RESEARCH ARTICLE

Macromolecular Chemistry and Physics
www.mcp-journal.de

Oxidation of Monoterpenes to Form Diols and Triols: A Versatile Toolbox for Polymer Synthesis

Harriet R. Fowler, Dara M. O'Brien, Daniel J. Keddie, Cameron Alexander, Derek J. Irvine, Robert A. Stockman, Steven M. Howdle,* and Vincenzo Taresco**

Polyols and polyacrylates have a wide range of applications in polymer synthesis as monomers, initiators, or building blocks in a variety of polymerization reaction types. With an ever-growing need to reduce the global dependency on fossil fuels, finding bio-based/renewable sources for these compounds is now critical. Herein, the alkene moieties of common, abundant terpenes are functionalized via oxidation to expand the "toolbox" of bio-based diols and triols. These polyol compounds are readily converted into the corresponding terpene-derived diacrylates using mild conditions. As a proof of concept, it is demonstrated that these monomers can be used in aza-Michael polymerizations, forming new (bio)degradable poly-β-amino esters.

1. Introduction

Since their commercialization, the production and application of polymeric materials have increased exponentially.[1,2] Polymers have become ubiquitous, causing their expansion into ever-broader and more versatile applications due to their unparalleled properties.[3] However, the vast majority of polymers are made from building blocks derived from petrochemical resources.[2] Bio-based raw materials are now considered the preferred alternative to fossil-fuel carbon sources and could provide renewable carbon in sufficient quantities to cover some of society's future requirements.[4,5]

Terpenes and terpenoids are an attractive source of renewable, bio-based polymeric building blocks that are applicable to a variety of fields, and have been the subject of many reviews.[2,6–8] Terpene feedstocks offer an array of small molecules with a variety of double bonds and chiral centers.[9] Furthermore, they are naturally abundant, inexpensive, and do not compete directly with food sources.[10,11] Commercially, terpenes are derived from turpentine, the volatile fraction isolated from pine resin on a scale of about 330 000 tons per year,[12] and from the peel of waste citrus fruit[2,13] or essential oils extracted from waste flower petals.[14,15]

Despite significant efforts to make polymers directly from terpenes,[16] they do not readily homopolymerize and are prone to rearrangements/undergoing polymerization at multiple sites to give a range of polymeric products.[17] Thus, polymers often lack the desired properties to compete with commercial alternatives.[18,19] However, the functionalization of terpenes can bring huge potential for polymerization. Synthetic methods have been developed, which, over the past 20 years, have seen terpenes undergo facile and robust (as well as bespoke) chemical modifications, to arrive at a wealth of monomer compounds.[20–25] Primarily, this has been achieved via the oxidation of the alkene moieties, which has been particularly successful. To give only a small handful of examples: the Baeyer–Villiger oxidation has been employed by the Hillmyer group to arrive at a number of terpene-based lactones, derived from carvone and menthone, these were used to produce polyesters by ring-opening polymerization (ROP).[10,16,26–28] Similarly, terpenoids with a ketone functionality can be converted to oximes, which can in turn undergo the Beckmann rearrangement, resulting in the corresponding lactams.[16,29–31] These can undergo ROP to produce polyamides.[16,29–31] Epoxidation of terpenes has resulted in polycarbonates,[32–35] polyurethanes,[36,37] polyethers,[38] and poly-β-amino alcohols.[39] Epoxidized terpenes also have applications as bio-based crosslinkers in epoxy-resin chemistry.[40,41]

Much of the research into the oxidation of terpenes has focused on green and sustainable methods of accessing these monomers, often independent of the investigations into their suitability for polymerization.[42,43] Typically, research has focused on the functionalization of terpenes to produce monomers that can be used in well-established polymerization methods.[18,19] For example, terpenes and their (meth)acrylate derivatives have frequently

H. R. Fowler, D. M. O'Brien, D. J. Keddie, R. A. Stockman, S. M. Howdle, V. Taresco
School of Chemistry
University of Nottingham
Nottingham NG7 2RD, UK
E-mail: robert.stockman@nottingham.ac.uk;
steve.howdle@nottingham.ac.uk; vincenzo.taresco@nottingham.ac.uk

