

Muconic acid esters as bio-based acrylate mimics

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Over the course of the last centuries, a wide number of synthetic polymers has been developed and introduced. Yet, most polymer materials are based on fossil fuels as raw material and are associated with a considerable environmental impact. *trans,trans*-muconic acid esters are interesting plant-based monomers that have not received much attention yet. The synthesis of a series of dialkyl muconates from muconic acid is described, following by an optimization of the solution free-radical polymerization of these monomers. Unlike claimed in previous studies, dialkyl muconates can be polymerized efficiently in solution to polymers with significant molecular weight above 10⁵ g/mol. Polymerizations are, however, relatively slow, as can be expected for diene monomers (48h at 120 °C). Mark-Houwink coefficients have been determined for diethyl muconate, dibutyl muconate and di(2-ethylhexyl) muconate. Further, glass transition temperatures and thermal stability are assessed for the polymers, showcasing that polymuconates can serve as alternatives to polyacrylate materials. In a last step, also the reversible addition-fragmentation chain transfer (RAFT) polymerization of the muconates is investigated, showing excellent control over molecular weight when a conventional trithiocarbonate is used to control polymerizations.

Introduction

Green polymer chemistry has received an ever growing interest in the last decade. Due to ecological and environmental issues, combined with the depletion of oil-based feedstocks, the shift towards greener chemical processes unavoidable.¹ Progressively, bio-based alternatives to fossil feedstock-derived established polymer products are developed and slowly enter the market. Ideally, a biobased material will not only mimic a conventional product, but even outperform the latter, in order to speed up industrial conversion.² In bio-based polymers the raw materials are typically derived from plant material.³ Sugar^{4,5} and cellulose⁶ are thereby interesting sources due to their simple harvesting and high abundance in nature. While using food products for chemical conversion isn't unproblematic, such approach is still highly attractive from a commercial point of view, as these feedstocks are reliable and available in relatively constant quality. Polymerizable building blocks can be obtained from these bio-feedstocks via chemical or enzymatic catalysis. A good example of such a bio-based compound is muconic acid (MA, see Figure 1). MA is produced from bio-fermentation of sugar⁷, lignin⁸ or their derived compounds.⁹ MA is interesting as it features high functionality, and is polymerizable via different modes of reaction. The acid groups offer a simply access to polycondensations with suitable diols or diamines.¹⁰ On the other hand, the conjugated double bonds present in the structure makes the molecule also suitable for radical chain growth polymerization. In both polymerization

modes, the final polymer contains unsaturations in the backbone, making the materials available for post-polymerization modification, and hence increased tunability or properties. Polycondensation reactions using muconic acid as a building block for the production of polyesters¹¹ or polyamides¹² are already described in literature. Also post-polymerization reactions using condensation products from *cis,cis*-muconic acid are studied toward resin applications via crosslinking of the polymer backbone.¹¹ However, free radical polymerization¹³ (FRP) of muconic acid derivatives is surprisingly less studied. While FRP is favourable in industry due to the ability to reach high molecular weights under relatively simple reaction conditions, only a few older reports exist describing free radical polymerization of muconic acid or its esters with limited success. Radical polymerization of muconic acid itself is challenging due to the polyelectrolyte nature of the resulting product, and difficulties in solubility of monomer and polymer. Hence, it is more straightforward to polymerize esters of MA, specifically alkyl muconates. Interestingly, the polymers obtained from such polymerization are structurally similar to alkyl acrylates and can thus serve as a convenient alternative to these established polymers. Polymuconates also still contain a double bond in each backbone unit, giving in principle access to post-polymerization modification and hence can be used for facile product design. This presents a distinct advantage of polymuconates over polyacrylates. Yet, this advantage only unfolds if the radical polymerization can be carried out successfully, for which literature studies claimed significant problems.

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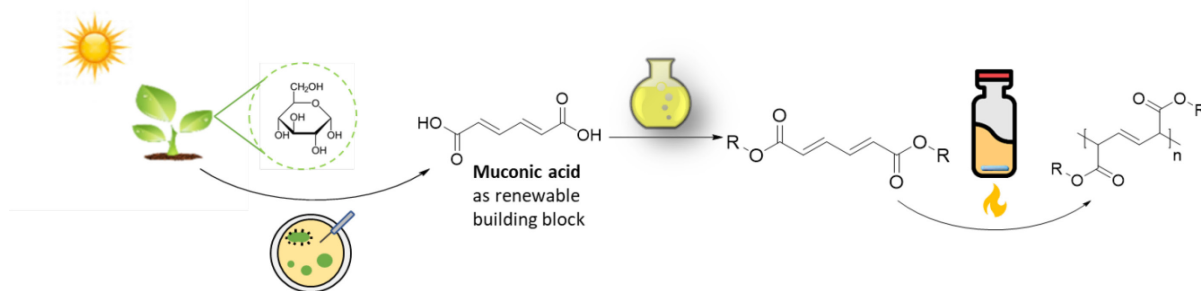


Figure 1 Overview of the value chain of deriving novel bio-based polymers via muconic acid as central building block.

