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Multicatalytic Transformation of (Meth)acrylic Acids: a One-Pot Approach to Biobased Poly(meth)acrylates

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Abstract: *Shifting from petrochemical feedstocks to renewable resources can address some of the environmental issues associated with petrochemical extraction and make plastics production sustainable. Therefore, there is a growing interest in selective methods for transforming abundant renewable feedstocks into monomers suitable for polymer production. Reported herein are one-pot catalytic systems, that are active, productive, and selective under mild conditions for the synthesis of copolymers from renewable materials. Each system allows for anhydride formation, alcohol acylation and/or acid esterification, as well as polymerization of the formed (meth)acrylates, providing direct access to a new library of unique poly(meth)acrylates.*

Introduction

Cheap, light and versatile plastics are the dominant materials of our modern economy.[1] The vast majority of these commodity materials are obtained from fossil fuels.[2] In order to remedy some of the environmental challenges associated with petrochemical extraction, an alternative to fossil feedstocks involves using chemicals from renewable resources.[3] In particular, the development of new methods for transforming biomass into resources suitable for polymer production is a critical hurdle along the path to a more sustainable chemical economy. The main challenge is then to design efficient and selective transformations of abundant, renewable, low-cost raw materials into innovative polymeric products.[4] Catalysis is as an important tool to support a more sustainable plastics production and in this case should ideally be efficient, convenient, and versatile, using common reagents. In this regard, one-pot catalytic transformations have significant advantages over conventional multi-step syntheses such as time- and cost-savings, waste reduction and energy consumption.[5] These synthetic schemes, which proceed through two or more consecutive catalytic steps, may serve as a versatile method in polymerization reactions, enabling the production of polymers with new structures and functions.[6] However, the one-pot synthesis of a target (macro)-molecule is not simply a linear combination of each optimized reaction.[7] The different catalytic systems used must be compatible with each other but also with the solvent, substrate, and reaction side products in order to obtain high activity and selectivity.[8] A one-pot synthesis is thus not only a useful methodology to follow for the production of (macro)molecules, but also a promising green approach for polymer synthesis.[9]

Poly(meth)acrylates are a major class of commodity plastics.[10] Numerous studies have led to the discovery of multiple commercial applications for poly(meth)acrylates ranging from functional coatings to energy storage materials, high-performance engineering plastics and biomaterials.[10a,11] The diversity of pendent ester groups that can be inserted into the (meth)acrylic repeat unit is one of the features that allows poly(meth)acrylates to exhibit varied properties. Due to the vast number of alcohols that can act as precursors of (meth)acrylate ester monomers, the potential number of unique poly(meth)acrylates is large and only a small part of this extensive series of polymers has been investigated. This widely unexplored polymer library offers the possibility to identify original materials with interesting properties, particularly from renewable resources. Fully sustainable poly(meth)acrylates can nowadays theoretically be obtained by producing (meth)acrylic acid from renewable resources,[12] efficiently coupling it with biobased alcohols,[13] and polymerizing the resulting monomer.[14] However, most research groups investigating the properties of biobased poly(meth)acrylates usually prepare their materials stepwise, starting from acryloyl chloride or methacrylic anhydride as these procedure require only a simple workup.[12] Although one of the methods of choice for modifying poly(meth)acrylates properties remains copolymerization, no examples of copolymerization of (meth)acrylate derivatives from carboxylic acid precursors have yet been reported via a one-pot procedure. Herein we present a practical route to biobased poly(meth)acrylates by way of a one-pot reaction using simple commercial catalysts and we demonstrate that these requirements can be met using, inter alia, the synthesis of intermediate anhydride derivatives. This process provides direct access to (meth)acrylates and the corresponding (co)polymers in high yields.