C. Alexander
School of Pharmacy
University of Nottingham
Nottingham NG7 2RD, UK

D. J. Irvine
Faculty of Engineering
University of Nottingham
Nottingham NG7 2RD, UK

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.202200446

DOI: 10.1002/macp.202200446

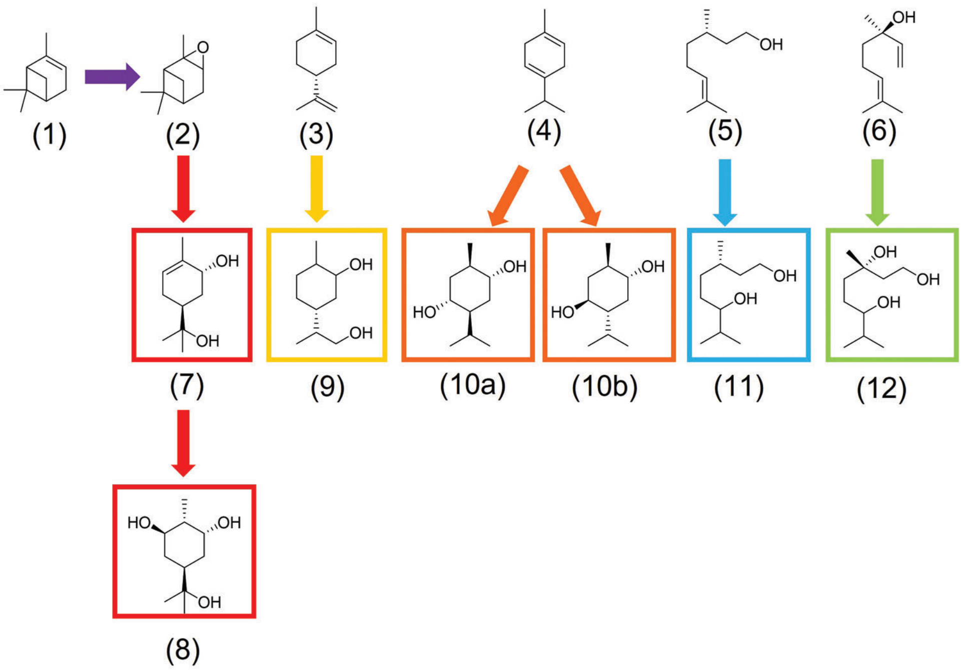

Figure 1. The terpene and terpenoid-based starting materials and their corresponding polyols.

been used in reversible addition–fragmentation chain-transfer (RAFT) polymerizations.[44,45] The authors have demonstrated that Brown hydroboration/ oxidation could be used to produce terpene-alcohols, which are easily converted to (meth)acrylate monomers for radical polymerization.[19] Furthermore, similar conditions were adopted to synthesize a limonene-based diol, which could be further oxidized to the hydroxy-acid, or used as the diol with a diacid co-monomer, in the synthesis of bio-based polyesters by condensation polymerization methods.[18] Lanteri et al. have also reported recent methods for producing citronellol-based diols via photooxidation and reduction, which were shown to readily produce co-polyesters by polycondensation.[46]

In this work, we further expanded upon the variety of terpenes that can undergo these robust, well-established oxidations including cyclic, acyclic, oxygenated, and chiral starting materials. However, we aimed at the production of a series of terpene-derived diols and triols using mild reaction conditions, which produce environmentally benign by-products.[47] These polyols were functionalized with acrylate moieties suitable to use in aza-Michael polymerization, via well-known procedures. This was demonstrated to allow easy access to renewable polymer materials derived from bio-based terpene-derived monomers.

Furthermore, the incorporation of terpenes has been recognized, not only as single molecules but also when they are present in polymers, to impart new chemical, physical, and biological properties.[48,49] This is an advantage over common, simple diol, and triol molecules such as ethylene glycol, glycerol, and propanediol among others. In accordance with previous work, we aimed to produce low molecular weight oligomers which have shown potential for use as surfactants and dispersants with improved biological properties.[48,49] These molecules can also be exploited to produce final polymers with tuneable mechanical and thermal properties for various applications.[11,24]

2. Results and Discussion

Initially, five common and inexpensive terpenes were selected as key starting materials for diol/triol monomer synthesis: a-pinene (**1**), (*R*)-limonene (**3**), *γ*-terpinene (**4**), (*S*)-citronellol (**5**), and linalool (**6**) (see **Figure 1**).

In this work, *trans*-sobrerol **(7)** was synthesized from *α*-pinene oxide **(2)**, which was purchased from Merck. Alternatively, **2** can easily be synthesized in high yields from **1** using meta- chloroperoxybenzoic acid (*m*CPBA) and after treatment with acidified water, using a flow of CO_2 in water, carbonic acid is generated.[12] Recently, an enzymatic synthesis for **7** directly from **1** has been reported, however, this is currently only feasible on a small scale.[45]

Previous work in our group has shown that *trans*-sobrerol **(7)** and limonene **(3)** can be readily converted to their corresponding triol **8** and diol **9** compounds, respectively.[18] The oxidations of the remaining terpenes were achieved using similar anti-Markovnikov hydroboration/oxidation methodologies (see Figure 1).[50]

Beginning the expansion of this toolbox of polyols, *γ*-terpinene-derived diols **(10a)** and **(10b)** were synthesized using a procedure based upon a previously reported example with limonene.[11] Following purification by chromatography, we were able to isolate two separate samples, **10a** and **10b**, which are diastereomeric racemates, in 27% and 28% yields, respectively (i.e., 56% for the combination). Analysis by NOESY NMR allowed for the identification of the respective diastereomers (Figures S5 and S6, Supporting Information).