Focusing on copolymerization reactivity, Bando and co-workers reported the synthesis of low molecular weight oligomers of diethyl muconate in 1977.¹⁴ Afterwards Matsumoto et al, performed the thermal FRP in the melt and in solution as well as solid-phase polymerization from crystals under UV irradiation¹⁵ using different dialkyl muconates.¹⁶ Relatively high molecular weights were achievable though. To reach this aim, the polymerizations was started partially from the melt, transitioning into homogeneous solution after heating. However, they could only achieve molecular weights of around $15\,000\text{ g}\cdot\text{mol}^{-1}$, which is not significantly higher than typically for polycondensations products. Radical polymerization of muconates is somewhat difficult as dienes do not polymerize easily in radical polymerization. The simplest liquid diene, isoprene, requires sometimes days to polymerize in a radical pathway and is often difficult to control in molecular weight. Generally, controlled polymerizations of dienes in reversible deactivation radical polymerizations (RDRP)¹⁷ – that allow to tune average molecular weight and dispersity – are more tedious than for other vinyl monomers) to achieve (see discussion below for details. Over the last years, various RDRP methods were developed including nitroxide mediated polymerization (NMP),^{18,19} atom transfer radical polymerization (ATRP)^{20,21,22} and reversible addition-fragmentation chain transfer (RAFT) polymerization.^{23,24} Being able to perform RDRP of muconates is an important evolution step in use of this monomer class, as any newly developed material should not fall behind the synthetic scope developed for their oil-based monomer counterparts.

In this paper we describe first the synthesis of *trans,trans*-muconic acid esters as alkyl acrylate mimics. The *trans,trans* conformation is favoured because it is the most stable isomer and features minimal steric hindrance. Use of muconates compared to pristine MA also promotes better solubility of monomers and polymers, and removes the complicating influences of polyelectrolytes on polymerization kinetics. By optimizing the polymerization conditions, an industrial applicable production mode is introduced that allows to obtain materials with relatively high molecular weights from free-radical polymerization. To investigate if these polymers can be used as potential bio-based replacements for their oil-based counterparts, the thermal properties of the residual materials are determined. Differential scanning calorimetry²⁵ (DSC) and thermal gravimetric analysis²⁶ (TGA) are used in order to

determine the glass transition temperature (T_g) and the thermal stability, respectively, as a function of the alkyl chain substituent. In addition, the Mark-Houwink parameters from different polymuconates are measured via size exclusion chromatography²⁷ and multi angle light scattering²⁸ (SEC-MALS). As a last step, not only FRP but also controlled polymerization is investigated. RAFT is employed to target increasing molecular weights to elucidate if molecular weight control is possible for the muconates under investigation.

Experimental

Materials and methods

trans,trans-muconic acid (>98%, Carbosynth), anisole (99% Acros), 1,4-dioxane (analytical reagent grade, Fisher), ethyl acetate (EtOAc, 99%, Fisher), toluene ($\geq 99.8\%$, Fisher), tetrahydrofuran (THF, analytical reagent grade, VWR), dimethylformamide (DMF, $\geq 99.5\%$, Fisher), ethanol (EtOH, 99.8%, Fisher), 1-butanol (lab reagent grade, Fisher), 2-ethylhexanol (99%, Acros), thionyl chloride (SOCl_2 , 99.7%, Acros), triethylamine (Et_3N , 99%, Acros), methanol (MeOH, technical reagent grade, VWR), hexane (laboratory reagent grade, Fisher), dichloromethane (DCM, 99%, Fisher), magnesium sulfate (MgSO_4 99%, extra pure, dried, Acros), 2,2'-azobis-[2-methyl-N-(2-hydroxyethyl)-propionamide] (VA-086, WAKO chemicals), di-*tert*-butyl peroxide (DTBPO, 99%, Acros). All chemical listed above were used without further purification. Azobisisobutyronitrile (AIBN, Glentham life Sciences) was precipitated 2 times from MeOH as extra purification step.

All polymerizations were performed under inert nitrogen atmosphere. The synthesized polymers were dried under vacuum after purification by precipitation. Nuclear magnetic resonance (NMR) chemical shifts (δ , in ppm) were determined relative to the residual CHCl_3 (7.26 ppm) absorption or the ^{13}C resonance shift of CDCl_3 (77.16 ppm). ^1H and ^{13}C NMR spectra were recorded in deuterated chloroform with a 400 MHz Jeol spectrometer. Analysis was realized with the program MestReNova®. All NMR spectra are shown in the Supporting Information Figure S 1 – Figure S 13. Analytical THF-SEC (Size Exclusion Chromatography) was performed on a Tosoh EcoSEC

HLC-8320GPC, comprising an autosampler, a PSS guard column SDV (50 x 7.5 mm²), followed by three PSS SDV analytical linear XL (5 μm, 300 x 7.5 mm²) columns thermostated at 40 °C (column molecular weight range: 1 x 10² – 1 x 10⁶ g·mol⁻¹) and a differential refractive index detector using THF as the eluent at with a flow rate of 1 mL·min⁻¹. Toluene was used as a flow marker. Differential scanning calorimetry (DSC) was performed with a Q200 (TA Instruments, 10 °C·min⁻¹, 20–180 °C, 3 cycles) using hermetic aluminum cups. Thermogravimetric analysis (TGA) was performed using a Q500 (TA Instruments, 20 °C·min⁻¹, room temperature–660 °C) using platinum cups.