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Pagina: 2
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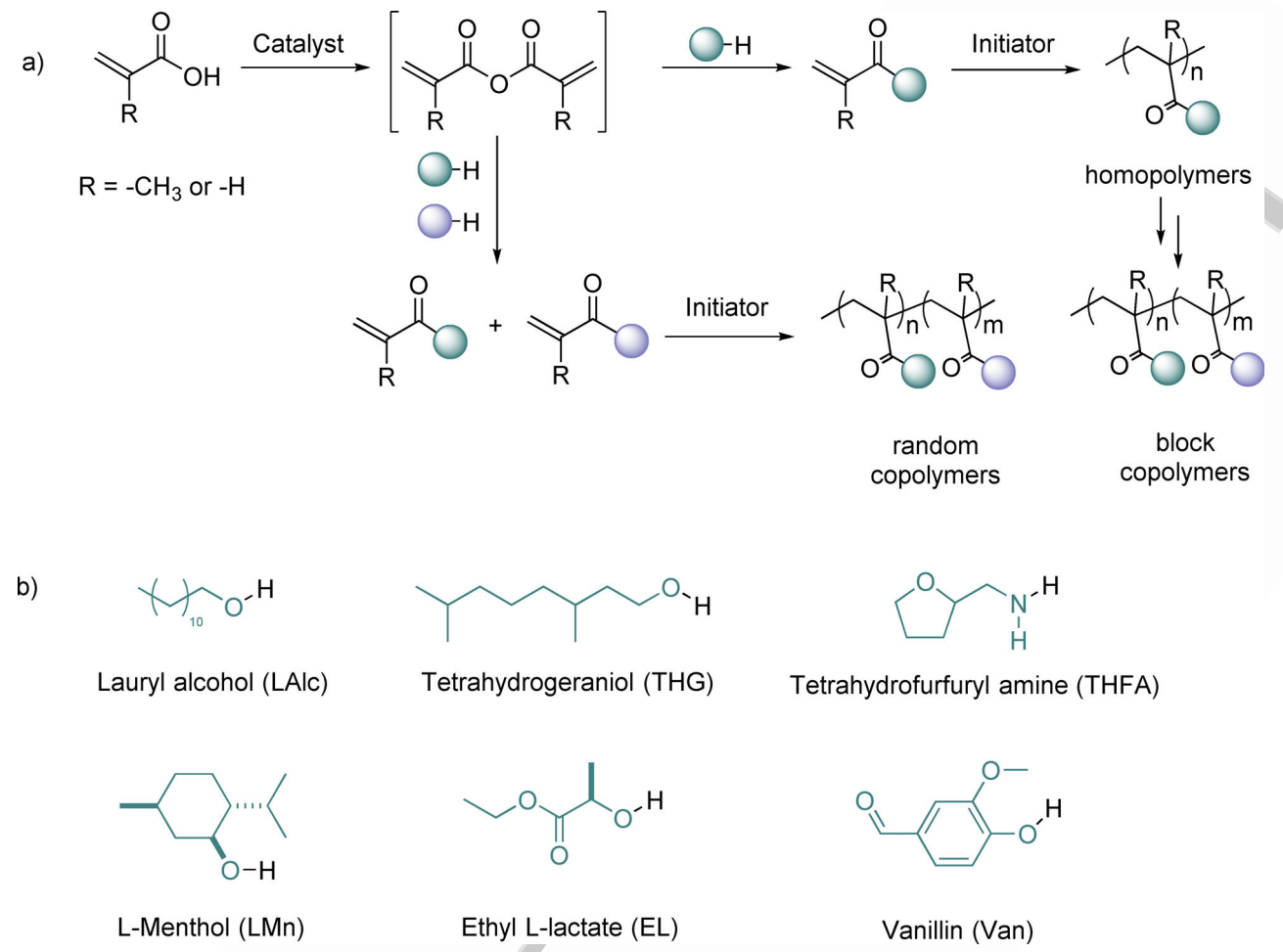

Scheme 1. a) One-pot synthesis of (meth)acrylate copolymers from biobased alcohols and (meth)acrylic anhydride. b) Biobased building block scope demonstrating generality of the methodology.

Results and Discussion

Monomer Formation Sequence

Formation of (meth)acrylic anhydrides

In order to generate (meth)acrylate monomers directly ready for copolymerization, the first objective of our one-pot approach was the synthesis of (meth)acrylic anhydrides from (meth)acrylic acids, able to act as intermediates for the synthesis of one or more esters (Scheme 1). This reaction is a known transformation that can only be achieved by dehydration of the starting compound under acidic conditions and at high temperature. To complete a one-pot procedure, it is therefore necessary to have an anhydride synthesis process that is efficient and produces anhydrides with a high yield. We have recently reported effective protocols for the preparation of cyclic anhydrides from the reaction of dicarboxylic acids in the presence of dialkyl dicarbonates under weak Lewis acid (LA) catalysis.[6a,15] Inspired by these previous results, it was envisaged that commercially available catalysts, such as magnesium chloride or triflate, could provide direct access to (meth)acrylic anhydrides with high selectivity and activity from the corresponding carboxylic acids.[16]

By reacting two equivalents of (meth)acrylic acid with di-*tert*-butyl dicarbonate (Boc_2O) and a suitable catalyst, it is indeed possible to obtain quantitatively acrylic or methacrylic anhydrides. For instance, the mild Lewis acid $MgCl_2$ catalyzes selectively the formation of the anhydride within 20 minutes at 30 °C (Table 1, entries 1&2). Magnesium triflate proved to be much slower for this reaction, reaching full conversion after 18 h (Table 1, entry 3). Traces of tert-butyl methacrylate were also observed. This by-product formation becomes even more pronounced when using strong Lewis acids (Table S1), as observed with $La(OTf)_3$ which cannot convert all the acid and only achieves 86 % selectivity (Table 1, entry 4).