The linear terpene citronellol **(5)** also easily underwent oxidation, producing the diol **(11)** in a 78% yield after purification by chromatography. This product saw the production of a new stereocentre at the secondary alcohol and was synthesized as a 1:1 mixture of diastereomers, which was not separated further.

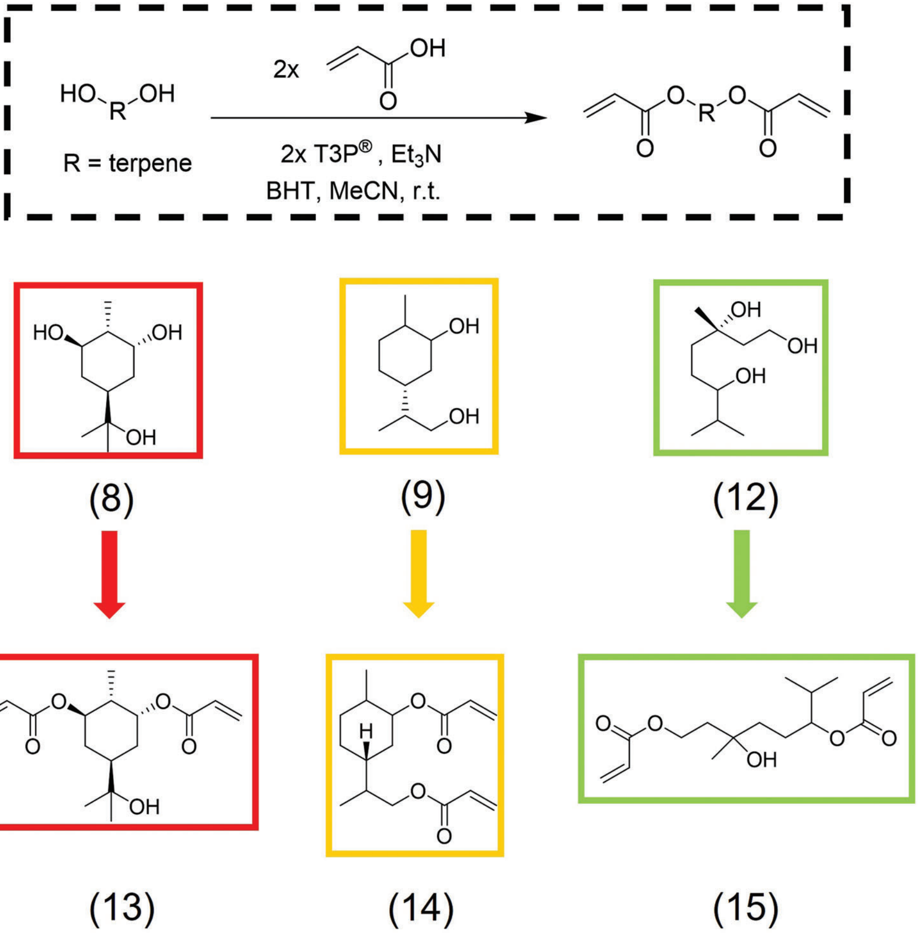

Figure 2. The general syntheses of terpene-based di-acrylates **13–15** from their corresponding terpene polyols **8, 9, and 12**, via esterification using acrylic acid.

We initially postulated that the linalool-derived triol **(12)** would be highly polar and difficult to isolate. However, we found **12** could be extracted by using diethyl ether. Purification via chromatography gave the product a yield of 25%. As with the synthesis of the citronellol-derived diol **(11)**, this reaction is not stereoselective, and so a new stereocentre was introduced to the molecule, with **12** isolated as a 1:1 diastereomeric mixture of racemates (diastereomers **12a** and **12b**) (Figure S8, Supporting Information).

The synthesized diols (**7**, **9–11**) and triols (**8** and **12**) can be utilized in a variety of ways. For example, we have previously demonstrated that terpene-based alcohols can be used as initiators for ROP reactions and for monomers in polycondensation reactions.[12,13,51,52]

We could further functionalize these compounds to produce (meth)acrylate molecules. The functionalization of terpenes with (meth)acrylate groups has led to a variety of polymers via a range of approaches, demonstrating the wide scope of materials and potential applications of these renewably sourced monomers.[53–55] Differently from the previous literature, we now combine our toolbox of terpene-based polyols with the aza-Michael polymerization, a well-known reaction that has been applied to biobased diacrylate monomers to produce degradable polymers.[56] To investigate this, three of the polyols (**8**, **9**, and **12**) were first converted into their corresponding di-acrylate compounds (see **Figure 2**) using mild, environmentally benign conditions; the esterification was carried out using acrylic acid, which can be biorenewably resourced, and propyl phosphonic acid (T3P), which promotes ester coupling. T3P produces an environmentally benign, water-soluble triphosphate by-product, which is considerably more sustainable than the chlorinated by-products formed when acryloyl chloride is used.[47] Good to excellent yields (72–92%) were achieved in each case, and the crude samples were all found to be of a high degree of purity (>94% by ^{1}H NMR), removing the need for further purification steps (Sections 5–7, Supporting Information).