Monomer synthesis

Synthesis of trans,trans-diethyl muconate

30 g trans,trans-muconic acid (0.21 mol) was suspended in a large excess of SOCl₂. A few drops of DMF were added as catalyst and the mixture was refluxed at 88 °C until a homogenous solution was obtained. Hereafter, the remaining SOCl₂ was removed under reduced pressure to obtain muconoyl chloride as a brown solid. The muconoyl chloride was dissolved in DCM and added drop wise to a cooled solution of excess ethanol and 2 equivalents of triethyl amine (0.42 mol, 58.8 mL). The reaction mixture was stirred for 1 hour at room temperature and hereafter, the remaining solvent was removed again under reduced pressure. The residue was dissolved and extracted 3 times with a water/ethyl acetate (50/50) mixture. The combined organic layers were dried with MgSO₄ and filtered. As a purification step, the solution was further filtered 2 times over basic alumina. After removal of the solvent (EtOAc) via reduced pressure, 39 g diethyl muconate (0.196 mol) was obtained as an off-white solid after crystallization while cooling in an ice bath with 93% yield. ¹H NMR (CDCl₃): δ 7.23 (m, 2H, R-O₂-C-CH=CH-), 6.11 (m, 2H, R-O₂-C-CH=CH-), 4.14 (q, 4H, ³J=7.2 Hz, -CH₂-) 1.22 (t, 6H, ³J=7.2 Hz, -CH₂-CH₃). ¹³C NMR (CDCl₃): δ 165.53 (C=O), 140.41 (-CH=CH-C=O), 128.03 (-CH=CH-C=O), 60.48 (-CH₂-), 13.84 (-CH₃).

Synthesis of trans,trans-dibutyl muconate

Trans,trans-dibutyl muconate was synthesized using the same procedure as the diethyl ester, starting from 10 g (0.070 mol) trans,trans-muconic acid. Trans,trans-dibutyl muconate (16 g, 0.063 mol) was obtained with 90% yield. ¹H NMR (CDCl₃): δ 7.23 (m, 2H, R-O₂-C-CH=CH-), 6.11 (m, 2H, R-O₂-C-CH=CH-), 4.18 (t, 4H, ³J=6.7 Hz, -O-CH₂-) 1.66 (m, 4H, -O-CH₂-CH₂), 1.40 (m, 4H, -O-CH₂-CH₂-CH₂-), 0.95 (t, 6H, ³J=7.4 Hz, -CH₃). ¹³C NMR (CDCl₃): δ 165.99 (C=O), 140.80 (-CH=CH-C=O), 128.42 (-CH=CH-C=O), 64.74 (-O-CH₂-), 30.66 (-O-CH₂-CH₂-), 19.15 (-O-CH₂-CH₂-CH₂-), 13.71 (-CH₃).

Synthesis of trans,trans-di-(2-ethylhexyl) muconate

Trans,trans-di-(2-ethylhexyl) muconate was synthesized using mainly the same procedure as the other esters. starting from 10 g (0.070 mol) trans,trans-muconic acid. Because the 2-ethylhexanol cannot be removed by using reduced pressure, the product was purified 2 times by column chromatography (100%

hexane). After removal of hexane via reduced pressure, di-(2-ethylhexyl) muconate (12 g, 0.033 mol) was obtained as an off-white oil with 47% yield. ¹H NMR (CDCl₃): δ 7.26 (m, 2H, RO₂C-CH=CH-), 6.17 (m, 2H, R-O₂-C-CH=CH-), 4.05 (m, 4H, -O-CH₂-) 1.58 (m, 2H, -CH-), 1.30 (m, 16H, -CH₂-), 0.85 (m, 12H, -CH₃). ¹³C NMR (CDCl₃): δ 166.16 (C=O), 140.81 (-CH=CH-C=O), 128.51 (-CH=CH-C=O), 67.35 (-O-CH₂-), 38.85 (-O-CH₂-CH-), 30.48 (-CH-CH₂-CH₂-CH₂-CH₃), 29.0 (-CH-CH₂-CH₂-CH₂-CH₃-), 23.86 (-CH-CH₂-CH₃), 23.03 (-CH-CH₂-CH₂-CH₂-CH₃), 14.12 (-CH-CH₂-CH₂-CH₂-CH₃), 11.05 (-CH-CH₂-CH₃).

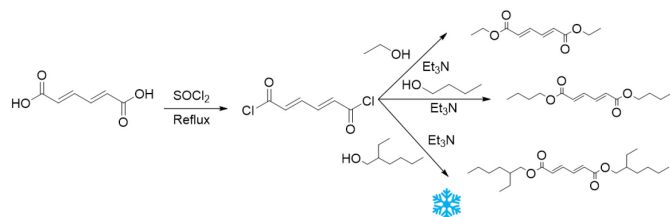
Polymerization

Polymerization of dialkyl muconates

In a typical procedure, polymerizations were performed as follows. In a volumetric flask of 5 mL, 2 g diethyl muconate (0.01 mol) was dissolved in less than 5 mL anisole. A stock solution of the initiator was prepared by dissolving 46 μL of di-*tert*-butyl peroxide in 10 mL anisole. Hereafter, 0.1 mL of the stock solution was added to the flask. Anisole was added to obtain a reaction mixture of 5 mL to give a solution of 2 mol·L⁻¹ diethyl muconate and 0.5 x 10⁻³ mol·L⁻¹ di-*tert*-butyl peroxide. The reaction mixture was poured in a small vial with a stir bar, equipped with a septum and flushed with nitrogen for 15 min. Hereafter, the reaction mixture was heated at 120 °C for 48 h. The polymer was precipitated 3 times in hexane to remove anisole and the unreacted monomer. The conversion of 78% was calculated via ¹H NMR. Other dialkyl muconates were synthesized using the same polymerization procedure (2 mol·L⁻¹ monomer, 0.5 x 10⁻³ mol·L⁻¹ di-*tert*-butyl peroxide at 120 °C and 48 h reaction time) precipitating the polymers in methanol.