Acylation with anhydrides

Encouraged by these first results, we investigated the next step of our one-pot approach: the acylation of a biobased alcohol with (meth)acrylic anhydride. We hypothesized that triflate complexes would have the potential to act as catalysts given their unique robustness and versatility,[17] as well as their activity in the acylation of alcohol.[18] The catalytic performances of different triflate complexes were therefore evaluated in the presence of commercially available alcohols and

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Datum: 29 KW., 12. Juli 2021 (Montag)
Pagina: 3
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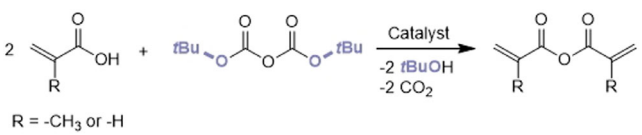
Zeit: 10:54:18 Uhr

Table 1: Catalytic formation of (meth)acrylic anhydride with different catalysts.[a]



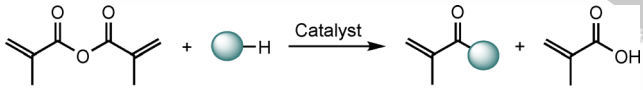
Entry	Catalyst	Acid	Acid Conversion (Time)	Selectivity [%][b]
1	$MgCl_2$ (4 mol%)	Methacrylic	100% (0.33 h)	>99
2	$MgCl_2$ (4 mol%)	Acrylic	100% (0.33 h)	>99
3	$Mg(OTf)_2$ (4 mol%)	Methacrylic	100% (18 h)	98
4	$La(OTf)_3$ (0.5 mol%)	Methacrylic	77% (7 h)	86

[a] All reactions were performed under argon in acetonitrile, at $T = 30\,°C$, with [Acid] = 2 × [Boc_2O] = 3 mol L^{-1}. [b] Selectivity was determined by ^1H NMR spectroscopy, calculating the integral ratio of the signals of the vinylic protons of (meth)acrylic anhydride and the by-product tert-butyl (meth)acrylate.

methacrylic anhydride. Representative results are summarized in Table 2.

We first investigated the use of strong Lewis acids as catalysts, such as scandium, yttrium and lanthanum triflate: the reaction of 50 equiv of methacrylic anhydride with lauryl alcohol was quantitative within 3, 19 and 86 h, respectively (Table 2, entries 1–3). This trend likely reflects the influence of the metal center Lewis acidity for rare-earth elements.[19] Under the same reaction conditions, lauryl methacrylate was also obtained in the presence of mild Lewis acids such as magnesium triflate and magnesium chloride, but in lower yields (Table 2, entries 4&5). Tetrahydrogeraniol, another primary biobased alcohol, was found as reactive as lauryl alcohol using yttrium triflate (Table 2, entry 6). Secondary alcohols, such as L-menthol and ethyl-L-lactate, could also be acylated (Table 2, entries 7&8), requiring a longer time than primary alcohols to give 100% of the corresponding biobased methacrylate, supposedly due to their lower nucleophilicity. This trend is confirmed by the faster acylation of amines, which are known to be better nucleophiles (Table 2, entry 9).

Table 2: Catalytic acylation of various alcohols/amine with different catalysts.[a]



Entry	Catalyst	Alcohol	Time [h]	Conversion [%][b]
1	$Sc(OTf)_3$	Lauryl alcohol	3	100
2	$Y(OTf)_3$	Lauryl alcohol	19	100
3	$La(OTf)_3$	Lauryl alcohol	86	100
4	$Mg(OTf)_2$	Lauryl alcohol	120	86
5	$MgCl_2$	Lauryl alcohol	120	95
6	$Y(OTf)_3$	Tetrahydrogeraniol	20	100
7	$Y(OTf)_3$	L-Menthol	39	100
8	$Y(OTf)_3$	EthyL L-lactate	72	100
9	$Y(OTf)_3$	Tetrahydrofurfuryl amine	3	100
10[c]	$MgCl_2$	Tetrahydrogeraniol	15	100

[a] All reactions were performed under argon in acetonitrile, at $T = 40\,°C$, with [Methacrylic Anhydride] = [Alcohol] = 1 mol L^{-1} and a catalyst loading of 2 mol%. [b] Conversion was determined by ^1H NMR spectroscopy, calculating the integral ratio of the signals of the vinylic protons of methacrylic anhydride and the products formed. [c] From the reaction mixture of the anhydride formation step. After addition of THG, T was raised to 50 °C.

Finally, we were pleased to find that this acylation reaction can also be carried out from the reaction mixture of the previous anhydride formation step using $MgCl_2$ (Table 2, entry 10). Increasing the temperature to 50 °C in this second step even reduces the reaction time. Therefore, these results allowed us to confirm that the acylation of biobased alcohols/amine with (meth)acrylic anhydride can be carried out under mild conditions, is rapid in processing and suitable for the one-pot preparation of relevant methacrylate monomers.

Esterification of (meth)acrylic acids

We then studied the esterification of methacrylic acid using dimethyl dicarbonate (Moc_2O) and Boc_2O as coupling agents (Scheme 1). Based on the mechanism proposed by Bartoli,[20] we assumed that the presence of a Lewis acid could cause the activation of the added dicarbonate, allowing the nucleophilic attack of the (meth)acrylic acid and ultimately leading to the formation of a mixed anhydride as a reaction intermediate (Figure 1). Then, the attack of a second (meth)-acrylic acid generates the corresponding symmetrical anhydride, which can then react with the in situ released alcohol (i.e., methanol) in the case of Moc_2O, or with an alcohol more nucleophilic than tBuOH in the case of Boc_2O, as already observed in the acylation step.