The step-growth aza-Michael polymerization of these compounds was investigated using 1,6-dimethyl hexane diamine **(16)** as a model co-monomer (see **Figure 3**); a molecule we previously exploited in the generation of β-amino alcohol oligomers from terpenes for anti-fungal purposes.[39] The amphiphilic balance of polymers is important for their self-assembly and plays an important role in the biocidal or anti-microbial activity,[57] which we envisage could be a future application of these new polymeric materials.

Several screens were conducted using **13** to optimize the polymerization conditions. We found that conventional heating at

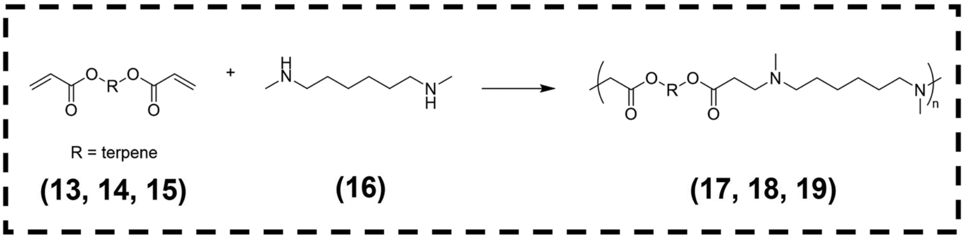

Figure 3. Reaction of terpene diacrylates **13, 14, 16** with 1,6-dimethyl hexane diamine **17** to generate poly-(β-amino ester)s **18, 19, 20**.

Table 1. The series of aza-Michael polymerizations conducted with compounds **13**, **14**, and **15** with diamine **16** to generate the poly-(β-amine ester)s, using both conventional and microwave heating.

Terpene	Temperature [°C]	Heating method	Time	Et_3N	MeCN [M]	M_n [g mol^{-1}]	Đ
13	90	CH	7 days	–	–	3200	2.04
13	70	CH	7 days	–	1	2900	1.96
13	70	CH	7 days	5 equiv.	1	1800	1.98
13	90	MWH	12 h	–	–	2600	1.52
13	90	MWH	12 h	–	1	2200	1.55
13	120	MWH	12 h	5 equiv.	1	2700	1.35
14	120	MWH	12 h	5 equiv.	1	4000	1.52
15	120	MWH	12 h	5 equiv.	1	4900	1.62

CH = conventional heating; MWH = microwave heating

70–90 °C over 1 week produced polymers with a similar structure and molar masses to those made by microwave heating at 90–120 °C for 12 h (see **Table 1**). These observations are in line with the results already present in literature for the improved synthesis of poly(amidoamine)s via aza-Michael polymerization conducted using microwave heating.[58] This allows higher temperatures to be accessed within a shorter heat-up timescale (solvent evaporation being an issue with conventional heating in an oil bath). This reduces reaction times which is more convenient and lowers energy costs, resulting in more efficient heating.[59] These higher temperatures are reached because of volumetric heating which ensures that the entire bulk of the reaction mixture is being heated, rather than relying on the conductive/convective heating mechanisms of the conventional heating system.[59] When volumetrically heated, the molecular friction, caused by the relative movement between the molecules in the reaction mixture as the oscillating magnetic field causes their dipoles to align with the electric field, results in rapid internal heating.[59] Furthermore, it has been recently reported in the literature that the addition of triethylamine (Et_3N) can help to catalyze the aza-Michael reaction and generate higher molecular weight polymers, likely because of the increased basicity of Et_3N facilities faster proton transfer.[60] This was not observed under conventional conditions, possibly as a result of the dilution of the sample, however, an increase in molecular weight was observed under microwave heating (see Table 1). Additionally, a solvent screen was carried out with the following solvents: acetonitrile (MeCN), 2-methyltetrahydrofuran (2-MeTHF), methanol (MeOH), ethanol (EtOH), and water (Table S2, Supporting Information). We found acetonitrile to be optimal for achieving the highest molecular weights, followed closely by the bio-based solvent 2-MeTHF (Table S2, Supporting Information). We postulate this is due to more efficient stabilization of the charged intermediate, which is formed during the aza-Michael addition. Using these conditions with **13**, polymers of up to 2700 g mol^{-1} (M_n) with dispersities of 1.35 were formed over 12 h (see Table 1). The reported dispersities are lower than expected for step-growth polymerization due to the low molecular weight of the polymers and are therefore not fully resolved in the gel permeation chromatography (GPC) traces (Table S1, Supporting Information and related GPC traces).