Reversible addition fragmentation chain transfer (RAFT) polymerization

2 g diethyl muconate (0.01 mol) and 0.069 g (0.2 mmol) RAFT agent 2-cyano-2-propyl dodecyl trithiocarbonate (CPD-TTC) was dissolved in less than 5 mL anisole. A stock solution of the initiator was prepared by dissolving 46 μL of di-*tert*-butyl peroxide in 10 mL anisole. Hereafter, 0.1 mL of the stock solution was added to the flask. Anisole was added to obtain a reaction mixture of 5 mL to give a solution of 2 mol·L⁻¹ diethyl muconate, 0.5 x 10⁻³ mol·L⁻¹ di-*tert*-butyl peroxide and 0.04 mol·L⁻¹ RAFT agent. Also 3 other solutions with 0.08 mol·L⁻¹ (0.14 g), 0.2 mol·L⁻¹ (0.345 g) and 0.02 mol·L⁻¹ (0.0345 g) RAFT agent were prepared by using the same procedure. The different reaction mixtures were poured in small vials with a stir bar, equipped with a septum and flushed with nitrogen for 15 min. Hereafter, the vials were heated for 48 h at 120 °C and samples were taken after 1, 5, 24, 30 and 48 hour(s).



Scheme 1 Reaction procedure to convert muconic acid into dialkyl muconates

Results and discussion

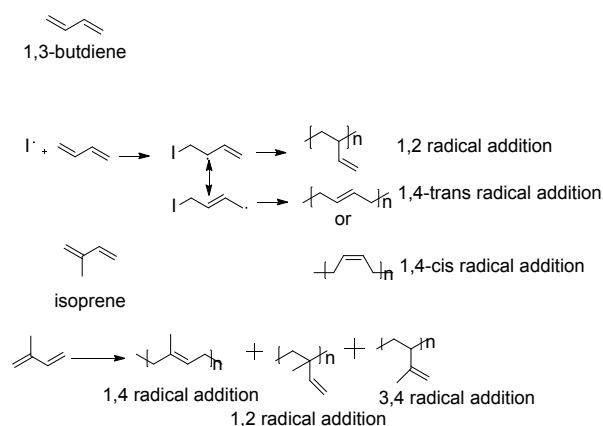
Polymerization of conjugated dienes such as butadiene and isoprene have been studied extensively in the past.²⁹ Due to the diene conjugation, different resonance structures can be considered after radical addition of the initiator. Radical polymerization of 1,3-butadiene will result in 1,2- and 1,4 radical addition products. Note that 1,4-addition can result in cis and trans conformation products. (see Scheme 2).³⁰ Free radical polymerization of butadiene at 100 °C typically yields about 28% 1,4-cis, 51% 1,4-trans and 21% of the 1,2 addition polymer.^{31,32} By increasing the polymerization temperature to 233 °C, the amount of 1,4-cis product can be increased (43%) with concomitant decrease of the 1,4-trans product (39%).³¹ Formation of 1,2 radical addition products seems not to change significantly upon increasing the polymerization temperature to above 200 °C. In case of polyisoprene, similar product mixtures are typically obtained. Again, at 100 °C, formation of 23% 1,4-cis, 66% 1,4-trans, 5% 1,2 and 6% 3,4 addition polymer has been reported.³¹ While an increase in temperature in butadiene polymerization affected the ratios of the different polymer structures, variations are less pronounced for isoprene polymerization (i.e. at 203 °C 19 % 1,4-cis, 69% 1,4-trans, 3% 1,2 and 9% 3,4 radical addition product).³¹

Since muconic esters are also conjugated dienes, the same polymerization pathways can be expected as described above. The polymerization of diethyl muconate (leading to poly(diethyl muconates), PDEM) was already investigated by Matsumoto and coworkers with respect to the type of radical addition products.¹⁶ These authors reported not only 1,4-addition occurred during polymerization but also a small percentage of 1,2-addition. ¹H and quantitative ¹³C NMR confirmed the presence of approximately 2% of the 1,2-addition product. By determination via quantitative ¹³C NMR, PDEM was found to contain 11 % of the 1,4-cis polymer relative to the 1,4-trans addition product. The ratio of 1,4-cis product appears to increase with increasing temperature.¹⁶ Presence of these inseparable structures should be considered while analyzing the thermal properties of the synthesized polymers, even if their contribution seems to be smaller compared to classical dienes (see above). 1,4 radical addition in muconates is likely to be

favoured as the electron withdrawing ester groups can stabilize the radicals, hence giving the 1,4 adduct a significant stability advantage over the 1,2-addition product. Influence on the thermal properties can be confirmed likewise using butadiene and isoprene as an example. Even the small changes in composition between the 1,4-trans and 1,4-cis addition products have a significant effect on T_g . 1,4-trans-polybutadiene has a T_g of -83 °C while the 1,4-cis isomer has a T_g of -95 °C.³¹ The same trend can be observed for isoprene. The T_g of 1,4-cis isomer (-73 °C) is again lowered compared to the 1,4-trans-polyisoprene (-58 °C).³¹ The 1,2 polymer has further impact. The variation in T_g for mixtures of 1,2, 1,4-trans and 1,4-cis polymers is extensively studied for polybutadiene.³³ A polymer mixture with a low amount of 1,2 polymer (molar fractions: 1,2 = 0.005, 1,4-cis = 0.976, 1,4-trans = 0.020) shows a T_g of -111 °C. while a high amount of 1,2 product (molar fractions: 1,2 = 0.790, 1,4-cis = 0.107, 1,4-trans = 0.103) results in a significantly higher T_g value (-28 °C).³³