As control experiments, scandium, yttrium and lanthanum triflate derivatives were first evaluated for the esterification of methacrylic acid with Moc_2O (Table S2, entries 1–3): methyl methacrylate was the main product, with traces of dimethylcarbonate (Figure S1), as a result of the nucleophilic attack of the released methanol on the mixed anhydride intermediate or on Moc_2O itself (vide infra). As the non-sequential addition did not lead to 100% conversion of methacrylic acid into MMA with neither of the catalysts studied, sequential addition of Moc_2O was therefore performed in order to avoid the decomposition of the dicarbonate. Under these conditions, $Y(OTf)_3$ was able to convert 100% of methacrylic acid into MMA within 4 h using a slight excess of Moc_2O (Table 3, entry 1). For $Sc(OTf)_3$ and $La(OTf)_3$ catalysts, a slightly higher excess of Moc_2O (i.e., 1.5 equivalents with respect to methacrylic acid) is necessary to obtain quantitative yields (Table S2, entries 5&6).

In order to directly produce (meth)acrylates from the corresponding acid, we then investigated the use of Boc_2O as a coupling agent (Table 3, entries 2–6). Gratifyingly, esterification of methacrylic acid by primary biobased alcohols such as lauryl alcohol or THG is efficiently and selectively carried out by $La(OTf)_3$ and $MgCl_2$, within 9 and 15 h, respectively (Table 3, entries 2&3). $Sc(OTf)_3$ and $Y(OTf)_3$ also catalyzed

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Seite: 3 te von 10
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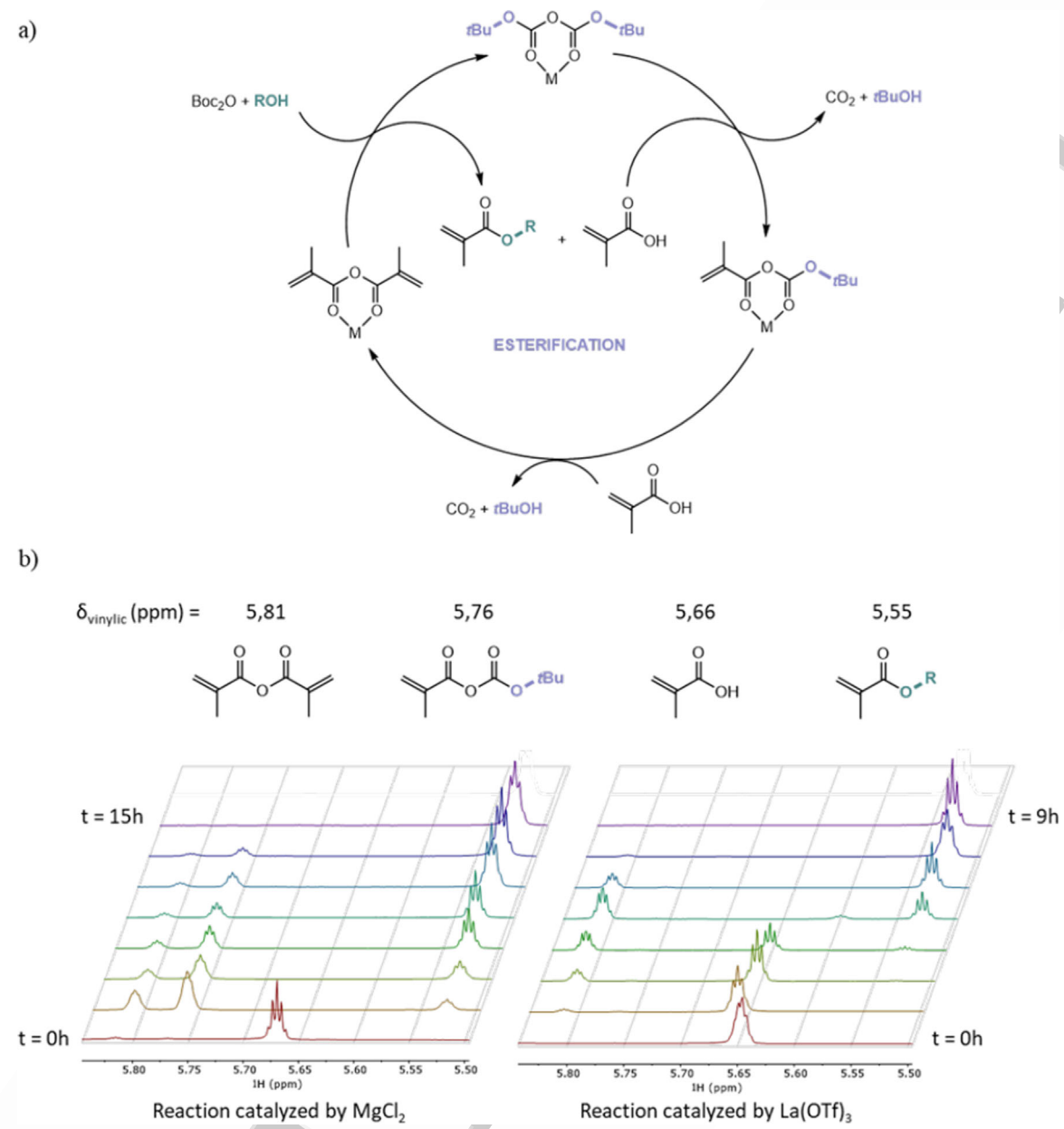

