 h. Subsequently, the reaction mixture was diluted with water (100 mL) and extracted and dried using ethyl acetate over anhydrous Na_2SO_4. The product was dried under medium vacuum and no further purification was required. Yield: 0.27 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.38 (m, 3H), 4.34 (m, 2H), 4.60 (m, 2H), 5.40 (m, 2H), 6.04 (m, 1H), 6.94 (m, 2H), 7.99 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 13.47, 60.74, 70.69, 115.18, 117.95, 119.13, 121.93, 130.59, 131.14, 132.7, 161.1, 165.45. FT-IR: 2983, 2905, 1709, 1505, 1248, 1158, 1100, 1015, 847, 758 cm^{-1}.

Synthesis of 1-azidopropan-2-ol (9). In a 250 mL round-bottomed flask, commercially available 2-methyloxirane

(0.172 mol), sodium azide (0.86 mol), and water (120 mL) were mixed and heated to 75 °C for 24 h. Afterwards, the product was extracted and dried using ethyl acetate over anhydrous Na_2SO_4. The product was concentrated using a rotary evaporator to obtain the pure product. Yield: 15.49 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.19 (m, 3H), 2.86 (m, 1H), 3.22 (m, 1H), 4.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 20.28, 58.29, 66.81. FT-IR: 3368, 2985, 2903, 2085, 1748, 1251 cm^{-1}.

Synthesis of an AB-type alkene–azide-derived monomer (10). In a 5 mL round-bottom flask, both the synthesized ethyl-4-(allyloxy)benzoate (**8**, 0.0015 mol) and 1-azidopropan-2-ol (**9**, 0.0015 mol) were mixed and heated to 80 °C overnight. The reaction mixture was then cooled to room temperature, characterized, and stored at 4 °C for further use. Yield: 0.42 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.02 (m, 3H), 1.36 (m, 3H), 3.38 (m, 4H), 3.49 (m, 1H), 3.87 (m, 1H), 4.12 (m, 2H), 4.27 (m, 2H), 6.91(m, 2H), 7.96 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 13.47, 47.26, 49.76, 50.18, 53.42, 58.8, 66.14, 67.33, 115.67, 117.43, 123.4, 129.56, 131.84, 161.09, 166.35. FT-IR: 3357, 2974, 2931, 2098, 1707, 1603, 1245, 1158, 1102, 758 cm^{-1}.

Synthesis of an alkene–azide-derived polyester polymer (11). To a 5 mL round-bottom flask, the synthesized AB-type "Click-ene" monomer (**10**, 0.00081 mol) and a catalytic amount (0.0000088 mol) of titanium(IV) isopropoxide were mixed and heated to 100 °C for 6 h under continuous N_2 flow. The reaction mixture was then placed under vacuum (0.2 mm Hg^{-1}) for 6 h, maintaining the same temperature. The resulting polymer was found to be soluble in DMF, DMSO, and chloroform, while it was insoluble in water. The polymer was purified *via* a mixed solvent precipitation method using a concentrated solution of the polymer in DMF precipitated in water. The resulting product was centrifuged, dried under vacuum, characterized, and stored at 4 °C for further use. Yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.19 (m, 3H), 1.41 (m, 3H), 1.45 (m, 3H), 3.51 (m, 2H), 3.79 (m, 1H), 4.14 (m, 1H), 4.26 (m, 2H), 7.07 (m, 2H), 7.96 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.47, 55.18, 57.32, 58.8, 60.68, 62.72, 65.12, 67.73, 114.11, 115.22, 123.4, 130.56, 133.59, 162.09, 166.35. FT-IR: 3357, 2974, 2931, 2098, 1707, 1603, 1529, 1245, 1158, 1102, 758 cm^{-1}.

Synthesis of 1,4-bis(allyloxy)benzene (13). To a 100 mL round-bottom flask, commercially available hydroquinone (**12**, 0.0182 mol), allyl chloride (0.0545 mol), potassium carbonate (0.091 mol), and 25 mL of DMF were mixed and refluxed at 80 °C for 12 h. The resulting mixture was then filtered, diluted with water, extracted, and dried using ethyl acetate over anhydrous Na_2SO_4. The mixture was concentrated using the rotary evaporator and purified by flash column chromatography with hexane/ethyl acetate as the eluent. Yield: 2.839 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 4.51 (m, 4H), 5.21 (m, 2H), 5.35 (m, 2H), 6.07 (m, 2H), 6.86 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 69.54, 114.71, 116.31, 117.65, 132.44, 135.17, 152.89. FTIR: 2929, 2856, 1666, 1507, 1385, 1258, 1090 cm^{-1}.

Synthesis of 1,6-diazidohexane (14). To a 250 mL round-bottom flask, commercially available 1,6-dibromohexane (0.041 mol), sodium azide (0.182 mol), and DMF (100 mL) were mixed and heated at 75 °C for 24 h. Following this, the reaction mixture was diluted with water, extracted, and dried using ethyl acetate over anhydrous Na_2SO_4. The resulting solution was concentrated *via* the rotary evaporator and stored at 4 °C for characterization and further use. Yield: 6.9 g (95%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.4 (m, 8H), 1.61 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 26.42, 28.81, 51.30. FT-IR: 2938, 2853, 2088, 1737, 1677, 1240, 1088, 1043 cm^{-1}.