To probe the versatility of these reaction set-ups, we applied these conditions to monomers **14** and **15** for 12 h yielding polymers of similar molecular weight and dispersity (see Table 1).

The polymerization pathway adopted here is just one example of a possible synthetic strategy where these materials could be exploited. Due to the chemical nature of these di-acrylates compounds, their use in the broad field of additive manufacturing may be foreseeable. In fact, despite the growing interest in more environmentally friendly materials, the applications of terpene-based (macro)monomers in photo-cross-linkable systems have been limited.[58,61] Indeed, there is ongoing research looking at the use of these new monomers in additive manufacturing where there are only a few biobased polymers for 3D printing.[62]

3. Conclusions

A series of diol and triol compounds were synthesized from terpene-based feedstocks using a robust and facile protocol, resulting in six compounds, each with two nucleophilic alcohol groups.

To exploit these terpenes for polymerization, as a proof of concept, selected polyols were converted into their corresponding di-acrylate compounds. These compounds were then employed in aza-Michael polymerizations with 1,6-dimethyl hexane diamine to yield intrinsically (bio) degradable poly-β-amino esters. It was found that the use of microwave heating reduced the reaction time from 7 days to 12 h.

The "toolbox" of bio-based polyols could have a wide range of applications in polymer synthesis, beyond the one shown in the work, such as ROP and polycondensations. These materials could also undergo further functionalization and optimization to have advantageous properties in a range of new fields such as additive manufacturing and tissue engineering.

4. Experimental Section

Materials: All reagents were purchased from a chemical supplier and used without further purification. Water was deionized before use. Dry solvents were obtained from drying towers and contained <17 parts per million (ppm) of water. TLCs were performed on silica gel mounted on aluminum and visualized using potassium permanganate with gentle heating. Experiments carried out using inert conditions employed nitrogen by means of a Schlenk line. Solvent evaporation was performed using a rotary evaporator under reduced pressure.

Analytical Techniques: Nuclear magnetic resonance spectroscopy was recorded in deuterated chloroform ($CDCl_3$) at 25 °C, with Bruker 400 MHz (^{1}H) and 100 MHz (^{13}C) spectrometers. Chemical shifts were assigned in ppm. All spectra were obtained at ambient temperature (22 °C). MestReNova 6.0.2 copyright 2009 (Mestrelab Research S. L.) was used for analyzing the spectra.

Fourier-transform infrared spectroscopy was recorded using a Bruker Tensor 27 using an ATR attachment and peaks are quoted as υ_{max} in cm^{-1}.

High-resolution mass spectrometry was recorded using a Bruker MicroTOF spectrometer operating in electrospray ionization (ESI) mode.

GPC was performed in $CHCl_3$ (HPLC grade, Fisher Scientific) with 1% v/v Et_3N as the eluent at room temperature using two Agilent PL-gel mixed-D columns in series with a flow rate of 1 mL min^{-1}. A differential refractometer (DRI) was used for 255 sample detection. The system was calibrated using polycaprolactone standards.

*General Procedure for the Synthesis of Poly-ol Compound **8***: Dry THF (60 mL) was added to a pre-dried flask of *trans*-sobrerol under argon. The mixture was stirred on ice and borane solution (1 м in THF; 117.7 mmol; 118 mL) was added dropwise via syringe. This was then stirred at room temperature for 3 h before 2 м sodium hydroxide solution was added (88 mL, 176.5 mmol) at 0 °C, followed by hydrogen peroxide solution (30% v/v, 18 mL, 176.5 mmol). The mixture was further stirred for 16 h before sat. aq. Na_2SO_3 was added (50 mL) and following further stirring for 10 min, the volatiles and water were removed by reduced pressure. The remaining material was re-dissolved in hot MeCN (80 °C) and undissolved solids were filtered while keeping the glassware hot. The filtrate was then kept at −20 °C for 4 h before the recrystallized title compound was formed as a white, solid precipitate and collected by Büchner filtration. Products analysis can be found in Supporting Information.

*General Procedure for the Synthesis of Poly-ol Compounds **10–12***: Borane solution (1 м solution in THF; 73.53 mmol) dropwise at 0 °C was added to a solution of starting terpene (36.77 mmol) in dry THF (40 mL) under argon. The solution was stirred for 2 h before 2 м NaOH solution was added (74 mL, 147.05 mmol) at 0 °C, followed by H_2O_2 solution (30% v/v, 15 mL, 147.05 mmol). The solution was stirred at room temperature for 2 h before extracting the water later with diethyl ether (2 × 100 mL). The organic layer was washed with Na_2CO_3 solution (2 × 100 mL) and brine (2 × 200 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and purified by silica gel chromatography. Products analysis can be found in Supporting Information.