Figure 1. a) Envisaged mechanism for the esterification of methacrylic acid by an alcohol using Boc_2O, catalyzed by a metal-based complex M; b) ^1H NMR monitoring (400 MHz, $CDCl_3$, 20 °C) of the reaction of methacrylic acid/tetrahydrogeraniol (1:1.2) with $MgCl_2$ or $La(OTf)_3$, using Boc_2O.

this reaction, although the selectivity was lower (ca. 97%, Table S3, entries 1&2). Acrylic acid is esterified under the same conditions, although it requires a longer reaction time for $La(OTf)_3$ than $MgCl_2$, with 87 and 15 h, respectively (Table S3, entries 3&4). These two catalysts are in fact quite complementary to produce a diverse library of (meth)acrylates. On the one hand, $La(OTf)_3$ is indeed more selective than $MgCl_2$ for the esterification of MAA with bulky (and less reactive) secondary alcohols such as L-menthol (Table 3, entry 4 and Table S3, entry 5). On the other hand, $MgCl_2$ is more functionally tolerant, as it could selectively produce methacrylates of ethyl-L-lactate and vanillin (Table 3, entries 5&6). It should be noted that the use of a slight excess of alcohol and Boc_2O (ca. $1.2 \times$ [Acid]) is mandatory to achieve complete conversion of (meth)acrylic acid, as the secondary reaction involving an alcohol attacking the activated Boc_2O to produce an unsymmetrical carbonate is observed to a small extent. Finally, although the use of amines in combination with Boc_2O is unsuitable (Table S3, entry 6), our methodology however makes it possible to obtain methacrylamides together with another methacrylate, by first the reaction of the amine with the anhydride and then esterification of the remaining acid.

To verify the mechanistic pathway during the first three steps, we performed the ^1H NMR kinetic monitoring of the esterification of methacrylic acid by tetrahydrogeraniol, in the presence of $La(OTf)_3$ or $MgCl_2$ (Table 3, entries 2&3). The nature of the resulting intermediates was assessed by

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Datum: 29 KW., 12. Juli 2021 (Montag)
Pagina: 5
Seite: 4 te von 10
Umfang (Seiten): 10
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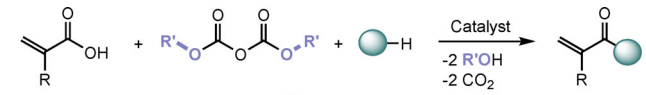
Table 3: Catalytic esterification of methacrylic acid with different alcohols, dicarbonates and catalysts.[a]



Entry	Roc_2O	Alcohol	Catalyst (Loading)	T [°C]	Time [h]	Selectivity [%][b]
1	Moc_2O[c]	–	$Y(OTf)_3$ (2 mol%)	40	4	>99
2	Boc_2O	THG	$La(OTf)_3$ (0.5 mol%)	30	9	>99
3	Boc_2O	THG	$MgCl_2$ (4 mol%)	30	15	98
4	Boc_2O	LMn	$La(OTf)_3$ (0.5 mol%)	30	41	96
5	Boc_2O	EL	$MgCl_2$ (4 mol%)	40	7	>99
6	Boc_2O	Van	$MgCl_2$ (4 mol%)	40	84	>99

[a] All reactions were performed under argon in acetonitrile. [Methacrylic Acid] = 1.4 mol L^{-1} for entries 2 to 6. [Roc_2O] = [Alcohol] = 1.2 × [Acid] for all entries. [b] Selectivity of the corresponding methacrylate was determined by ^{1}H NMR spectroscopy, calculating the integral ratio of the signals of the vinylic protons of the methacrylates involved, methacrylic acid and methacrylic anhydride. [c] 1.2 equivalent of Moc_2O with respect to methacrylic acid, added sequentially after the end of the first acylation step: 0.5 equivalents at t = 0, 0.25 equivalents at t = 0.5 h, 0.25 equivalents at t = 1.5 h, 0.2 equivalents at t = 3 h.