Synthesis of a "click-ene" polymer (15). To a 5 mL round-bottom flask, synthesized 1,4-bis(allyloxy)benzene (**13**, 0.0018 mol) and 1,6-diazidohexane (**14**, 0.0025 mol) were mixed and heated at 100 °C under a N_2 atmosphere for 12 h. Following this, the reaction mixture was placed under vacuum (0.2 mm Hg^{-1}) for 6 h, maintaining the aforementioned temperature. The resulting polymer was soluble in DMF and DMSO, while being insoluble in acetonitrile and water. The polymer was purified *via* a mixed solvent precipitation method by precipitating a concentrated polymer/DMF solution in acetonitrile, followed by centrifugation and drying under vacuum to get the pure polymer. The pure polymer was then characterized and stored at 4 °C for further use. Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.29 (m, 8H), 1.5 (m, 2H), 2.23 (m, 2H), 2.51 (m, 2H), 3.28 (m, 2H), 3.75 (m, 1H), 4.41 (m, 2H), 5.23 (m, 2H), 5.99 (m, 1H), 6.71 (m, 4H). ^{13}C NMR (75 MHz, DMSO, δ ppm): 25.61, 27.72, 28.98, 30.11, 48.59, 51.36, 56.77, 60.03, 67.86, 71.14, 116.27, 117.63, 134.89, 151.28. FT-IR: 2931, 2856, 2093, 1657, 1594, 1505, 1456, 1385, 1215 cm^{-1}.

Synthesis of 3-(allyloxy)-2-((allyloxy)methyl)-2-methylpropanoic acid (17). To a 500 mL round-bottom flask, commercially available 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid (**16**, 0.149 mol), KOH (1.191 mol), allyl chloride (0.744 mol), a catalytic amount of DABCO, and toluene (150 mL) were mixed and heated at 110 °C for 48 h with continuous stirring. Following this, the reaction mixture was concentrated *via* the rotary evaporator and purified by flash column chromatography using neutral silica gel and 30% ethyl acetate in hexane as the eluent. Yield: 21.70 g (68%), ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.24 (s, 3H), 3.61 (m, 4H), 4.00 (s, 4H), 5.21 (m, 4H), 5.85 (m, 2H), 10.5 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 17.98, 48.23, 71.90, 72.46, 116.94, 134.64, 180.53. FT-IR: 2920, 1709, 1458, 1350, 1250, 1097 cm^{-1}.

Synthesis of an aliphatic "click-ene" polymer (18). To a 25 mL round-bottom flask, the synthesized compounds 3-(allyloxy)-2-((allyloxy)methyl)-2-methylpropanoic acid (**17**, 0.0234 moles) and 1,6-diazidohexane (**14**, 0.0234 moles) were mixed and heated at 100 °C under a N_2 atmosphere for 12 h, followed by 3 h under vacuum (0.2 mm Hg^{-1}), maintaining the aforementioned temperature. The resulting polymer was soluble in DMF and DMSO, and insoluble in ethyl acetate and water. The polymer was purified *via* a mixed solvent precipitation method by precipitating a concentrated polymer/DMF solution in ethyl acetate, followed by centrifugation and drying under vacuum to get the pure polymer. The pure polymer was then characterized and stored at 4 °C for further use. Yield: 82%, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.14 (m, 3H), 1.23 (m, 8H), 1.34 (m, 2H), 2.62 (m, 2H), 2.90 (m, 2H), 3.54 (m, 4H), 3.96 (m, 1H), 4.13(m, 2H), 5.21(m, 2H) 5.85 (m, 1H). ^{13}C NMR

(75 MHz, $CDCl_3$, δ ppm): 14.32, 20.79, 26.42, 28.63, 48.75, 51.13, 60.17, 72.10, 117.81, 135.99, 170.96. FT-IR: 3305, 2969, 2929, 2857, 2092, 1735, 1365, 1219 cm^{-1}.

Conclusions

We successfully established "click-ene" chemistry by synthesizing 1,2,3-triazoline ring containing small molecules using solvent and catalyst-free conditions. The synthesized monomers were characterized without any purification steps. Spectroscopic methods performed showed a reduction of vinyl and azide functionalities in the small molecule products, confirming triazoline ring formation. The capabilities of this chemistry were expanded through the successful synthesis of a functional AB-type monomer, indicating that the presence of other functional groups do not interfere with the proposed alkene–azide chemistry. Further expanding on the applications of this chemistry, the proposed methodology was used for synthesizing polymers without the use of traditional polymerization catalysts. We were able to synthesize two vinyl terminating monomers (aryl/aliphatic) which were each polymerized with a diazide, both forming high molecular weight products, confirmed by spectroscopic data. This shows that the alkene–azide chemistry can not only be used for synthesizing small molecule conjugates and functional monomers, but is also applicable for synthesizing macromolecular compounds. Most importantly, this work presents an alternative and effective approach for the Hüisgen 1,3-dipolar cycloaddition reaction, without using any laborious purification steps or toxic solvents and catalysts. Our chemistry is orthogonal, highly efficient, and reaction yields are high; therefore, this chemistry would have a high impact in the pharmaceutical and industrial settings, where the use of toxic solvents and heavy-metal catalysts is not advised. Further research is in progress to validate this "click-ene" chemistry using non-terminal aliphatic and aromatic alkenes.

Conflicts of interest

There are no conflicts to declare.

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