*General Procedure for the Synthesis of Diacrylate Compounds **13–15***: To a round bottom flask charged with terpene poly-ol (≈35 mmol), acetonitrile (80 mL), Et_3N (≈210 mmol), acrylic acid (≈77 mmol), and BHT (≈0.35 mmol) were added. T3P (∼80 mmol) was added dropwise on ice. The mixture was stirred, and exposed to air for 16 h. Et_2O (2 × 75 mL) was added and the mixture was washed with 1 м HCl (2 × 50 mL), sat. $NaHCO_3$ (2 × 50 mL), and brine (100 mL). The organic extracts were collected and dried over $MgSO_4$. The volatiles were removed with a flow of air to produce the diacrylate compounds. Products analysis can be found in Supporting Information.

Synthesis of Terpene-Derived Poly β-(Amino Ester)s via the aza-Michael Polymerization by Conventional Heating (Oil Bath): Terpene diacrylate (1 equiv.) and 1,6-dimethyl hexane diamine (1 equiv.) were measured into an 8-dram vial, which was heated in an oil bath to the required temperature. The reaction was stirred for 7 days, after which time the polymer was isolated without further purification. Products analysis can be found in Supporting Information.

Synthesis of Terpene-Derived Poly β-(Amino Ester)s via the aza-Michael Polymerization by Microwave Heating: To a microwave vial charged with acetonitrile (1.7 mL, 1 м) and Et_3N (1.2 mL, 8.44 mmol), terpene diacrylate (1.69 mmol) and 1,6-dimethyl hexane diamine (1.69 mmol) were added. The vial was sealed, and the sample was heated under microwave radiation to 120 °C for 12 h. After this time, the mixture was precipitated into cold petroleum ether and the sample was stored at −20 °C for 2 h, before centrifugation at 4500 g for 5 min. The organic layer was decanted to yield the polymer product. Products analysis can be found in Supporting Information.

Supporting Information

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

Acknowledgements

H.R.F. and D.O.B. contributed equally to this work. S.M.H. acknowledges the Engineering and Physical Sciences Research Council (grant numbers EP/N019784/1). D.O.B. acknowledges the Engineering and Physical Sciences Research Council (grant numbers EP/N006615/1). H.R.F. acknowledges EPSRC/SFI CDT in Sustainable Chemistry – Atoms 2 Products (EP/S022236/1) for their funding support. V.T. would like to thank the University of Nottingham for his Nottingham Research Fellowship. C.A. acknowledges the Engineering and Physical Sciences Research Council (grant numbers EP/N006615/1) and Royal Society (Wolfson Research Merit Award WM150086). The authors thank Mark Guyler (University of Nottingham) for his technical support with all laboratory equipment. The authors are indebted to Shazad Aslam and Dr. Kevin Butler (University of Nottingham) for their technical expertise in NMR spectroscopy.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aza-Michael polymerizations, diol-terpenes, terpene-diacrylates, terpenes, triol-terpenes