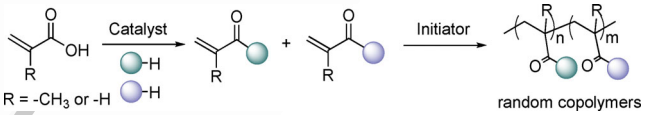
examination of the vinylic and *tert*-butylic regions of the ^{1}H NMR spectra (Figures 1, S2 and S3). Remarkably, all reagents, products and hypothetical intermediates of this esterification reaction can be observed and distinguished solely by ^{1}H NMR spectroscopy. However, notable discrepancies are observed between the reaction catalyzed by $MgCl_2$ and $La(OTf)_3$. In the case of $MgCl_2$, the mixed anhydride and methacrylic anhydride are rapidly produced early in the reaction, and then gradually consumed. With $La(OTf)_3$, the mixed anhydride is difficult to detect, and the methacrylic anhydride is formed more slowly. These observations are consistent with the mechanism proposed by Bartoli *et al*, where the authors suggested that the Lewis acidity affects the reactivity of the intermediates differently. Mixed anhydride formation is probably the fastest step when catalyzed by $MgCl_2$, while methacrylic anhydride formation can be fast but slower, and alcohol acylation appears to be the rate-determining step. In the case of a stronger Lewis acid such as $La(OTf)_3$, consumption of the mixed anhydride is supposedly the fastest step, which should explain why it is observed in only small amounts. However, acylation of the alcohol seems to remain the rate determining step.

Thus, biobased (meth)acrylate monomers in solution, ready for polymerization without purification, could be obtained smoothly and quantitatively using our one-pot methodology. Starting from (meth)acrylic acid, the use of either $MgCl_2$ or $La(OTf)_3$ provides one or several biobased (meth)acrylate(s), with excellent selectivity and a wide scope of reagents.

Polymer Formation Step

With an efficient and quantitative synthesis of (meth)-acrylates in hand, we then explored the radical polymerization of the resulting monomer mixtures using 2,2′-azobis(2-methylpropionitrile) (AIBN) and various control agents. To assess the feasibility of the overall process, we conducted preliminary experiments with the rare earth triflate catalysts capable of performing the first two steps with a [catalyst]/[AIBN] ratio of 2:1 (Table 4, entry 1 and Table S4, entries 1–3). We first tested the copolymerization of LMA with MMA. Indeed, these copolymers could be of great interest to industry, since the resulting poly(meth)acrylate will have "soft" (or low T_g) segments of LMA associated with "hard" (higher T_g) segments of MMA. Remarkably, all three one-pot systems were active for the polymerization step and exhibited comparable reactivities. Also, a similar experiment using $MgCl_2$ for the monomer formation steps yielded comparable results (Table S4, entry 4). As a control experiment, we then performed a polymerization reaction using a clean combination of isolated methacrylates in the presence of AIBN (Table S4, entry 5). In marked contrast to what has been observed for other LA-mediated radical polymerizations of methacrylates,[21] we noticed that direct polymerization gives poly(MMA-*co*-LMA) with a reactivity (i.e., molar masses and reaction rates) close to that obtained with one-pot systems.[22] A conventional free radical pathway can also be suggested for these one-pot polymerizations, as the polymers obtained with

Table 4: Radical polymerization of various monomer mixtures with different control agents.[a]



Entry	M_1-M_2	AIBN [mol%]	Control Agent [mol%]	X_{M1}–X_{M2} [%][b]	M_n^{exp} (M_n^{th}) [g/mol][c]	$Đ$[c]
1	LMA-MMA	0.5	–	85–90	35 600 (30 600)	2.0
2	THGMA-ELMA	0.5	–	83–95	27 200 (36 500)	2.7
3	ELA-EL-MA	0.5	–	97–99	57 500 (35 100)	1.7
4	LMA-MMA	0.25	DDM (4)	71–75	5 000 (5 700)	1.5
5	LMA-MMA	0.5	CPDB (1.5)	82–88	9 800 (12 900)	1.1
6	THGMA	1	CPDB (3)	97	6 200 (4 900)	1.2
7	THGMA	0.25	CPDB (0.75)	87	16 300 (17 100)	1.2

[a] All reactions were performed under Ar, adding to the previously prepared monomer mixture in acetonitrile a solution of AIBN in toluene ($V_{toluene}/V_{MeCN}$ = 3) and a control agent, and heating at T = 70 °C for 20 h. [b] Conversion was determined by ^{1}H NMR spectroscopy, calculating the integral ratio of the signals of the alkyl ester protons of the monomers and the polymers formed. [c] M_n^{exp} and $Đ$ of polymer determined by SEC-RI in THF calibrated with polystyrene standards at 35 °C. M_n^{th}: for detailed calculations see the Supporting information.

