



HAL
open science

An Expedient Route to Bio-Based Polyacrylate Alternatives with Inherent Post-Chemical Modification and Degradation Capabilities by Organic Catalysis for Polymerization of Muconate Esters

Thomas Dardé, Émilie Diomar, Xavier Schultze, Daniel Taton

► To cite this version:

Thomas Dardé, Émilie Diomar, Xavier Schultze, Daniel Taton. An Expedient Route to Bio-Based Polyacrylate Alternatives with Inherent Post-Chemical Modification and Degradation Capabilities by Organic Catalysis for Polymerization of Muconate Esters. *Angewandte Chemie International Edition*, 2024, 63 (50), <10.1002/anie.202411249>. <hal-04835567>

HAL Id: hal-04835567

<https://hal.science/hal-04835567v1>

Submitted on 13 Dec 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY-NC-ND 4.0 - Attribution - Non-commercial use - No Derivative Works - International License

An Expedient Route to Bio-based Polyacrylate Alternatives with Inherent Post-chemical Modification and Degradation Capabilities by Organic Catalysis for Polymerization of Muconate Esters

Thomas Dardé,^[a] Émilie Diomar,^[a] Xavier Schultze,^[b] and Daniel Taton*^[a]

[a] T. Dardé, E. Diomar, Prof. D. Taton
Laboratoire de Chimie des Polymères Organiques (LCPO), Université de Bordeaux INP-ENSMAC, 16 av. Pey Berland, 33607 Pessac cedex, France
Email: taton@enscbp.fr

[b] Dr. X. Schultze
L'Oréal Research & Innovation, 1 Avenue Eugène Schueller, 33601 Aulnay Sous-Bois, France

Supporting information for this article is given via a link at the end of the document.

Abstract: The quest for polymers that would be at the same time bio-based and degradable after usage, in addition to offering chemical post-modification options, remains a daunting challenge in contemporary polymer science. Despite advances in polymer chemistry, attempts at controlling the chain-growth polymerization of muconate esters remain unexplored. Here we show that dialkyl muconates can be rapidly polymerized by organocatalyzed group transfer polymerization (O-GTP). O-GTP is conducted to completion at room temperature in toluene within a few minutes, using 1-ethoxy-1-(trimethylsiloxy)-1,3-butadiene (ETSB) as initiator and 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2,2,5,4,15 catenadi(phosphazene) ($P_4-t\text{-Bu}$) as catalyst. Chain extension experiments and synthesis of all muconate-type block copolymers can also be achieved. Furthermore, polymuconates are amenable to facile post-polymerization modification reactions. This is showcased through the hydrolysis of the ester side chains leading to well-defined poly(muconic acid), and by epoxidation of the C=C double bonds of the main chain. Last but not least, these internal alkene groups can be selectively cleaved by ozonolysis, demonstrating the upcyclability of polymuconates under oxidative conditions. This work demonstrates that polymuconates constitute a unique platform of bio-based polymers, easily modifiable in addition to being chemically degradable under user friendly experimental conditions.

Introduction

Plastics have developed in a strictly linear economic mode, with far too little being truly recycled (< 20%)^[1,2] and using mostly fossil resources for their production.^[3] The awareness that end-of-life of plastics is causing a major environmental threat has sparked new initiatives to position them at the heart of a circular economy.^[4–6] Hardly a week goes without an article appearing in leading journals, dealing with mechanical recycling of polymers, chemical recycling to monomer, or upcycling of polymers to value-added chemicals.^[7–24] In this context, polymerization methods enabling to install degradable bonds in the polymer backbone and aiming to program the (bio)degradation of the final material, while maintaining its functional properties during service, appear very attractive.^[25–32] New classes of chemically recyclable, upcyclable or biodegradable polymers have thus

emerged. For instance, some aliphatic polyesters made by ring-opening polymerization of moderately strained cyclic esters hold great promises as closed-loop recyclable polymers.^[9,10,33] As for vinyl polymers, which are constituted of robust C-C bonds, they can be made more easily degradable by incorporating weak bonds (e.g. esters, thioesters, etc.) through the use of specific co-monomers, following a copolymerization strategy (Figure 1).^[34,35] Representative co-monomers endowing degradability to vinyl polymers include cyclic ketene acetals,^[36–39] thiolactones,^[38,40–42] or carbon monoxide (CO) when copolymerized with ethylene.^[43] Labile halogens groups can also be incorporated in the copolymer backbone for further chemical degradation by a radical mechanism.^[44–50] Although very elegant, this bottom-up approach is sometimes restrictive in terms of monomer and/or catalyst design, cost and scale-up. These limitations might be overcome if commercial monomers could be used from the outset, with the resulting polymers providing both the desired application performance and degradability properties. Such an “ideal plastic”, *i.e.*, combining suitable thermomechanical properties, low production costs and programmed degradation/recycling capabilities, while reducing our dependence on fossil resources, remains a major challenge for future research and development in polymer science. To tackle this challenge, at least in part, we hypothesized that the potential of dialkyl muconate esters could be better explored. By virtue of their structure, these monomers indeed incorporate multiple options and functionalities, including i) the ability to control the structure of the resulting polymers, ii) a variation of the nature of the alkyl side groups, iii) a modularity for post-chemical modification of polymuconates, iv) a facile degradation after usage, in addition to their v) bio-sourced origin. All these attributes could make polymuconates a new platform of bio-sourced alternatives of poly(meth)acrylates, the physicochemical properties of which can be modulated at will. Muconate esters derive from muconic acid (MA), referred to as 2,4-hexadienedioic acid, a high-value compound that is both a conjugated diene and a dicarboxylic acid. Several bio-sourced synthesis routes to MA have been developed since the 1980s^[51,52] and many production sources are currently being considered, in particular biotechnologies through fermentation (bacteria, yeast) of lignin or glucose derivatives.^[53–56]

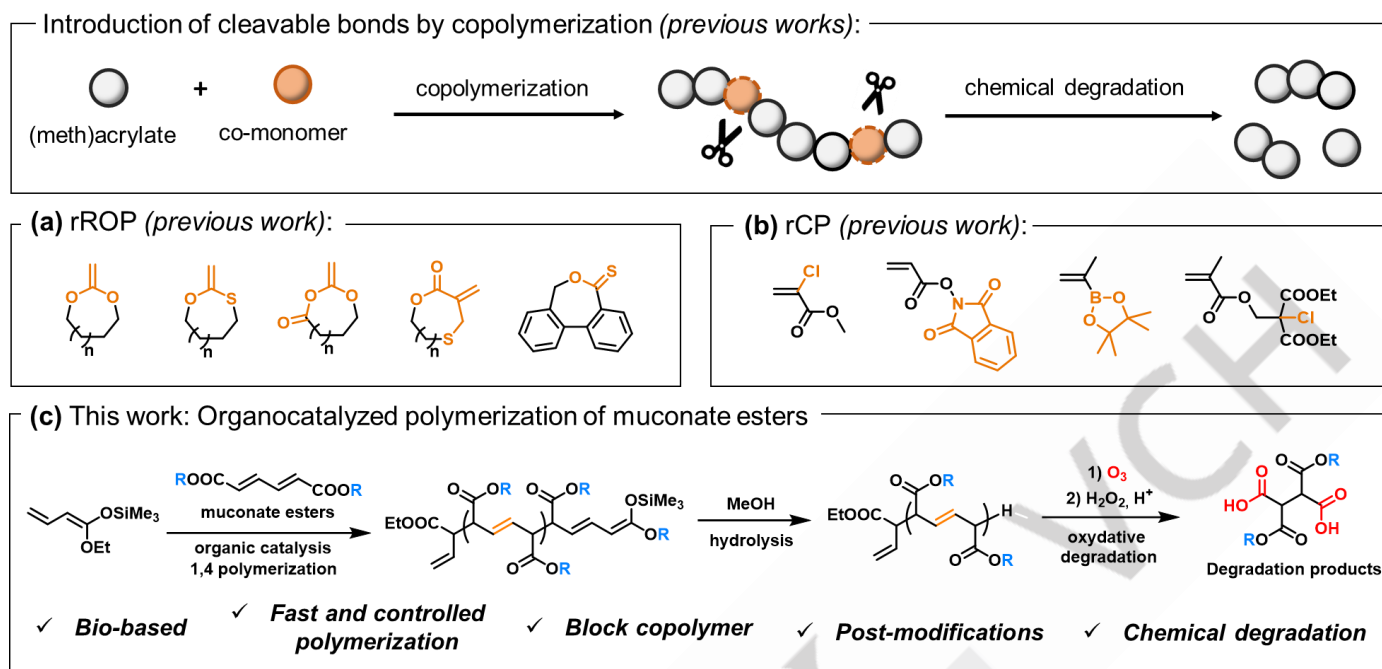


Figure 1. Strategies for introducing cleavable units into a vinyl chain by copolymerization and representative examples of monomers used for: (a) radical ring-opening (co)polymerization (rROP) and (b) radical copolymerization with a (meth)acrylate; (c) organocatalyzed group transfer polymerization (O-GTP) of bio-based muconate esters developed in this work, introducing cleavable unsaturation-containing units in the polymer backbone.