Monomer Synthesis

Within this study, the trans,trans isomer of muconic acid was employed as mentioned above. This isomer is only poorly soluble in organic solvents and to increase solubility and to avoid interference of ionic charges during the polymerization, dialkyl muconates were synthesized via esterification. First, diethyl muconate (DEM) was synthesized to optimize the monomer synthesis as well as the polymerization procedures. Afterwards, the length and the bulkiness of the ester side chain was varied by synthesizing dibutyl muconate (DBM) and di-2-ethylhexyl muconate (DEHM) to investigate the influence of the ester chain on essential thermal properties such as T_g and thermal stability.



Scheme 2 Polymerization products of butadiene and isoprene.

Table 1 Overview of the outcome of free-radical polymerizations of DEM for various reaction conditions

Entry	T (°C)	[Monomer] (mol·L ⁻¹)	Initiator/ [Initiator] (mol·L ⁻¹)	Reaction time (h)	Conversion (%)	M _n (g·mol ⁻¹)
1	70	2.5 ^b (dioxane)	AIBN/ 2 × 10 ⁻³	24	18	5.9 × 10 ⁴
2	110	2.5 ^b (toluene)	VA-086/ 3.5 × 10 ⁻³	48	68	9.9 × 10 ⁴
3	130	3.36 ^a (anisole)	VA-086/ 1.2 × 10 ⁻³	48	86	6.9 × 10 ⁴
4	130	3.36 ^a (anisole)	DTBPO/ 1.2 × 10 ⁻³	48	90	7.3 × 10 ⁴
5	120	3.36 ^a (anisole)	DTBPO/ 1.2 × 10 ⁻³	48	86	1.04 × 10 ⁵
6	120	3 ^a (anisole)	DTBPO/ 1 × 10 ⁻³	48	88	1.33 × 10 ⁵
7	120	2.5 ^a (anisole)	DTBPO/ 0.5 × 10 ⁻³	48	80	1.27 × 10 ⁵
8	120	2 ^b (anisole)	VA-086/ 0.5 × 10 ⁻³	48	66	1.07 × 10 ⁵
9	120	2 ^b (anisole)	DTBPO/ 0.5 × 10 ⁻³	48	78	1.23 × 10 ⁵

^a Partially polymerized from the melt, no homogeneous solution at room temperature. ^b Homogeneous and stable if dissolved at room temperature.

The esters were synthesized via two distinct approaches, the first being an acid catalyzed esterification using H₂SO₄ and via muconoyl chloride as a reactive intermediate. The drawbacks of the acid catalyzed reaction are the long reaction times and high temperatures. Although SOCl₂ is needed in the alternative route, the reaction conditions as shown in Scheme 1 are favorable due to the fast reaction times and decrease in heat exposure. To speed up the muconoyl chloride formation, DMF was added. Using this reaction procedure, all esters are obtained with high purity and reasonable yields on a multigram scale. In principle, this reaction is well scalable by use of flow chemistry, as was recently shown.³⁴

Optimization of FRP conditions in solution

Since the previous work reported in literature did not result in satisfying polymers with respect to reaction rates and molecular weights obtained, we first focused on obtaining improved reaction conditions for the polymerization. Various parameters were screened for the synthesis of PDEM, this being temperature, initiator, solvent, reaction time and concentration of both monomer and initiator. Representative results for these screenings are summarized in Table 1.

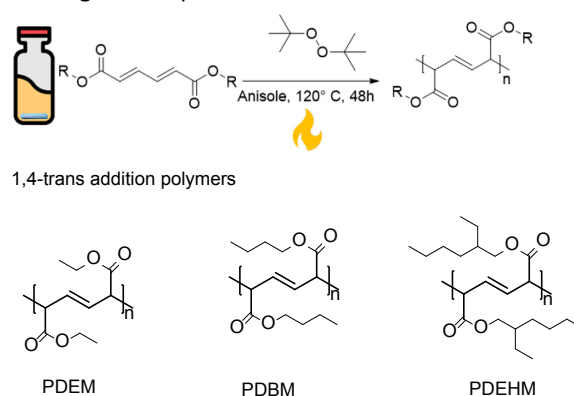
Polymerization for 24h at comparatively low temperature (70 °C) using azobisisobutyronitrile (AIBN) as initiator (hence rather standard conditions for radical polymerizations), resulted in a rather low molecular weight polymer (M_n = 5.9 × 10⁴ g·mol⁻¹ and low monomer conversion of only 18% (Table 1, entry 1). Thermal free radical polymerizations of isoprene and butadiene are likewise slow and DEM fits well into the series of diene monomers. Even at 100 °C reaction times >100 h are needed to obtain equal conversions for isoprene.²⁹ Already at this stage, it