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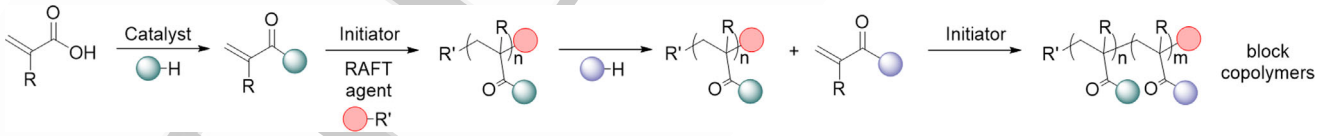
Datum: 29 KW., 12. Juli 2021 (Montag)
Pagina: 6
Seite: 5 te von 10
Umfang (Seiten): 10
Zeit: 10:54:20 Uhr

LA/AIBN were syndiotactically-enriched (*rr:rm:mm* = 60:40:0), such as PMMAs prepared with AIBN in the literature.[23] In addition, increasing the catalyst loading to 5 mol% shows no significant difference (Table S4, entry 6). These results indicate that the active species formed during the (stepwise) copolymerization process might be the same species as that of the one-pot process, therefore suggesting that the coordination of a Lewis acid to the conjugate -C=O electron-withdrawing group of either an alkene or radical is not effective.[21] This lack of effect can be attributed to the presence of a Lewis base (e.g., traces of alcohol or dimethylcarbonate), that can compete with MMA and LMA for coordination to the Lewis acid. By varying the initiator loading, we were then able to obtain copolymers of different molar masses (Table S4, entries 7–9), with increasing dispersity as the amount of AIBN decreases. Various mixtures of comonomers could be randomly copolymerized, starting from one acid and two (or more) alcohols (Table 4, entry 2), or from one alcohol and acrylic and methacrylic acids (Table 4, entry 3). These examples illustrate the wide variety of combinations possible with a one-pot system.

In order to extend the versatility of our approach, we then decided to test the reactivity of different control agents and monomer mixtures for the polymerization step.[24] A chain transfer agent, dodecyl mercaptan (DDM), and a RAFT agent, cyanopropyl dithiobenzoate (CPDB), were thus evaluated (Table 4, entries 4–7).[25] These control agents were efficient in controlling the homo- and copolymerization process (predictable M_n and narrow $Đ$), with various molar masses accessible depending on the loadings of chain transfer agent and initiator. The evolution of M_n^{exp} as a function of THGMA conversion was also assessed to show the control of the polymerization process using the RAFT agent (Figure S4). Overall, the radical polymerization process is efficient and not affected by the different byproducts of our one-pot methodology.

Thanks to the ability of RAFT agent-capped polymers to act as macroinitiators, we then decided to explore the one-pot synthesis of block copolymers. We envisioned that, after an initial sequence of esterification (30–40 °C) and RAFT polymerization (70 °C), the reaction temperature could be reduced to 30–40 °C and new reagents could be added to perform such a sequence again. The macroinitiator obtained upon the first sequence could then act as a RAFT agent and form block copolymers with the newly synthesized monomer (Table 5). This was first confirmed by the fact that the catalysts used for the initial sequence (i.e., $MgCl_2$ or La(OTf)$_3$) were still active for a second esterification, in the same reaction mixture (Table S5). Slightly longer reaction times were required to achieve complete conversion, as the reaction medium was more diluted than under optimal conditions (Table 3). By increasing the reaction temperature again to 70 °C after adding the initiator, we then successfully obtained block copolymers. Di-block copolymers of various compositions were accessible in two sequences, depending on the RAFT agent used (Table 5). Dithioesters such as CPDB were preferred for the copolymerization of methacrylates, while trithiocarbonates such as 2-(2-cyanoprop-2-yl)-S-dodecyltrithiocarbonate (CPDTC) provided a better balance between activity and control for acrylate polymerization. If a block copolymer of methacrylate and acrylate monomers is targeted, it is mandatory to use CPDTC and start with the poly(methacrylate) block (Table 5, entries 1–4), as the poly(methacrylate) chain is a better homolytic leaving group than the poly(acrylate) chain (Table 5, entries 5&6).[26] For the precise formation of blocks, it is crucial to attain near complete conversion of the first monomer before starting the synthesis of the second one. Depending on the monomers targeted, the catalyst must also be chosen carefully to obtain good selectivity in the esterification step. Notably, no change of molar mass was observed after the second esterification (Figures S5&S6), meaning that the macroinitiator previously formed is inactive and unaffected under the conditions of the esterification step. As already reported by Perrier, some low-molar mass tailings may appear after multiple polymerization steps, due to the accumulation of dead polymer chains, initiator-derived chains or possible interactions of the multi-block copolymer with the SEC column.[27] As in all systems

Table 5: One-pot synthesis of various monomers and their block copolymerization.[a]



Entry	Cat.	Control agent	M_1	X_{M1} [%][b]	M_n^{exp} [g/mol][c]	$Đ$	M_2	X_{M2} [%][b]	M_n^{exp} [g mol^{-1}][c]	$Đ$[c]
1	La(OTf)$_3$	CPDB	L-MnMA	92	8300	1.3	THGMA	92	14800	1.6
2[d]	La(OTf)$_3$	CPDB	THGMA	97	6200	1.2	LMA	96	11400	1.3
3[e]	$MgCl_2$	CPDB	VMA	96	3800	1.1	ELMA	96	4700	1.3
4	$MgCl_2$	CPDB	VMA	86	7400	1.4	LMA	75	13600	1.8
5	$MgCl_2$	CPDTC	THGA	90	6900	1.2	ELA	98	10300	1.5
6	$MgCl_2$	CPDTC	ELMA	90	16200	1.6	THGA	95	24100	1.5