MA in fact exists in three distinct isomeric forms, namely, *cis,cis*-MA, *cis,trans*-MA and *trans,trans*-MA, which can serve as important synthons of platform chemicals, such as adipic acid and terephthalic acid.^[52,57,58] Polymers resulting from both step- and chain-growth polymerization modes feature C=C double bonds in the backbone, allowing for further post-polymerization modifications as a means to tune the properties of poly(muconates). Whereas step-growth polymerization by polycondensation of MA is documented,^[59] poly(muconate) synthesis by chain-growth polymerization of MA and muconate esters remains underexplored. The Matsumoto group developed the so-called topochemical 1,4-polymerization of dialkyl muconates consisting in photo-irradiating the monomers in their crystalline-state, forming stereoregular polymer chains.^[60–64] More recently, Junkers *et al.* reported the solution free-radical polymerization of dialkyl muconates, forming high molecular weight polymers (>100 000 g mol⁻¹).^[65] Monomers could also be polymerized in a controlled fashion by the reversible addition fragmentation chain transfer (RAFT) process. However, polymerization reactions proved very sluggish, *i.e.* 48 h at 120 °C to reach high monomer conversion.^[65]

Alkyl sorbates show structural analogies with alkyl muconates as polar conjugated dienes. Unlike muconates, however, alkyl sorbates have been the subject of a number of polymerization studies, either by living anionic polymerization (LAP),^[66] anionic-coordinated polymerization,^[67,68] Lewis pair polymerization (LPP)^[69,70] or group transfer polymerization (GTP).^[71,72] The latter method contrasts with many “controlled/living” polymerization methods, as GTP can be

conducted at room temperature and does not employ any sulfur-containing controlling agent, or a metallic catalyst or a halogenated initiator^[73,74]. This is particularly important for specific applications, *e.g.*, in cosmetics, electronics or food applications, where the presence of contaminants may be detrimental and require additional purification steps. GTP is industrially developed to produce methacrylate-based copolymers used as dispersants for pigments,^[75] emulsifiers^[76] and cosmetic stabilizing agents.^[77] With the emergence of organic catalysts for polymerization,^[78–84] the GTP route has seen further advances over the past 15 years, including a wider range of polymerizable monomers^[85–88] and a variety of readily available block copolymers.^[87,89–94] To our knowledge, only one reference mentions a GTP process involving *trans,trans*-diethyl muconate. The few examples of polymerization in THF report polymers with low molar mass and high dispersity, indicating a lack of control over the reaction.^[95] Thus, rapid and efficient controlled polymerization of muconate esters is still lacking. Here, we report suitable conditions for very fast organocatalyzed GTP (O-GTP) of various dialkyl muconate esters. The resulting poly(muconate ester)s represent a very rare example of vinyl polymers being at the same time bio-based, subject to facile post-polymerization modification reactions and chemically degradable.

Results and Discussion

Synthesis and organocatalyzed group transfer polymerization (O-GTP) of *trans,trans*-dialkyl muconates.

All monomers were readily synthesized in high yields from the esterification of MA with the corresponding alcohol, following the procedure described in the supporting information. In all cases, solid compounds were obtained and could all be purified by recrystallization to obtain white solid crystals, as illustrated in Figure 2 (see also Figures S3 to S10). Monomers were conceived by varying the length of the alkyl chains, in order to vary the final properties of the corresponding polymers. Monomers thus synthesized in this work include diethyl muconate (DEM), di-*iso*-propyl muconate (DIM), di-*tert*-butyl muconate (DtBuM) and di-*n*-octyl muconate (DOM). The advantages of handling pure solids are obvious, especially when compared with standard alkyl acrylates and methacrylates, which are often toxic and smelly liquids.

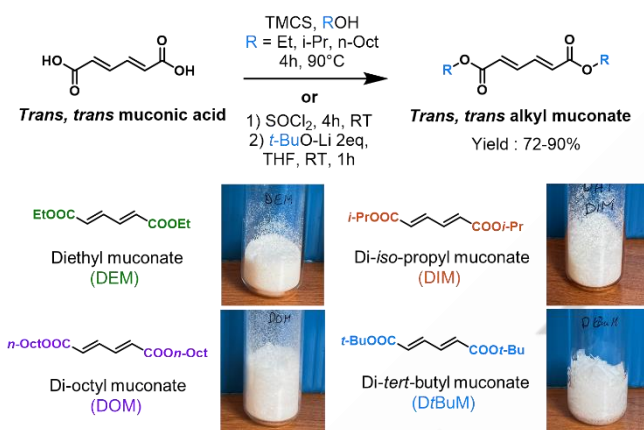


Figure 2. Synthesis of crystallized alkyl muconate esters from muconic acid.

We then focused our efforts on screening different organic catalysts to attempt controlling the polymerization of *trans,trans*-diethyl muconate (DEM). As a reminder, the GTP method uses small amounts of catalyst compared to the silyl ketene acetal (SKA) as an initiator, typically under the following conditions: [Monomer]/[Initiator]/[Catalyst] = 20-500/1/0.01-0.1. GTP of DEM was first investigated in toluene at room temperature (RT) using 1-ethoxy-1-(trimethylsiloxy)-1,3-butadiene, denoted as ETSB, as SKA initiator. ETSB was selected rather than 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (MTS), because the structure of ETSB better mimics the expected growing poly(muconate) chains, while MTS is the benchmark GTP initiator for methacrylics. Out of the different organic catalysts we tested, only the strong organic base P₄-*t*-Bu led to the formation of polymer (Table 1). Neither the Lewis acid Me₃NTf₂, in contrast to the GTP of alkyl sorbates,^[71] nor bases such as tetrabutyl ammonium fluoride (TBAF), P₁-*t*-Bu and P₂-*t*-Bu phosphazene bases, were indeed able to polymerize DEM under these conditions (Table 1, entries 1-4), already highlighting a specific

reactivity of this monomer, compared to others previously examined by GTP.^[71,82,92] Remarkably, the polymerization of DEM catalyzed by P₄-*t*-Bu proved to be very fast, *i.e.*, achieving full conversion of DEM in less than a minute (Figure 3a), contrasting with results obtained by RAFT polymerization.^[65] The linear evolution of Ln[M]₀/[M] as a function of time, on the one hand, and of molar masses with monomer conversion, on the other, indicate the virtual absence of termination and transfer reactions, during this GTP process (Figure 3c and Figure S16, respectively). Using a [P₄-*t*-Bu]₀/[ETSB]₀ molar ratio higher than 1 mol.% did not improve the control, while a lower ratio of 0.5 mol.% did not achieve complete monomer conversion (Table 1, entries 5-8) under otherwise identical conditions. Analysis by ¹H NMR spectroscopy of a typical poly(diethyl muconate) (PDEM, Table 1, entry 7, Figure S19) showed the presence of both alkene protons, H_a at 4.98-5.85 ppm, and methine protons H_b at 3.10-3.89 ppm of the polymer backbone, as a result of exclusive 1,4-conjugated addition reactions of the polar dienic monomer. Protons of ester-bonded ethyl groups (H_c) were also distinguished at 3.89-4.28 ppm. Further analysis by ¹³C NMR spectroscopy allowed us to determine the *trans*-to-*cis* ratio of the C=C double bonds of PDEM obtained in this way. Multiplet peaks assignable to the methine carbon atom -CHCO₂- (Figure 3b, peak d) were found at 51.3 and 46.8 ppm, corresponding to the *trans* and the *cis* structure, respectively (Figure 3b; see also Figure S23). Integration of these peaks led to a *trans* content equal to 80.2 %. Next, polymerization of DEM carried out in the presence of increasing amounts of [DEM]₀/[ETSB]₀ ratio, at [P₄-*t*-Bu]₀/[ETSB]₀ molar ratio equal to 1 mol.%, led to the formation of PDEM's with increasingly higher molar masses, suggesting some degree of control over the poly(muconate) chain size (Table 1, entries 8-11; Figure 3d). PDEM₁₀₀ and PDEM₃₀₀ were characterized by SEC using two laser light scattering (LS) detectors, *a priori* enabling true molar mass values to be calculated. Such a LS/SEC analysis required prior determination of the PDEM refractive index increment (dn/dc value) in THF at 658 nm, using a differential refractometer (ESI, Fig. S26). The M_{n,SEC,LS} values thus determined (Figure S27) turn out to be higher than the apparent molar masses M_{n,SEC,PS} and M_{n,SEC,PMMA} (Table S2); they are also higher than the theoretical values calculated from the initial molar ratio of monomer to the initiator. These results could be explained by a non-quantitative initiation of the O-GTP of DEM by ETSB. On the other hand, GTP-derived PDEM's exhibit relatively high dispersity values (*D*), *i.e.*, ranging from 1.50 to 1.72 (Table 1). Due to the strongly basic character of P₄-*t*-Bu (pK_a = 42.1), GTP catalysis by this base follows an anionic-like dissociative mechanism,^[82] involving active centers, namely, phosphazanium diene-enolate anions, and dormant phosphazanium silyl bis-(diene-enolate) siliconate anionic species (Scheme 1). In order to achieve optimal "controlled/living" polymerization, exchange reactions between bare active diene-enolates and dormant species should be faster than the rate of propagation. This is probably not the case here, as P₄-*t*-Bu-catalyzed GTP of DEM is particularly fast, and therefore probably faster than these exchange reactions, which may explain the somewhat high dispersity values of the PDEM samples.