could thus be concluded that high temperatures are needed in order to achieve faster propagation and hence higher overall polymerization rates. However, higher temperatures lead to an increase of termination due to higher radical concentrations being present (if the same initiator is used) and therefore may likewise result in low molecular weight polymers. Hence the half-life (τ) of the initiator must be chosen accordingly. To this end, a high temperature initiator with a high half-life value is needed to allow for extended reaction times. In here, the peroxide initiator di-*tert*-butyl peroxide (DTBPO) with a half-life of 10 h at 123 °C and azo initiator 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086) with a half-life of 10 h at 86 °C were investigated for a 48 h reaction time. Polymerization with AIBN, VA-086 or DTBPO as initiator were tested at different concentrations as well as increasing temperatures (70 to 130 °C). Despite the high polymerization temperature, long reaction times up to 48 h are still needed to obtain reasonable conversions above 70%. Using VA-086 at 110 °C, a polymer with an M_n = 9.9 × 10⁴ g·mol⁻¹ could be obtained (Table 1, entry 2). Increasing the temperature to 130 °C indeed reduced the average molecular weight to 6.9 × 10⁴ g·mol⁻¹. However, the conversion increased from 68% to 86% (48 h reaction time) (see Table 1, entry 3). Changing the initiator (entry 4) to DTBPO increased the molecular weight somewhat to 7.3 × 10⁴ g·mol⁻¹ with 90% monomer conversion.

Polymerizations auto-accelerate due to the onset of the gel-effect at high polymer content.³⁵ High monomer concentrations are hence favorable to reduce the reaction time. At the same time, high initial monomer concentrations will result in higher initial polymerization rates. High reaction temperatures require a compatible solvent with a high boiling point and good solubility for the monomer, initiator and the polymer as well. The polymerization at lower temperatures below 110 °C were tested in 1,4-dioxane ($bp = 101$ °C) and toluene ($bp = 111$ °C) as solvent. The polymerizations above 110 °C were tested in DMSO ($bp = 189$ °C), butyl acetate ($bp = 126$ °C) and anisole ($bp = 156$ °C) as solvent. DMSO is not preferred due to difficulties in removal of the solvent after polymerization. Although polymerization in butyl acetate was possible, anisole was preferred as solvent. Anisole is considered to be a green solvent which can be recycled resulting in a lower environmental impact and is perfectly in line with the greener mindset of the research.³⁶ Keeping in mind that monomer concentrations should be chosen as high as possible, we found that with monomer concentration $> 2 \text{ mol}\cdot\text{L}^{-1}$ no homogeneous monomer solution could be obtained at room temperature and heating was needed to dissolve the monomer. This can potentially lead to reproducibility issues and hence a series of concentrations in homogenous solution (Table 1, entries 5-9) were tested. Best results were obtained with molecular weights of $M_n = 1.23 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, see SI Figure S 14) and 78% monomer conversion (see Table 1, entry 9) with DTBO as initiator. The somewhat lowered monomer conversion was accepted as a compromise as larger molecular weights and homogenous polymerization conditions were prioritized over residual monomer content. Following these conditions, also DBM and DEHM were polymerized using the same optimized conditions to obtain poly(dibutyl muconate) (PDBM) and poly(di-2-ethylhexyl muconate) (PDEHM), respectively. PDBM ($M_n = 1.17 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, 88% conversion) showed no significant difference in molecular weight (see SI Figure S 15). However polymerizing the more bulky DEHM resulted in a M_n of $3.10 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ (see SI Figure S 16) with a conversion of 90%.

Thus, unlike postulated in the early reports on melt-state polymerization of muconates, high molecular weight polymers are readily obtainable from (homogenous) solution polymerization of dialkyl muconates if conditions are chosen accordingly. A general overview of the reaction conditions and the residual 1,4-trans polymuconate structures are shown in Scheme 3. As already mentioned in the research of Matsumoto, and also in line with alkyl acrylate polymerization,³⁷ changes in the size of the alkyl ester chain affects the polymerization rate.¹⁶ This is an interesting observation, as this behavior has so far only been observed for alkyl (meth)acrylates. As a result, the reaction time of DEHM in solution could be reduced from 48 h to 24 h to reach already a conversion of 89%, also due to a stronger gel-effect.³⁵ Note that the purity of the monomer is very important to obtain molecular weights above $100\,000 \text{ g}\cdot\text{mol}^{-1}$. To investigate batch to batch variations, reproducibility was tested using muconic acid from another supplier. While using the first commercial batch PDEM was again synthesized and this time an M_n value of $1.13 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ was obtained

using the same conditions as showed in Table 1, entry 9. The 2nd batch (of muconic acid then also converted into the ester) gave only $6.6 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ using the same monomer synthesis and polymerization procedure. However after extra purification via two liquid-liquid extractions (the first using a saturated solution of NaHCO_3 /ethyl acetate and a second one with water/ethyl acetate) and an extra filtration over basic alumina, the polymerization of the diethyl muconate from the 2nd batch was repeated two times using the same conditions to give polymers of $1.15 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ and $1.18 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$. Results of the reproducibility test are shown in the SI in Figure S 17. These high molecular weights obtained in solution polymerization are a major improvement compared to an M_n value of PDEM of just $7.1 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ reported earlier.¹⁶



Scheme 3 Polymerization of a dialkyl ester using optimal reaction conditions within this research.