Received: December 13, 2022
Revised: January 5, 2023

[1] Ellen Macarthur Foundation, *The New Plastics Economy, Rethinking the Future of Plastics* **2016**, https://ellenmacarthurfoundation.org/the-new-plastics-economy-rethinking-the-future-of-plastics (accessed: December 2022).
[2] Y. Zhu, C. Romain, C. K. Williams, *Nature* **2016**, *540*, 354.
[3] M. Peplow, *Nature* **2016**, *536*, 266.
[4] S. B. P. Kabasci, in *Plastic Waste and Recycling*, Elsevier, New York **2020**, pp. 67–96.
[5] A. Llevot, P.-K. Dannecker, M. von Czapiewski, L. C. Over, Z. Söyler, M. A. R. Meier, *Chemistry* **2016**, *22*, 11510.
[6] M. R. Thomsett, T. E. Storr, O. R. Monaghan, R. A. Stockman, S. M. Howdle, *Green Mater.* **2016**, *4*, 115.
[7] C. Williams, M. Hillmyer, *Polym. Rev.* **2008**, *48*, 1.
[8] K. Yao, C. Tang, *Macromolecules* **2013**, *46*, 1689.
[9] M. Belgacem, A. M. Gandini, in *Polymers and Composites from Renewable Resources, in Monomers, Polymers and Composites from Renewable Resources*, 1st ed., Elsevier, New York **2008**, pp. 17–38.
[10] J. R. Lowe, W. B. Tolman, M. A. Hillmyer, *Biomacromolecules* **2009**, *50*, 2003.
[11] M. R. Thomsett, J. C. Moore, A. Buchard, R. A. Stockman, S. M. Howdle, *Green Chem.* **2019**, *21*, 149.
[12] D. M. O'brien, R. L. Atkinson, R. Cavanagh, A. A. C. Pacheco, R. Larder, K. Kortsen, E. Krumins, A. J. Haddleton, C. Alexander, R. A. Stockman, S. M. Howdle, V. Taresco, *Eur. Polym. J.* **2020**, *125*, 109516.
[13] V. Negro, G. Mancini, B. Ruggeri, D. Fino, *Bioresour. Technol.* **2016**, *214*, 806.
[14] M. Ghannadnia, R. Haddad, F. Zarinkamar, M. Sharifi, *Ind. Crops Prod.* **2014**, *53*, 65.
[15] O. Boussaada, R. Chemli, *J. Essent. Oil-Bear. Plants* **2006**, *9*, 133.
[16] M. Winnacker, B. Rieger, *ChemSusChem* **2015**, *8*, 2455.
[17] K. Adlington, J. El Harfi, J. Li, K. Carmichael, J. A. Guderian, C. B. Fox, D. J. Irvine, *Biomacromolecules* **2016**, *17*, 165.
[18] M. R. Thomsett, J. C. Moore, A. Buchard, R. A. Stockman, S. M. Howdle, *Green Chem.* **2019**, *21*, 149.
[19] M. F. Sainz, J. A. Souto, D. Regentova, M. K. G. Johansson, S. T. Timhagen, D. J. Irvine, P. Buijsen, C. E. Koning, R. A. Stockman, S. M. Howdle, *Polym. Chem.* **2016**, *7*, 2882.
[20] P. Sahu, P. Sarkar, A. K. Bhowmick, *ACS Sustainable Chem. Eng.* **2017**, *5*, 7659.
[21] O. R. Monaghan, S. T. Skowron, J. C. Moore, M. Pin-Nó, K. Kortsen, R. L. Atkinson, E. Krumins, J. C. Lentz, F. Machado, Z. Onat, A. Brookfield, D. Collison, A. N. Khlobystov, D. De Focatiis, D. J. Irvine, V. Taresco, R. A. Stockman, S. M. Howdle, *Polym. Chem.* **2022**, *13*, 5557.
[22] R. L. Atkinson, M. Elsmore, S. Smith, M. Reynolds-Green, P. D. Topham, D. T. W. Toolan, M. J. Derry, O. Monaghan, V. Taresco, D. J. Irvine, R. A. Stockman, D. S. A. De Focatiis, S. M. Howdle, *Eur. Polym. J.* **2022**, *179*, 111567.
[23] U. Montanari, V. Taresco, A. Liguori, C. Gualandi, S. M. Howdle, *Polym. Int.* **2021**, *70*, 499.
[24] R. L. Atkinson, O. R. Monaghan, M. T. Elsmore, P. D. Topham, D. T. W. Toolan, M. J. Derry, V. Taresco, R. A. Stockman, D. S. A. De Focatiis, D. J. Irvine, S. M. Howdle, *Polym. Chem.* **2021**, *12*, 3177.
[25] M. Firdaus, L. M. De Espinosa, M. A. R. Meier, *Macromolecules* **2011**, *44*, 7253.
[26] D. Zhang, M. A. Hillmyer, W. B. Tolman, *Biomacromolecules* **2005**, *6*, 2091.
[27] J. R. Lowe, M. T. Martello, W. B. Tolman, M. A. Hillmyer, *Polym. Chem.* **2011**, *2*, 702.
[28] M. A. Hillmyer, W. B. Tolman, *Acc. Chem. Res.* **2014**, *47*, 2390.
[29] P. N. Stockmann, D. Van Opdenbosch, A. Poethig, D. L. Pastoetter, M. Hoehenberger, S. Lessig, J. Raab, M. Woelbing, C. Falcke, M. Winnacker, C. Zollfrank, H. Strittmatter, V. Sieber, *Nat. Commun.* **2020**, *11*, 509.