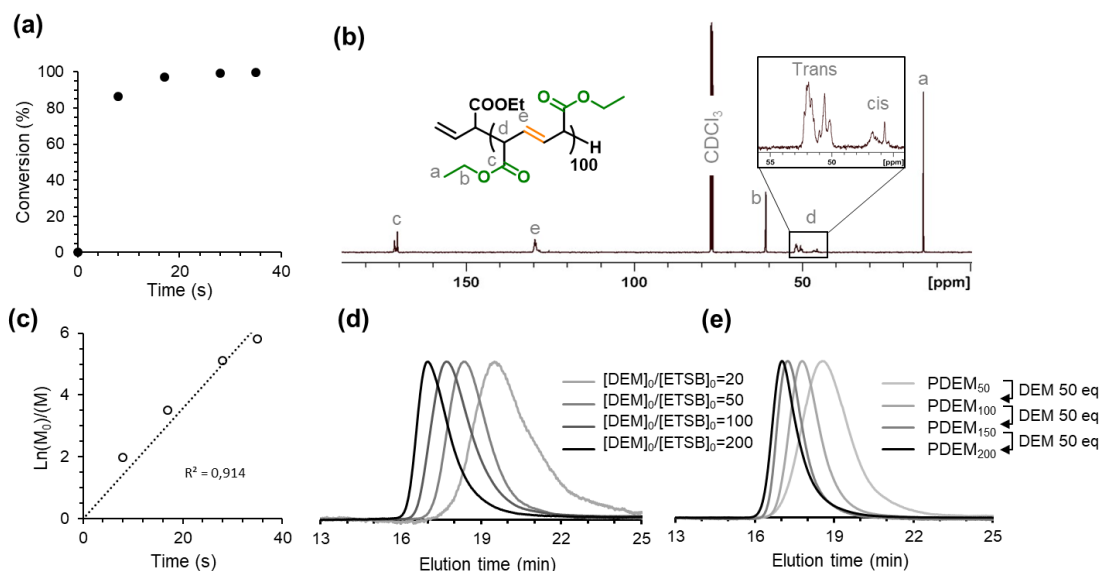


Figure 3. (a) Monomer conversion vs. time for the GTP of DEM in toluene at RT; [DEM]₀/[ETSB]₀/[P₄-t-Bu]₀ = 100/1/0.01; (b) ¹³C NMR spectrum of PDEM₁₀₀ in CDCl₃; (c) Evolution of ln([M]₀/[M]) vs. time for the GTP of DEM in toluene at RT; [DEM]₀/[ETSB]₀/[P₄-t-Bu]₀ = 100/1/0.01 (d) SEC traces of PDEM's from [DEM]₀/[ETSB]₀/[P₄-t-Bu]₀ = 20-200/1/0.01. (e) SEC traces of a parent GTP-derived PDEM (PDEM₅₀) and PDEM's after chain extension experiments involving subsequent additions of 50 eq. of DEM in each case, after 1 min of reaction.

A similar observation was made by Chen *et al.* in the case of the dissociative GTP of alkyl sorbates mediated by the same P₄-t-Bu base.^[71] One can thus hypothesize that both dormant and active species deriving from muconate esters exhibit a higher stability due to conjugation, compared to enolate-type species involved in GTP of (meth)acrylic monomers, and even perhaps to those deriving from alkyl sorbates.^[71,84]

To assess further the degree of control of these GTP reactions using ETSB and P₄-t-Bu, chain extension experiments were performed. After synthesis of a PDEM₅₀ by GTP in toluene, several successive additions of DEM yielded chain-extended PDEM samples showing a systematic shift of SEC traces towards the higher molar mass region. A symmetric and unimodal distribution was maintained ($\mathcal{D} \leq 1.5$; Table S4), attesting to an efficient re-initiation of GTP from the parent PDEM chains (Figure 3e). This GTP method proved to be compatible with a range of muconate esters. The three other dialkyl muconates synthesized, DIM, DfBuM and DOM, could indeed be polymerized very rapidly, as summarized in Table 1 (entries 12-21; see also Figure 4). The same conditions set up for the GTP of DEM allowed us to achieve almost quantitative yields with similar reaction rates, *i.e.*, complete monomer conversion was reached within 5 min. Figure 4 shows that SEC traces of the resulting PDIM's, PDfBuM's and PDOM's exhibit a relatively narrow and unimodal distribution of molar masses, along with a clear shift to the higher molar mass region upon increasing the initial [muconate ester]₀/[ETSB]₀ ratio (see also Figures S32-S35 and Table S2 for the determination of $M_{n,SEC/LS}$ for PDfBuM₁₀₀ and PDOM₁₀₀). Dispersity values are found in the same range as in the case of PDEM samples

described above, with the noticeable exception of PDfBuM's ($\mathcal{D} \leq 1.23$). One explanation in the latter case is that the GTP of DfBuM exhibits a lower propagation rate, compared, for example, with DEM. This is evidenced through the comparison of the first-order kinetic plot between the two monomers (Fig. S18). The rate of exchange between active and dormant species may be fast enough, relatively to the rate of propagation, in the case of the dissociative GTP of DfBuM. This consequently leads to lower dispersity values for PDfBuM's.

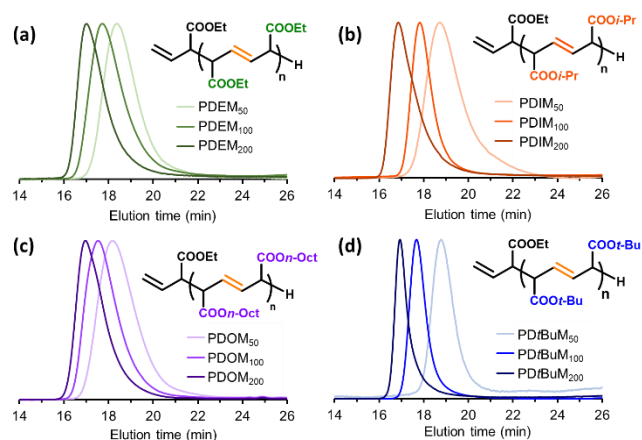


Figure 4. SEC traces of (a) PDEMs, (b) PDIMs, (c) PDOMs and (d) PDfBuMs obtained by GTP (Table 1, entries 7,9-21).

Table I. Group transfer polymerization of di-alkyl muconates at 25°C.

| Entry | Monomer | Catalyst | t. (h) | Conv. ^[a] (%) | [M] ₀ /[I] ₀ /[Cat.] ₀ ^[b] | M _{n,th.} ^[c] (g.mol ⁻¹) | M _{n,SEC} ^[d] (g.mol ⁻¹) | Đ ^[f] |
|-------|---------|----------------------------------|--------|--------------------------|--|--|--|------------------|
| 1 | DEM | TBAF | 72 | 34.9 | 100/1/0.1 | 19 900 | - | - |
| 2 | DEM | P ₁ - <i>t</i> -Bu | 72 | 4.5 | 100/1/0.05 | 19 900 | - | - |
| 3 | DEM | P ₂ - <i>t</i> -Bu | 72 | 1.8 | 100/1/0.05 | 19 900 | - | - |
| 4 | DEM | Me ₃ NTf ₂ | 48 | <1.0 | 100/1/0.05 | 19 900 | - | - |
| 5 | DEM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 100/1/0.05 | 19 900 | 18 100 | 1.75 |
| 6 | DEM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 100/1/0.02 | 19 900 | 26 300 | 1.77 |
| 7 | DEM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 100/1/0.01 | 19 900 | 29 400 ^[e] | 1.56 |
| 8 | DEM | P ₄ - <i>t</i> -Bu | 0.017 | 97.7 | 100/1/0.005 | 19 900 | 36 500 | 1.50 |
| 9 | DEM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 50/1/0.01 | 10 000 | 23 000 | 1.56 |
| 10 | DEM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 200/1/0.01 | 39 800 | 66 600 | 1.72 |
| 11 | DEM | P ₄ - <i>t</i> -Bu | 0.017 | 96.5 | 300/1/0.01 | 59 600 | 69 600 ^[e] | 1.56 |
| 12 | DOM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 50/1/0.01 | 18 400 | 25 500 | 1.49 |
| 13 | DOM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 100/1/0.01 | 36 800 | 42 800 ^[e] | 1.56 |
| 14 | DOM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 200/1/0.01 | 73 400 | 57 700 | 1.64 |
| 15 | DOM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 300/1/0.01 | 110 100 | 99 800 | 1.53 |
| 16 | DIM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 50/1/0.01 | 11 400 | 17 000 | 1.39 |
| 17 | DIM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 100/1/0.01 | 22 700 | 39 900 | 1.30 |
| 18 | DIM | P ₄ - <i>t</i> -Bu | 0.017 | 100 | 200/1/0.01 | 45 400 | 66 100 | 2.01 |
| 19 | DfBuM | P ₄ - <i>t</i> -Bu | 0.051 | 100 | 50/1/0.02 | 12 800 | 24 500 | 1.15 |
| 20 | DfBuM | P ₄ - <i>t</i> -Bu | 0.051 | 100 | 100/1/0.02 | 25 500 | 42 900 ^[e] | 1.21 |
| 21 | DfBuM | P ₄ - <i>t</i> -Bu | 0.051 | 100 | 200/1/0.02 | 51 000 | 93 500 | 1.23 |