With the ability to obtain polymuconates with significant molecular weight, it is worthwhile to continue to study their basic properties. While existing oil-based materials such as polyacrylates are well known in polymer chemistry and industry, polymuconates still require a detailed analysis to establish structure property relationships. First, we determined the Mark-Houwink (MH) parameters for the polymers under investigation in order to obtain correct molecular weights (in fact the molecular weights discussed above were already determined using the following MH parameters). Knowledge of MH parameters is detrimental to allow for simple and straight forward molecular analysis from universal SEC calibration. Usually triple detection SEC is used to determine the MH parameters as both absolute molecular weights and viscosity must be known to establish the MH relation. Due to technical restrictions in the laboratories, we refrained from only using Multi Angle Light Scattering (MALS) for absolute molecular weight determination. Intrinsic viscosities were obtained from universal calibration rather than measurement. Note that by using this technique, MH parameters are determined relative to polystyrene standards. Yet, values should be comparatively reliable as viscosity determination from universal calibration is fairly accurate. A full procedure is given in the SI, and the resulting MH parameters are collated in Table 2.

Table 2 Mark-Houwink parameters K and α obtained for the muconates under investigation using SEC-MALS.

Polymer	dn/dc ($mL \cdot g^{-1}$)	K ($cm^3 \cdot g^{-1}$)	α
PDEM	0.065	1.3×10^{-3}	0.88
PDBM	0.063	1.6×10^{-3}	0.86
PDEHM	0.065	1.8×10^{-3}	0.81

Thermal properties

An essential thermal property is the glass transition temperature, which was determined for all synthesized polymers using DSC measurements. Figure 2 shows the thermograms after removal of the thermal history of the polymers in a first heating cycle. The on-set and off-set of the T_g regions are indicated by the straight lines. The dashed lines indicate the inflection point and hence the respective T_g value. T_g decreases upon increasing the length of the ester side chain in the muconates (see also Table 3). PDEM with a short side chain showed a significant higher T_g value of 7 °C compared to PDBM ($T_g = -37$ °C) and PDEHM ($T_g = -60$ °C). Table 3 compares the glass transition temperatures of the muconates with the corresponding acrylate polymers.³⁸ The same trend is observed here, allowing for the conclusion that poly(muconates) behave similarly to polyacrylates, and show the same family-type behavior. Also, overall glass transitions temperatures are not too different, and poly(muconates) may thus indeed function as substitutes for polyacrylates.

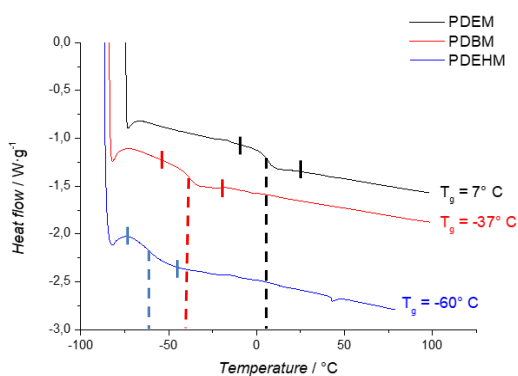


Figure 2 Combined DSC profiles for the poly(dialkyl muconates). Dotted lines indicate the glass transition temperatures

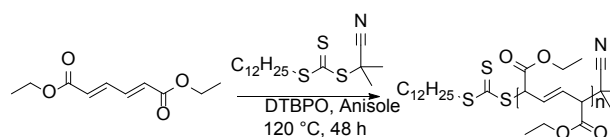
In addition, also TGA was measured under air atmosphere to determine the thermal stability of the obtained polymers. (see SI Figure S 18). The decomposition of PDEM was found to start at above 200 °C and the polymer is fully degraded at around 550 °C. The onset temperature is equal to 271 °C. Following the same trend, the onset of PDBM is at 262 °C. Going to the more

bulky ester chain, PDEHM shows a lowered onset temperature of 258 °C in air compared to the other poly(muconates).

Table 3 T_g of the synthesized poly(muconates) and corresponding acrylate homopolymers

Poly(muconates)	T_g (°C)	Acrylate counterpart ³⁸	T_g (°C) (literature) ³⁸
PDEM	7	Poly(ethyl acrylate)	-24
PDBM	-37	Poly(butyl acrylate)	-54
PDEHM	-60	Poly(2-ethyl-hexyl acrylate)	-64

RDRP: Reversible addition fragmentation chain transfer polymerization



Scheme 4 RAFT polymerization of diethyl muconate using CPD-TTC as RAFT agent.