[30] P. N. Stockmann, D. L. Pastoetter, M. Woelbing, C. Falcke, M. Winnacker, H. Strittmatter, V. Sieber, *Macromol. Rapid Commun.* **2019**, *40*, 1970025.
[31] M. Winnacker, S. Vagin, V. Auer, B. Rieger, *Macromol. Chem. Phys.* **2014**, *215*, 1654.
[32] C. M. Byrne, S. D. Allen, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2004**, *126*, 11404.
[33] M. Taherimehr, P. P. Pescarmona, *J. Appl. Polym. Sci.* **2014**, *131*, 41141.
[34] C. Martín, A. W. Kleij, *Macromolecules* **2016**, *49*, 6285.
[35] F. Parrino, A. Fidalgo, L. Palmisano, L. M. Ilharco, M. Pagliaro, R. Ciriminna, *ACS Omega* **2018**, *3*, 4884.
[36] M. Bähr, A. Bitto, R. Mülhaupt, *Green Chem.* **2012**, *14*, 1447.
[37] V. Schimpf, B. S. Ritter, P. Weis, K. Parison, R. Mülhaupt, *Macromolecules* **2017**, *50*, 944.
[38] H. J. Park, C. Y. Ryu, J. V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 109.
[39] D. M. O'brien, C. Vallieres, C. Alexander, S. M. Howdle, R. A. Stockman, S. V. Avery, *J. Mater. Chem. B* **2019**, *7*, 5222.
[40] H. Morinaga, N. Ogawa, M. Sakamoto, H. Morikawa, *J. Polym. Sci.* **2019**, *57*, 2466.
[41] R.m Carman, K.d Klika, *Aust. J. Chem.* **1991**, *44*, 1803.
[42] P. S. Löser, P. Rauthe, M. A. R. Meier, A. Llevot, *Philos. Trans. R. Soc., A* **2020**, *378*, 20190267.
[43] M. A. Droesbeke, F. E. Du Prez, *ACS Sustainable Chem. Eng.* **2019**, *7*, 11633.
[44] F. L. Hatton, *Polym. Chem.* **2020**, *11*, 220.
[45] A. Stamm, M. Tengdelius, B. Schmidt, J. Engström, P. O. Syrén, L. Fogelström, E. Malmström, *Green Chem.* **2019**, *21*, 2720.
[46] D. Lanteri, S. Quattrosoldi, M. Soccio, A. Basso, D. Cavallo, A. Munari, R. Riva, N. Lotti, L. Moni, *Front Chem.* **2020**, *8*, 85.
[47] M. F. Sainz, J. A. Souto, D. Regentova, M. K. G. Johansson, S. T. Timhagen, D. J. Irvine, P. Buijsen, C. E. Koning, R. A. Stockman, S. M. Howdle, *Polym. Chem.* **2016**, *7*, 2882.
[48] D. M. O'brien, C. Vallieres, C. Alexander, S. M. Howdle, R. A. Stockman, S. V. Avery, *J. Mater. Chem. B.* **2019**, *7*, 5222.
[49] V. C. Crucitti, A. Ilchev, J. C. Moore, H. R. Fowler, J.-F. Dubern, O. Sanni, X. Xue, B. K. Husband, A. A. Dundas, S. Smith, J. L. Wildman, V. Taresco, P. Williams, M. R. Alexander, S. M. Howdle, R. D. Wildman, R. A. Stockman, D. J. Irvine, *Biomacromolecules* **2023**.
[50] H. C. Brown, C. D. Pfaffenberger, *Tetrahedron* **1975**, *31*, 925.
[51] K. Fukushima, *Biomater. Sci.* **2016**, *4*, 9.
[52] P. McKeown, M. Kamran, M. G. Davidson, M. D. Jones, L. A. Román-Ramírez, J. Wood, *Green Chem.* **2020**, *22*, 3721.
[53] M. Von Czapiewski, K. Gugau, L. Todorovic, M. A. R. Meier, *Eur. Polym. J.* **2016**, *83*, 359.
[54] A. Stamm, M. Tengdelius, B. Schmidt, J. Engström, P. O. Syrén, L. Fogelström, E. Malmström, *Green Chem.* **2019**, *21*, 2720.
[55] M. S. Lima, C. S. M. F. Costa, J. F. J. Coelho, A. C. Fonseca, A. C. Serra, *Green Chem.* **2018**, *20*, 4880.
[56] L. Stricker, C. Taplan, Prez, F. E. Biobased, *ACS Sustainable Chem. Eng.* **2022**, *10*, 14045.
[57] A. Chen, H. Peng, I. Blakey, A. K. Whittaker, *Polym. Rev.* **2017**, *57*, 276.
[58] P. Gurnani, A. K. Blakney, J. Yeow, C. R. Bouton, R. J. Shattock, M. M. Stevens, C. Alexander, *Polym. Chem.* **2020**, *11*, 5861.
[59] K. Kempe, C. R. Becer, U. S. Schubert, *Macromolecules* **2011**, *44*, 5825.
[60] A. K. Blakney, Y. Zhu, P. F. Mckay, C. R. Bouton, J. Yeow, J. Tang, K. Hu, K. Samnuan, C. L. Grigsby, R. J. Shattock, M. M. Stevens, *ACS Nano* **2020**, *14*, 5711.
[61] A. C. Weems, K. R. D. Chiaie, J. C. Worch, C. J. Stubbs, A. P. Dove, *Polym. Chem.* **2019**, *10*, 5959.
[62] I. Louzao, B. Koch, V. Taresco, L. Ruiz-Cantu, D. J. Irvine, C. J. Roberts, C. Tuck, C. Alexander, R. Hague, R. Wildman, M. R. Alexander, *ACS Appl. Mater. Interfaces* **2018**, *10*, 6841.