^[a] Conversion determined by ¹H NMR. ^[b] [M]₀/[I]₀/[Cat.]₀ represents the [Monomer]₀/[Initiator]₀/[Catalyst]₀ ratio. ^[c] Theoretical number molar mass calculated with ([M]₀/[Initiator]₀) × (M_w of DEM = 198.22 g.mol⁻¹, DOM = 366.54 g.mol⁻¹, DIM = 226.27 g.mol⁻¹, DfBuM = 254.33 g.mol⁻¹) + chain ends (-C₆H₉O₂ and -H = 114.1 g.mol⁻¹). ^[d] Average number molar mass determined by SEC (THF, 40°C relatively to PMMA standards). ^[e] dn/dc values and molar masses determined by LS/SEC are provided in Figures S27, S34-35 and Table S2. ^[f] Dispersity value determined by SEC.

The chemical structures of these polymuconates were also confirmed by ¹H and ¹³C NMR spectroscopy (Figures S19-25). The presence of the characteristic peak due to the vinylic protons around 5.0–5.9 ppm could be assigned to monomer units resulting from 1,4-conjugated addition reactions, ruling out the occurrence of 1,2- and 3,4-additions. The *cis*-/*trans*-configuration ratio was also quantified through analysis by ¹³C NMR spectroscopy, to give the following results: 81.9 and 87.7% of *trans* units for PDIM and PDOM, respectively. It is worth of note that polymuconate chains are terminated by a SKA group right after the GTP reactions (Figure 1; see also Scheme 1). However, addition of benzoic acid or MeOH during workup enables to hydrolyze these SKA end groups to enol esters, rearranging into ester functions, hence the final polymuconates are free of silyl groups at their chain ends (Scheme 1).

The MALDI-TOF mass spectrum of a P₄-*t*-Bu-catalyzed GTP-derived PDEM, with a theoretical degree of polymerization equal to 8, is shown in Figure 5. The presence of a major population of peaks attributable to the expected polymer structure, *i.e.*, resulting from GTP initiation by ETSB, is clearly observed, with a peak-to-peak mass increment of 198.1 g.mol⁻¹, corresponding to the molar mass of a DEM unit, and both chain ends with a total molar mass of 114.1 g.mol⁻¹.

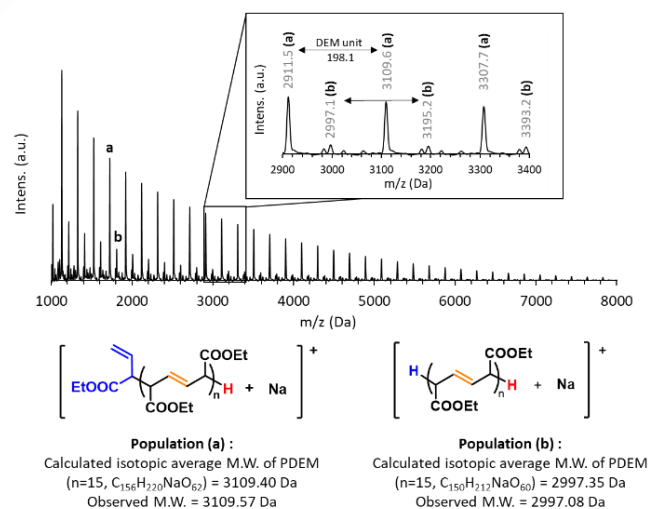
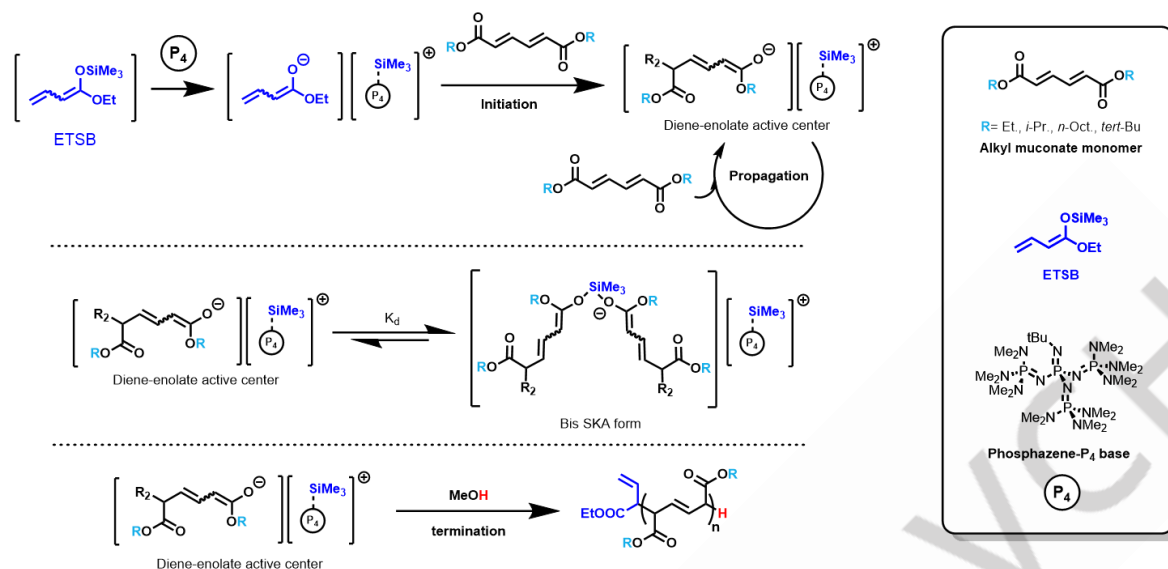


Figure 5. MALDI-TOF MS spectrum of PDEM₈ (M_{n,th.} = 1 700 g.mol⁻¹, M_{n,SEC}: 3 600 g.mol⁻¹, Đ = 1.32) synthesized by P₄-*t*-Bu-catalyzed GTP; the structure of the two populations (a) and (b) is also shown.



Scheme 1: Dissociative mechanism of P_4 -*t*-Bu catalyzed GTP of trans,trans-dialkyl muconates, initiated by 1-ethoxy-1-(trimethylsilyloxy)-1,3-butadiene (ETSB).

Another minor population was also noted in the MALDI-TOF mass spectrum though, which we attributed to polymuconate chains featuring a hydrogen atom at both chain ends (Figure 5, population (b); see also Figures S38). Although we cannot yet explain with certainty the origin of this low-intensity population, two hypotheses can be put forward. The first relates to the ionization of polymuconate chains during MALDI-TOF analysis, which may cleave relatively fragile bonds, in this case carbon-carbon bonds where each carbon atom carries a lateral ester function. A schematic representation of this putative C-C bond chain breaking is displayed in Scheme S2. This chain fragmentation occurring during MALDI-TOF analysis would explain the low molar mass value of the resulting PDEM chains. Another hypothesis is that these chains carrying a hydrogen atom at each end are generated during GTP synthesis *via* a side reaction, where a growing polymuconate chain could expel a hydride capable of initiating new chains. In other words, this would be a transfer reaction to the monomer (see Scheme S3 for a detailed mechanism). A new series of PDEM's were then synthesized using increasing amounts of P_4 -*t*-Bu, in this case 0.5, 1 and 5% relatively to ETSB, targeting DP = 100. Analysis MALDI-TOF MS of these samples revealed that a higher amount of catalyst increased the intensity of population (b) with a hydrogen atom at each chain end (Fig. S39), suggesting the possible occurrence of transfer reactions at too high concentration of catalytic base.

DSC analysis indicated that all poly(muconate ester)s were amorphous, with a broad range of values of their glass transition temperature (T_g), from -55 to 66°C, depending on the alkyl groups (Table S3 and Figure S40). The thermomechanical properties of polymuconates can therefore be adapted, as a function of the intended performances and related applications. As expected, and consistently with poly(meth)acrylate homologues, increasing the linear *n*-alkyl side chain caused a

significant decrease of the T_g value, e.g., $T_g = 9.3$ vs. -54.8 °C for PDEM₁₀₀ and PDOM₁₀₀, respectively. On the other hand, T_g values of polymuconates proved to be higher than those of polyacrylate analogues. Dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) of polymuconates were also performed, confirming that their thermomechanical properties strongly depend on the side alkyl chains (Fig. S41-S42 and Table S4). Below T_g , polymuconates exhibit a storage modulus one order of magnitude lower (10^8 - 10^9 Pa) to that of methacrylate-based materials.^[96] Their 5% weight loss decomposition temperature was found intermediate to that of polyacrylate and polymethacrylate counterparts, *i.e.* with the same side alkyl substituent (see degradation profile Fig. S43-S44).^[97] On the other hand, the decomposition temperature of PD*t*BuM proved to be lower than that of other polymuconates, as is also the case for poly(*tert*-butyl (meth)acrylate), which is explained by release of *tert*-butyl groups upon heating, forming volatile isobutene.