While high molecular weight polymers obtained via FRP are highly relevant for industrial production of bio-based materials, little control over molecular weight itself is achievable with respect to molecular weight targeting and dispersity control. For this reason, we also investigated reversible deactivation radical polymerizations (RDRP), more specifically reversible addition-fragmentation chain transfer (RAFT) polymerization as further method to obtain poly(muconates). This adds significant value to the polymers obtained, and gives rise to specialty applications. Generally, with higher prices associated with biobased building blocks, high-added value materials are better to target as those will be less dependent on cost of the monomer. RAFT of dienes has been demonstrated before, but is challenging due to the limited reactivity of the monomers as discussed above. Perrier and coworkers polymerized isoprene via thermal RAFT using two different RAFT agents at 60 and 120 °C, obtaining reasonable conversions after extended reaction times of several days. Using 2-cyano-2-propyl benzodithioate (CPBD) as RAFT agent at 60 °C and 93 h reaction time, only 14% conversion was obtained. Using 2-ethylsulfanylthiocarbonyl sulfanylpropionic acid ethyl ester (ETSPE) as RAFT agent at 120 °C and reaction times up to 72 h gave 97% monomer conversion.³⁹ More recently, Junkers and Abetz demonstrated that isoprene can be polymerized rapidly in high temperature photoflow polymerization.⁴⁰ In here, we refrained to thermal batch polymerization to remain consistent with the free-radical

Table 4 Summary of RAFT polymerization conditions for PDEM using CPD-TTC as RAFT agent. Reaction conditions are kept identical to the FRP polymerization: T = 120 °C, solvent = anisole, initiator = DTBPO, [initiator] = $0.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$. $M_n(\text{target})$ refers to molecular weights at 100 % conversion, whereas $M_n(\text{theoretical})$ is adjusted to the experimentally-derived monomer conversion.

Entry	[Monomer] ($\text{mol}\cdot\text{L}^{-1}$)	[RAFT] ($\text{mol}\cdot\text{L}^{-1}$)	Monomer/ RAFT ratio	$M_n(\text{target})$ ($\text{g}\cdot\text{mol}^{-1}$)	Conversion %	M_n (theoretical) ($\text{g}\cdot\text{mol}^{-1}$)	$M_n(\text{SEC})$ ($\text{g}\cdot\text{mol}^{-1}$)	\bar{D}	σ
1	2	0.2	10/1	1.982×10^3	89	1.76×10^3	2.5×10^3	1.2	1.1×10^3
2	2	0.08	25/1	4.955×10^3	78	3.87×10^3	4.2×10^3	1.3	2.3×10^3
3	2	0.04	50/1	9.911×10^3	76	7.53×10^3	7.5×10^3	1.3	4.1×10^3
4	2	0.02	100/1	19.82×10^3	77	15.3×10^3	14×10^3	1.4	8.8×10^3

polymerizations described above (see Scheme 4). Via adjustment of RAFT agent concentrations, we targeted 2000, 5000, 10000 and 20000 $\text{g}\cdot\text{mol}^{-1}$ in diethyl muconates polymerization with 2-cyano-2-propyl dodecyl trithiocarbonate (CPD-TTC) as control agent. The optimized FRP conditions are transferred to the RAFT polymerization as conditions should ideally hold for both reaction modes. An overview of the reaction conditions used is given in Table 4. In order to map the kinetics of the different polymerization reactions, samples were taken after 1, 5, 24, 30, 48 hour(s). The molecular weight evolution is shown in Figure 3, lines given in the Figure represent best linear fits of the data points (SEC results are shown in SI Figure S 19). For all polymerizations, linear progression of the number-average molecular weight is observed. The linearity of the data depicted in Figure 3 is indicative for a well-controlled RAFT polymerization. The slopes are closely approaching the theoretically expected behavior, which also can be used as indication for the excellent control exhibit of the trithiocarbonates over the RAFT polymerization.

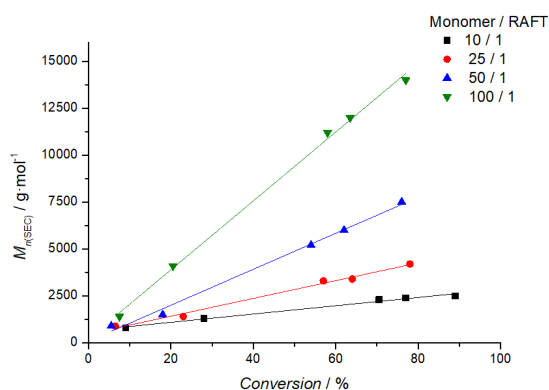


Figure 3 Molecular weight evolution in the RAFT polymerization of diethyl muconate under variation of the [Monomer]/[RAFT] ratio showing the best linear fit of the data points.

Table 4 summarizes the data given in Figure 3 for PDEM, underpinning the good match between theory and experiment. Also dispersities of the polymers are comparatively low, at least within the range seen in RAFT of other dienes, and for methacrylates. Dispersity does though increase when targeting higher molecular weights. This phenomenon is often observed

in controlled diene polymerizations. Butadiene RAFT polymerization yields polymers with dispersities in the range of 1.23-1.48 and isoprene likewise dispersities above 1.2 depending on the used polymerization conditions.^{32, 39}

Conclusions

Starting from muconic acid, a potential bio-based building block, different high molecular weight polyesters $> 100\,000 \text{ g}\cdot\text{mol}^{-1}$ were synthesized in a homogeneous solution using free radical polymerization. Based on the basic properties analyzed within this paper, these polymers are promising materials towards replacement of oil-based polyacrylates while concomitantly giving access to facile post polymerization modifications. Also, the possibility for molecular weight targeting was proven within this research using reversible addition fragmentation chain transfer (RAFT). Molecular weights could be controlled very well in the range of $2.5 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ up to $14 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$. However, further optimization of the polymerization conditions are recommended for industrial processing due to the long reaction times of 48 hours. Therefore, further optimization of the polymerization conditions and more in-depth measurement of the polymeric properties will be subject of future research.

Conflicts of interest

No conflict of interests to declare.

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