Synthesis of all polymuconate-based block copolymers by sequential O-GTP.

We sought to investigate the sequential GTP to achieve all-muconate block copolymers (BCP's). Table II summarizes the results of these P_4 -*t*-Bu-catalyzed sequential GTP attempts. Both well-defined AB and ABA-type BCP's could thus be synthesized sequentially in toluene (Table S7). Both monomers, namely DEM and DOM, were added either in this order, *i.e.*, DEM then DOM or in the other, *i.e.*, DOM then DEM. Synthesis of a well-defined PDEM-*b*-PDOM BCP was first achieved using 50 eq. of DEM rel. to ETSB as initiator, giving a PDEM precursor ($M_n = 19\,000$ g.mol⁻¹; $\bar{D} = 1.42$) after 1.0 min and full monomer conversion. Further addition of 50 eq. of DOM showed a shift to the higher molar masses ($M_n = 39\,600$ g.mol⁻¹; $\bar{D} = 1.48$; Figure 6b), demonstrating an effective crossover reaction.

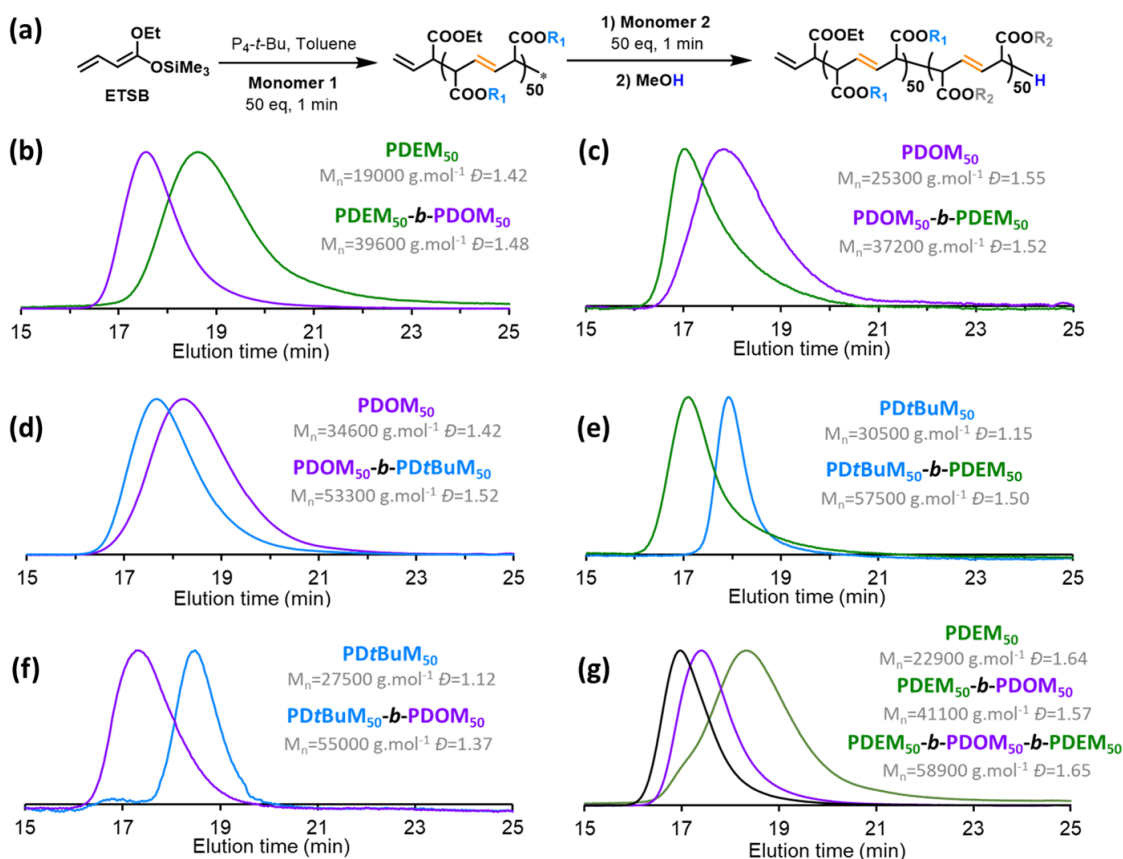


Figure 6. (a) Block copolymer synthesis by sequential P_4 -*t*-Bu-catalyzed GTP in toluene (Table S7); SEC traces in THF of (b) PDEM₅₀-b-PDOM₅₀ (entry 1); (c) PDOM₅₀-b-PDEM₅₀ (entry 2); (d) PDOM₅₀-b-PDtBuM₅₀ (entry 3); (e) PDtBuM₅₀-b-PDEM₅₀ (entry 4); (f) PDtBuM₅₀-b-PDOM₅₀ (entry 5); (g) PDEM₅₀-b-PDOM₅₀-b-PDEM₅₀ (entry 6).

Interestingly, a well-defined PDOM-*b*-PDEM BCP could also be achieved by reversing the order of addition of the two monomers (entry 2, Table S7, Figure 6c). Other BCP's were also achieved, namely, PDOM₅₀-*b*-PDtBuM₅₀ (entry 3, Figure 6d); PDtBuM₅₀-*b*-PDEM₅₀ (entry 4, Figure 6e) and PDtBuM₅₀-*b*-PDOM₅₀ (entry 5, Figure 6f). Thus, BCP's based on all-muconate units can be obtained in less than 3 minutes by a sequential GTP route, without the need to purify the block precursor for the growth of the next block, which greatly facilitate the synthesis procedure. This represents an undeniable advantage of the GTP route, compared in particular to controlled radical polymerization methods for which a progressive loss of control is often observed due to the occurrence of side reactions at high monomer conversions. On this basis, a PDEM-*b*-PDOM-*b*-PDEM triblock copolymer was also synthesized sequentially, namely, by adding DEM, DOM and DEM in this order (Table S7, entry 6). Monomers were again quantitatively consumed in less than 1 min. after each sequence. The resulting (co)polymers showed unimodal SEC traces, as illustrated in Figure 6g. Analysis by ¹H NMR spectroscopy confirmed the chemical structure of the different BCP's achieved and their composition could also be estimated. For instance, the proportion in each monomer unit was determined from the relative integrations of the signal at 5.19 - 5.87 ppm, assigned to both DEM and DOM methine proton of the

main chain, and the signal at 0.82-0.93 ppm due to the methyl protons of the DOM unit (Figure S63, peak g). Assuming the PDEM precursor has a total molar mass of 10 000 g.mol⁻¹ (Table S7, entry 1), the M_n value of the PDEM-*b*-PDOM BCP could be estimated at 28 400 g.mol⁻¹. Similarly, the composition of the other GTP-derived BCP's were estimated by ¹H NMR by the relative integrations of characteristic signals of methyl protons at 0.73 - 0.92 ppm for the DOM unit, or methyl protons of *tert*-butyl at 1.32 - 1.98 ppm for the DtBuM unit (Figures S64 - S66), compared with the methine protons of the main chain. In this manner, the M_n value of the PDEM-*b*-PDOM-*b*-PDEM BCP could be estimated at 58 900 g.mol⁻¹.

Post-polymerization modification and chemical degradation of polymuconates.

Another distinctive advantage of polymuconate esters, over poly(meth)acrylates, relates to the presence of internal C=C double bonds, making polymuconates amenable to many post-polymerization modification (PPM) reactions. As an example, we derivatized a parent PDtBuM into an epoxidized polymuconate, *i.e.*, by subjecting the double bonds of PDtBuM to an epoxidation reaction, by treatment with *m*-CPBA (Figure 7a). This PPM reaction was successfully accomplished, as confirmed by the complete disappearance of the vinylic protons (signal a at

RESEARCH ARTICLE

5.10–5.80 ppm) in the ^1H NMR spectra, before and after epoxidation (Figure 7).

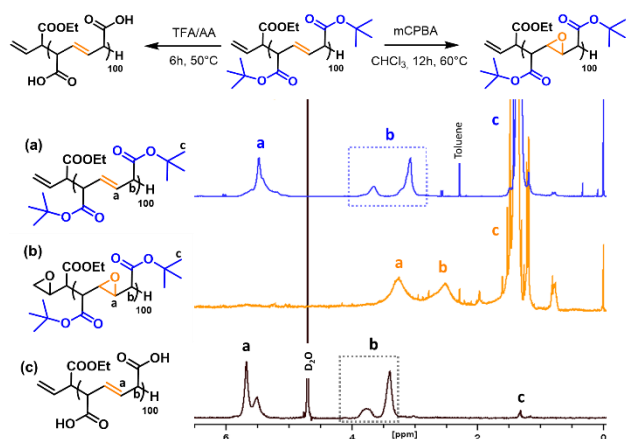


Figure 7. ^1H NMR of (a) PDtBuM₁₀₀ in CDCl_3 ; (b) PDtBuM in CDCl_3 after epoxidation with 4 eq of mCPBA, 12 h at 60 °C; (c) PMA₁₀₀ in D_2O from hydrolysis of PDtBuM₁₀₀ in acetic acid/trifluoroacetic acid solution (4:1, V/V).

In addition, diagnostic signals assigned to the epoxidic protons appeared at 3.0–3.7 ppm. Further analysis by FT-IR confirmed that signals due to the internal trans C=C double bonds (970 cm^{-1} , peak g, Figure S76) totally vanished after epoxidation, while a characteristic peak due to the epoxy group was detected at 910 cm^{-1} (peak h', Figure S76). As expected, the presence of internal epoxide functions, instead of double bonds, changed the T_g value, which increased from 9.3 to 29.2 °C, before and after epoxidation of PDEM₁₀₀ (Table S3), owing to the more rigid nature of the three-member ring epoxides. Many other PPM reactions of the internal double bonds of poly(muconates) could be envisaged, such as hydrogenation, hydroamination or hydrohalogenation reactions, or thiol-ene click chemistry reactions, which will be the topic of a forthcoming paper. Hydrolysis of ester groups represents another obvious possibility for the PPM of GTP-derived poly(muconates), leading to structurally well-defined poly(muconic acid) (PMA) chains. To account for this, two types of poly(muconates) were used as precursors to be hydrolyzed under different PPM reaction conditions, in this case, PDEM and PDtBuM (Figure 7 in the latter case; see also Scheme S5). PDEM was thus treated using NaOH in ethanol at RT, whereas PDtBuM was hydrolyzed under acidic conditions, with a mixture of acetic and trifluoroacetic acids (4:1 in vol.). The disappearance of the signals of the alkyl group (peak Figure 7c) in the ^1H NMR spectra confirmed the efficacy of the deprotection step (>98%), leading in both cases to a water-soluble PMA without affecting the internal C=C double bonds (peaks a and b, Figure 7c). Molar masses determined by SEC before and after modification did not reveal any degradation of the poly(muconate) chains, either for the epoxidation or for the hydrolysis reaction (Table S8, see also figure S77).

The final step in validating poly(muconates) as a versatile platform of new bio-sourced polymers was to demonstrate their chemical degradability. To this end, we again leveraged the

poly(muconate)'s internal alkene functions to efficiently cleave them with ozone (O_3). Ozonolysis is extensively applied for the oxidative cleavage of alkenes, a method showing broad substrate scope and that is relatively easy to implement, including at the industrial scale for the treatment of wastewater.^[98] Use of ozone to oxidize natural or synthetic dienic rubbers has been intensively investigated, as a means to understand the structure and monomer sequence of these rubbers and/or to synthesize telechelic oligomers.^[99,100] A PDEM precursor was thus used as a representative poly(muconate) ester to be cleaved by ozone (Figure 8).

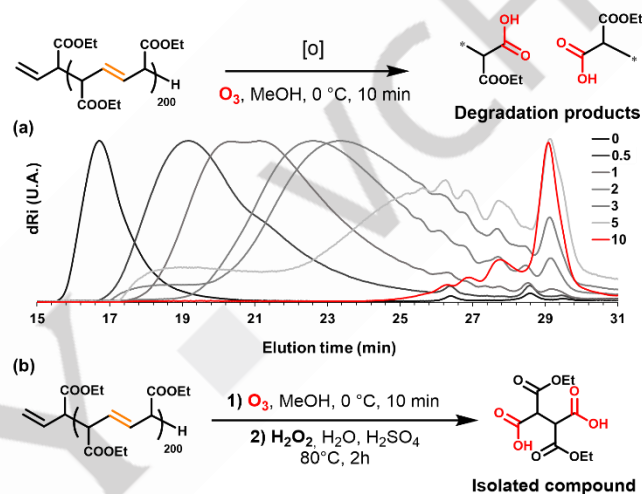


Figure 8. (a) Normalized SEC traces of PDEM₂₀₀ before and after different ozonolysis reaction times, without post-treatment; (b) upcycling of a PDEM₂₀₀ by ozonolysis, followed by treatment with H_2O_2 forming a defined product.

The ozonolysis reaction was readily performed by dissolving PDEM₁₀₀ in methanol at 0 °C, before adding ozone. SEC monitoring revealed that this PDEM chain degradation reaction was complete within a few minutes, confirming the remarkably high reaction rate of oxidative cleavage of the poly(muconate)'s internal double bonds. The parent PDEM₂₀₀ thus degraded into lower molar mass oligomers, then to molecular -likely carboxylated- compounds, as highlighted in Figure 8(a). As shown in Figure 8(b), a post ozonolysis treatment using H_2O_2 selectively oxidized the ozonide compounds, ultimately leading to a major product in the form of a dicarboxylic diester (see Figures S78–S79), which could be exploited as a value-added product. For instance, compounds of similar structure have been described as gemini surfactants with a low critical micellar concentration^[101] (See Fig. S80) to elaborate vesicular structures, for a potential use in medical or cosmetic applications.^[102] This method of oxidative post-treatment of poly(muconates) could thus represent a simple route for their upcycling. Other routes of chemical or biocatalytic degradation of the poly(muconate) backbone could be envisaged, notably *via* metathesis reactions or by exposing poly(muconates) to enzymes.

Conclusion

Poly(dialkyl muconate)s represent a rare example of vinyl polymer platform showing at the same time a bio-based character, chemical degradability of their polymeric backbone in addition to offering various post-functionalization options. The group transfer polymerization (GTP) of muconate esters using $P_4-t\text{-Bu}$ as an organic catalyst provides particularly fast reaction kinetics, marking the distinction with alkyl (meth)acrylates in terms of reactivity of the growing species. In just a few minutes, indeed, GTP achieves quantitative conversions of muconate esters and avoids the use of metal, sulfur or halogen atom. The production of poly(muconates) with a broader molar mass distribution than in the case of perfectly “controlled/living” polymerization can be explained by propagation rates higher than the exchange rates between dormant and active species, except for the GTP of di-*tert*-butyl muconate (DtBuM). Moreover, the stabilizing effect of the conjugation of active and dormant species could make them susceptible to side reactions. This GTP method is compatible with a range of odorless solid monomers that are easy to crystallize and handle, and which are obtained in a single step by esterification of muconic acid, a compound of bio-based origin. The physicochemical properties of poly(muconates) can be easily manipulated by varying, among other things, the nature of the alkyl side chains. For example, the glass transition temperature can be varied over a wide range of values. Synthesis of all-muconate block copolymers can also be achieved by sequential addition of different monomers, paving the way for nanostructures for high-value-added applications. As polar conjugated dienes, muconate ester units are linked by GTP in an exclusive 1,4-conjugated addition mode, effectively introducing internal alkene groups along their carbon-based polymeric backbone. The presence of these internal C=C double bonds offers relevant inherent options to further tune the properties of poly(muconates) by various post-polymerization modification reactions. For instance, epoxidation of a parent poly(diethyl muconate) significantly increases the rigidity of the epoxidized poly(muconate) derivative. Furthermore, internal alkene functions make poly(muconates) intrinsically degradable by a chemical pathway, as demonstrated in this work by the very rapid and efficient oxidative cleavage of a poly(diethyl muconate) upon its exposure to ozone. These findings break ground for a novel and promising family of versatile, bio-based and degradable polymers. All in all, the results we are unveiling here can form the basis for a new circular polymer chemistry, new markets and far-reaching innovations to reduce the impact of plastic waste accumulating in the environment.

Supporting Information

The data that support the findings of this study are available in the Supporting Information of this article. Materials, instrumentation, synthetic procedures, and additional characterization including, NMR spectra, SEC, MS and IR data. (PDF).

Acknowledgements

The authors are grateful to L'Oréal for funding (contract # 220674) and to Cédric Le Coz for his help in thermomechanical analyses.

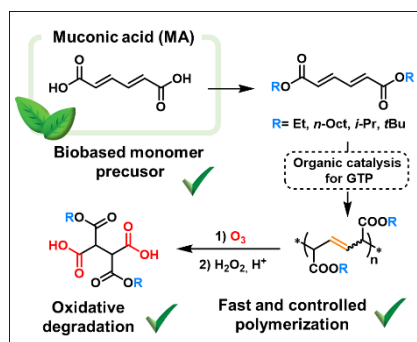
Keywords: Bio-based polymers • Degradable polymers • Organic catalysis • Group transfer polymerization

- [1] K. L. Law, R. Narayan, *Nat Rev Mater* **2021**, 7, 104–116.
- [2] B. von Vacano, H. Mangold, G. W. M. Vandermeulen, G. Battagliarin, M. Hofmann, J. Bean, A. Künkel, *Angew Chem Int Ed* **2022**, anie.202210823.
- [3] G. Hayes, M. Laurel, D. MacKinnon, T. Zhao, H. A. Houck, C. R. Becer, *Chem. Rev.* **2023**, 123, 2609–2734.
- [4] G. W. Coates, Y. D. Y. L. Getzler, *Nat Rev Mater* **2020**, 5, 501–516.
- [5] F. M. Haque, J. S. A. Ishibashi, C. A. L. Lidston, H. Shao, F. S. Bates, A. B. Chang, G. W. Coates, C. J. Cramer, P. J. Dauenhauer, W. R. Dichtel, C. J. Ellison, E. A. Gormong, L. S. Hamachi, T. R. Hoyer, M. Jin, J. A. Kalow, H. J. Kim, G. Kumar, C. J. LaSalle, S. Liffland, B. M. Lipinski, Y. Pang, R. Parveen, X. Peng, Y. Popowski, E. A. Prebivalo, Y. Reddi, T. M. Reineke, D. T. Sheppard, J. L. Swartz, W. B. Tolman, B. Vlaisavljevich, J. Wissinger, S. Xu, M. A. Hillmyer, *Chem. Rev.* **2022**, 122, 6322–6373.
- [6] V. Tournier, S. Duquesne, F. Guillamot, H. Cramail, D. Taton, A. Marty, I. André, *Chem. Rev.* **2023**, 123, 5612–5701.
- [7] M. R. Martinez, D. Schild, F. De Luca Bossa, K. Matyjaszewski, *Macromolecules* **2022**, 55, 10590–10599.
- [8] H.-Z. Fan, X. Yang, J.-H. Chen, Y.-M. Tu, Z. Cai, J.-B. Zhu, *Angewandte Chemie International Edition* **2022**, 61, e202117639.
- [9] X. Li, R. W. Clarke, H. An, R. R. Gowda, J. Jiang, T. Xu, E. Y. -X. Chen, *Angew Chem Int Ed* **2023**, 62, e202303791.
- [10] Y.-L. Su, L. Yue, H. Tran, M. Xu, A. Engler, R. Ramprasad, H. J. Qi, W. R. Gutekunst, *J. Am. Chem. Soc.* **2023**, jacs.3c03455.
- [11] G. R. Jones, H. S. Wang, K. Parkatzidis, R. Whitfield, N. P. Truong, A. Anastasaki, *J. Am. Chem. Soc.* **2023**, 145, 9898–9915.
- [12] L. Čamdžić, E. E. Stache, *J. Am. Chem. Soc.* **2023**, 145, 20311–20318.
- [13] Y. Chiba, R. Kawatani, Y. Kohsaka, *ACS Macro Lett.* **2023**, 12, 1672–1676.
- [14] F. Häfliger, N. P. Truong, H. S. Wang, A. Anastasaki, *ACS Macro Lett.* **2023**, 12, 1207–1212.
- [15] K. Parkatzidis, N. P. Truong, K. Matyjaszewski, A. Anastasaki, *J. Am. Chem. Soc.* **2023**, 145, 21146–21151.
- [16] F. De Luca Bossa, G. Yilmaz, K. Matyjaszewski, *ACS Macro Lett.* **2023**, 12, 1173–1178.
- [17] A. B. Korpusik, A. Adili, K. Bhatt, J. E. Anot, D. Seidel, B. S. Sumerlin, *J. Am. Chem. Soc.* **2023**, 145, 10480–10485.
- [18] J. Zhou, T. Hsu, J. Wang, *Angew Chem Int Ed* **2023**, 62, e202300768.
- [19] F. Eisenreich, *Angewandte Chemie International Edition* **2023**, 62, e202301303.
- [20] T. F. Nelson, D. Rothauer, M. Sander, S. Mecking, *Angewandte Chemie International Edition* **2023**, 62, e202310729.
- [21] A. M. Mineo, R. Katsumata, *Angew Chem Int Ed* **2024**, 63, e202316248.
- [22] V. Lohmann, G. R. Jones, N. P. Truong, A. Anastasaki, *Chem. Sci.* **2024**, 15, 832–853.
- [23] K. Parkatzidis, H. S. Wang, A. Anastasaki, *Angew Chem Int Ed* **2024**, 63, e202402436.
- [24] X. Zhang, Y. Xia, Y. Sun, C. Zhang, X. Zhang, *Angewandte Chemie International Edition* **2024**, 63, e202315524.
- [25] Y.-C. Wu, H.-Z. Fan, W. Zhang, M.-Y. Wang, Z. Cai, J.-B. Zhu, *Macromolecules* **2022**, 55, 9232–9241.

- [26] S. M. Parke, J. C. Lopez, S. Cui, A. M. LaPointe, G. W. Coates, *Angew Chem Int Ed* **2023**, *62*, e202301927.
- [27] H. Watanabe, M. Kamigaito, *J. Am. Chem. Soc.* **2023**, *145*, 10948–10953.
- [28] W. Wang, B. Rondon, Z. Wang, J. Wang, J. Niu, *Macromolecules* **2023**, *56*, 2052–2061.
- [29] K. R. Albanese, P. T. Morris, J. Read de Alaniz, C. M. Bates, C. J. Hawker, *J. Am. Chem. Soc.* **2023**, *145*, 22728–22734.
- [30] K. R. Albanese, Y. Okayama, P. T. Morris, M. Gerst, R. Gupta, J. C. Speros, C. J. Hawker, C. Choi, J. R. de Alaniz, C. M. Bates, *ACS Macro Lett.* **2023**, *12*, 787–793.
- [31] M. Eck, S. T. Schwab, T. F. Nelson, K. Wurst, S. Iberl, D. Schleheck, C. Link, G. Battagliarin, S. Mecking, *Angewandte Chemie International Edition* **2023**, *62*, e202213438.
- [32] L. Yu, Y. Wang, Q. Zhou, X. Wu, Z. Yu, Y. Xu, Z.-C. Li, J. Wang, *Macromolecules* **2024**, *57*, 6429–6438.
- [33] X. Wu, C. Yang, J. Xi, C. Shi, F. Du, Z. Li, *Angew Chem Int Ed* **2024**, *63*, e202404179.
- [34] T. Pesenti, J. Nicolas, *ACS Macro Lett.* **2020**, *9*, 1812–1835.
- [35] C. Lefay, Y. Guillauneuf, *Progress in Polymer Science* **2023**, *147*, 101764.
- [36] A. Tardy, J. Honoré, J. Tran, D. Siri, V. Delplace, I. Bataille, D. Letourneur, J. Perrier, C. Nicoletti, M. Maresca, C. Lefay, D. Giges, J. Nicolas, Y. Guillauneuf, *Angew Chem Int Ed* **2017**, *56*, 16515–16520.
- [37] A. W. Jackson, S. R. Mothe, P. Ang, L. R. Chennamaneni, A. M. V. Herk, P. Thoniyot, *Chemosphere* **2022**, *293*, 133487.
- [38] N. Gil, B. Caron, D. Siri, J. Roche, S. Hadiouch, D. Khedaoui, S. Ranque, C. Cassagne, D. Montarnal, D. Giges, C. Lefay, Y. Guillauneuf, *Macromolecules* **2022**, *55*, 6680–6694.
- [39] M. Uchiyama, Y. Murakami, K. Satoh, M. Kamigaito, *Angew Chem Int Ed* **2023**, *62*, e202215021.
- [40] H. Elliss, F. Dawson, Q. un Nisa, N. M. Bingham, P. J. Roth, M. Kopeć, *Macromolecules* **2022**, *55*, 6695–6702.
- [41] O. Ivanchenko, S. Mazières, R. Poli, S. Harrisson, M. Destarac, *Polym. Chem.* **2022**, *13*, 6284–6292.
- [42] O. Ivanchenko, S. Mazières, S. Harrisson, M. Destarac, *Macromolecules* **2023**, *56*, 4163–4171.
- [43] T. O. Morgen, M. Baur, I. Göttker-Schnetmann, S. Mecking, *Nat Commun* **2020**, *11*, 3693.
- [44] T. Kimura, K. Kuroda, H. Kubota, M. Ouchi, *ACS Macro Lett.* **2021**, *10*, 1535–1539.
- [45] H. Makino, T. Nishikawa, M. Ouchi, *Chem. Commun.* **2022**, *58*, 11957–11960.
- [46] S. Yamamoto, T. Kubo, K. Satoh, *Journal of Polymer Science* **2022**, *60*, 3435–3446.
- [47] T. Kimura, M. Ouchi, *Angew Chem Int Ed* **2023**, *62*, e202305252.
- [48] H. Makino, T. Nishikawa, M. Ouchi, *Macromolecules* **2023**, *56*, 8776–8783.
- [49] R. W. Hughes, M. E. Lott, I. S. Zastrow, J. B. Young, T. Maity, B. S. Sumerlin, *J. Am. Chem. Soc.* **2024**, *146*, 6217–6224.
- [50] R. W. Hughes, J. D. Marquez, J. B. Young, J. B. Garrison, I. S. Zastrow, A. M. Evans, B. S. Sumerlin, *Angew Chem Int Ed* **2024**, *63*, e202403026.
- [51] N.-Z. Xie, H. Liang, R.-B. Huang, P. Xu, *Biotechnology Advances* **2014**, *32*, 615–622.
- [52] I. Khalil, G. Quintens, T. Junkers, M. Dusselier, *Green Chem.* **2020**, *22*, 1517–1541.
- [53] Y. Chen, B. Fu, G. Xiao, L.-Y. Ko, T.-Y. Kao, C. Fan, J. Yuan, *ACS Food Sci. Technol.* **2021**, *1*, 382–387.
- [54] C. Ling, G. L. Peabody, D. Salvachúa, Y.-M. Kim, C. M. Kneucker, C. H. Calvey, M. A. Monninger, N. M. Munoz, B. C. Poirier, K. J. Ramirez, P. C. St. John, S. P. Woodworth, J. K. Magnuson, K. E. Burnum-Johnson, A. M. Guss, C. W. Johnson, G. T. Beckham, *Nat Commun* **2022**, *13*, 4925.
- [55] F. Weiland, N. Barton, M. Kohlstedt, J. Becker, C. Wittmann, *Metabolic Engineering* **2023**, *75*, 153–169.
- [56] C. R. Amendola, W. T. Cordell, C. M. Kneucker, C. J. Szostkiewicz, M. A. Ingraham, M. Monninger, R. Wilton, B. F. Pflieger, D. Salvachúa, C. W. Johnson, G. T. Beckham, *Metabolic Engineering* **2024**, *81*, 88–99.
- [57] D. R. Vardon, N. A. Rorrer, D. Salvachúa, A. E. Settle, C. W. Johnson, M. J. Menart, N. S. Cleveland, P. N. Ciesielski, K. X. Steirer, J. R. Dorgan, G. T. Beckham, *Green Chem.* **2016**, *18*, 3397–3413.
- [58] S. Capelli, A. Rosengart, A. Villa, A. Citterio, A. Di Michele, C. L. Bianchi, L. Prati, C. Pirola, *Applied Catalysis B: Environmental* **2017**, *218*, 220–229.
- [59] N. A. Rorrer, J. R. Dorgan, D. R. Vardon, C. R. Martinez, Y. Yang, G. T. Beckham, *ACS Sustainable Chem. Eng.* **2016**, *4*, 6867–6876.
- [60] A. Matsumoto, T. Matsumura, S. Aoki, *J. Chem. Soc., Chem. Commun.* **1994**, 1389.
- [61] A. Matsumoto, T. Matsumura, S. Aoki, *Macromolecules* **1996**, *29*, 423–432.
- [62] A. Matsumoto, T. Odani, M. Chikada, K. Sada, M. Miyata, *J. Am. Chem. Soc.* **1999**, *121*, 11122–11129.
- [63] A. Matsumoto, T. Odani, *Macromol. Rapid Commun.* **2001**, *22*, 1195.
- [64] A. Matsumoto, K. Sada, K. Tashiro, M. Miyata, T. Tsubouchi, T. Tanaka, T. Odani, S. Nagahama, T. Tanaka, K. Inoue, S. Saragai, S. Nakamoto, *Angew. Chem.* **2002**, *114*, 2612–2615.
- [65] G. Quintens, J. H. Vrijssen, P. Adriaenssens, D. Vanderzande, T. Junkers, *Polym. Chem.* **2019**, *10*, 5555–5563.
- [66] M. Farina, M. Grassi, G. Di Silvestro, L. Zetta, *European Polymer Journal* **1985**, *21*, 71–74.
- [67] A. Takasu, M. Ishii, Y. Inai, T. Hirabayashi, *Macromolecules* **2001**, *34*, 6548–6550.
- [68] Y. Hosoi, A. Takasu, S. Matsuoka, M. Hayashi, *J. Am. Chem. Soc.* **2017**.
- [69] W. Zhao, F. Li, C. Li, J. He, Y. Zhang, C. Chen, *Angewandte Chemie Intl Edit* **2021**, *60*, 24306–24311.
- [70] W. Zhao, Q. Wang, J. He, Y. Zhang, *Macromol. Rapid Commun.* **2022**, *43*, 2200088.
- [71] Y. Liu, Y. Li, Y. Chen, *Macromolecules* **2021**, *54*, 9039–9052.
- [72] L. Xu, Y. Takagi, X. Fu, Y. Wang, A. Narumi, S. Sato, X. Shen, T. Kakuchi, **2023**.
- [73] O. Webster, *Advances in Polymer Science* **2004**.
- [74] M. Rikkou-Kalourkoti, O. W. Webster, C. S. Patrickios, in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Ltd, **2013**.
- [75] T. Imai, R. Hata, *Diblock Copolymer, Method for Producing Diblock Copolymer, and Use of Diblock Copolymer*, **2023**, U.S. Patent US 20230174701A1.
- [76] T. Imai, *Emulsifier and Emulsion Composition Containing Same*, **2023**, U.S. Patent US 20230193138A1.
- [77] H. Ryunosuke, *Cosmetic*, **2023**, E. Patent EP4151279A1.
- [78] J. Raynaud, A. Ciolino, A. Baceiredo, M. Destarac, F. Bonnette, T. Kato, Y. Gnanou, D. Taton, *Angew Chem Int Ed* **2008**, *47*, 5390–5393.
- [79] M. D. Scholten, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2008**, *41*, 7399–7404.
- [80] J. Raynaud, Y. Gnanou, D. Taton, *Macromolecules* **2009**, *42*, 5996–6005.
- [81] J. Raynaud, N. Liu, Y. Gnanou, D. Taton, *Macromolecules* **2010**, *43*, 8853–8861.
- [82] T. Kakuchi, Y. Chen, J. Kitakado, K. Mori, K. Fuchise, T. Satoh, *Macromolecules* **2011**, *44*, 4641–4647.
- [83] M. Fevre, J. Vignolle, V. Heroguez, D. Taton, *Macromolecules* **2012**, *45*, 7711–7718.
- [84] K. Fuchise, Y. Chen, T. Satoh, T. Kakuchi, *Polym. Chem.* **2013**, *4*, 4278.
- [85] E. Kassi, M. S. Constantinou, C. S. Patrickios, *European Polymer Journal* **2013**, *49*, 761–767.
- [86] Y. Takenaka, H. Abe, *Macromolecules* **2019**, *52*, 4052–4058.
- [87] A. Narumi, S. Sato, X. Shen, T. Kakuchi, *Polym. Chem.* **2022**, *13*, 1293–1319.
- [88] L. Xu, F. Liang, Y. Wang, A. Narumi, S. Sato, X. Shen, T. Kakuchi, *Macromolecules* **2023**, *56*, 9196–9206.

- [89] J. Raynaud, N. Liu, M. Fèvre, Y. Gnanou, D. Taton, *Polym. Chem.* **2011**, *2*, 1706.
- [90] E. J. Kepola, K. Kyriacou, C. S. Patrickios, M. Simon, M. Gradzielski, M. Kushnir, C. Wesdemiotis, *Macromolecular Symposia* **2017**, *372*, 69–86.
- [91] A. P. Constantinou, B. Zhan, T. K. Georgiou, *Macromolecules* **2021**, *54*, 1943–1960.
- [92] M. S. Zaky, G. Guichard, D. Taton, *Macromol. Rapid Commun.* **2022**, 2200395.
- [93] A. Stiti, A. M. Cenacchi Pereira, S. Lecommandoux, D. Taton, *Angew Chem Int Ed* **2023**, *62*, e202305945.
- [94] A. Stiti, A. M. Cenacchi Pereira, G. Fleury, S. Lecommandoux, D. Taton, *Macromolecules* **2024**, *57*, 1713–1724.
- [95] W. R. Hertler, T. V. RajanBabu, D. W. Ovenall, G. S. Reddy, D. Y. Sogah, *J. Am. Chem. Soc.* **1988**, *110*, 5841–5853.
- [96] D. Ionita, M. Cristea, D. Banabic, *J Therm Anal Calorim* **2015**, *120*, 1775–1783.
- [97] F. Fleischhaker, A. P. Haehnel, A. M. Misske, M. Blanchot, S. Haremza, C. Barner-Kowollik, *Macromolecular Chemistry and Physics* **2014**, *215*, 1192–1200.
- [98] S. Lim, J. L. Shi, U. von Gunten, D. L. McCurry, *Water Research* **2022**, *213*, 118053.
- [99] H. Nor, *Progress in Polymer Science* **1998**, *23*, 143–177.
- [100] S. S. Solanky, R. P. Singh, *Progress in Rubber and Plastics Technology* **2001**, *17*, 13–58.
- [101] H. N. Chau, T. Kawase, T. Oida, *J. Oleo Sci.* **2013**.
- [102] M. In, R. Zana, *Journal of Dispersion Science and Technology* **2007**, *28*, 143–154.

Entry for the Table of Contents



Organocatalyzed group transfer polymerization (O-GTP) of muconic esters leads to bio-sourced and degradable polymers analogous to polyacrylates. This O-GTP method proves ultra-fast, converting 100% of the monomer in one minute in toluene at room temperature. Chemical modification of the internal double bonds offers additional leverage either for modulating polymer properties or for chemical degradation.