[a] All reactions were performed under Ar, adding to the previously prepared monomer mixture in acetonitrile a solution of AIBN in toluene ($V_{toluene}$/V_{MeCN} = 3) and a control agent ([Control agent]/ [AIBN] = 5), and heating at T = 70 °C for 20 h. Then, the reaction mixture was cooled back to 30 or 40 °C (depending on the monomer) and (meth)acrylic acid, Boc_2O and the desired alcohol were introduced (same ratios as in the 1st step). Finally, after the desired amount of time, a solution of AIBN in toluene is added and the mixture is heated at T = 70 °C for 20 h. [b] Conversion was determined by ^{1}H NMR spectroscopy, calculating the integral ratio of the signals of the alkyl ester protons of the monomers and the polymers formed. [c] M_n^{exp} and $Đ$ of polymer determined by SEC-RI in THF calibrated with polystyrene standards at 35 °C. [d] [Control agent]/ [AIBN] = 3. [e] [Control agent]/ [AIBN] = 12.

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Seite: 6 te von 10
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based on a degenerative transfer mechanism, this can be avoided by using a higher [RAFT agent]/[initiator] ratio, as the number of living chains is dictated by the initial number of chain transfer agent. Finally, in order to determine topology and end groups of the copolymers, a diblock copolymer poly(VMA-*b*-ELMA) was characterized by MALDI-ToF-MS (Figures S7–S9). Analysis of the major isotope distributions confirmed the presence of the block copolymers with cyanopropyl and thiol end-groups.[28]

New homo- and copolymers synthesized by our one-pot process were then characterized by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) (Table 6 & S6). The important range of T_g accessible confirms

Table 6: Thermal analyses of polymers obtained by one-pot catalysis.[a]

Entry	Type of (co)polymer	M_n^{exp} [g/mol]	T_{g1} [°C]	T_{g2} [°C]	$T_{-5\%}$ [°C]
1	poly(ELMA)	43900	47	–	247
2	poly(THGA)	25000	−61	–	272
3	poly(THGMA)	38300	−27	–	214
4	poly(ELMA-*r*-MMA)	37000	74	–	247
5	poly(ELMA-*r*-ELA)	60300	27	–	310
6	poly(VMA-*b*-ELMA)	21800	111	40	226
7	poly(ELMA-*b*-THGA)	24100	40	−50	291
8	poly(ELMA-*b*-THGMA-*b*-ELMA)	22100	28	−31	208

[a] M_n^{exp} of polymer determined by SEC-RI in THF calibrated with polystyrene standards at 35 °C. T_g of polymer determined by DSC on second heating cycle (10 °C/min, N_2 flow). $T_{-5\%}$ of polymer determined by TGA (20 °C/min, N_2 flow).

the wide variety of characteristics that can be obtained using our synthetic method. Starting from acrylic acid, methacrylic acid or both, coupling it with various biobased alcohols (or amines) to obtain (random or block) homo- or copolymers, the possibilities are numerous. For instance, the homopolymer of ethyl-L-lactate methacrylate displays a T_g at 47 °C, while the homopolymer of tetrahydrogeraniol acrylate has a glass transition at −61 °C, due to its more flexible side chain and the less rigid nature of the polyacrylate backbone (Table 6, entries 1&2). The T_g of poly(ELMA) could either be increased or decreased by random copolymerization of ethyl-L-lactate methacrylate with other suitable comonomers (Table 6, entries 4&5). Also, all of our di- and tri-block copolymers exhibited several glass transition temperatures, instead of a single T_g for fully miscible copolymers (Table 6, entries 6 to 8).[29] Interestingly, the significant increase in the glass transition temperature of the VMA-ELMA copolymer supports the hypothesis that the T_g of these copolymers is strongly dependent on their aromatic nature (Table 6, entry 6). In addition, the double bonds in these structures can provide a functional handle for subsequent modification or cross-linking of the material. For poly(ELMA-b-THGA), two glass transitions were observed at −50 °C and 40 °C (Table 6, entry 7). As compared to the T_gs of poly(THGA) (−61 °C) and poly(ELMA) (47 °C) homopolymers, the small shifts indicate that the blocks of poly(THGA) and poly(ELMA) are only slightly miscible with each other. An increased thermal stability is observed for this copolymer when compared to poly(ELMA) and poly(THGA) (Figure S10). The block copolymer shows indeed a 5% weight-loss temperature of 291 °C, much higher than the ones of its respective homopolymers (248 °C and 272 °C for poly(ELMA) and poly(THGA), respectively). Such a synergy between these two blocks is noteworthy and provides better processability to the final material, as the operational window between the second glass transition temperature and the degradation temperature is expanded. The microphase separation was also confirmed for the triblock copolymer poly(ELMA-*b*-THGMA-*b*-ELMA), since two transitions are clearly observed, which are characteristic of the glass transition of the THGMA soft phase at the lower temperature (−31 °C) and the transition of the ELMA hard phase at a higher temperature (28 °C) (Table 6, entry 8).

Remarkably, all homopolymers and random copolymers described in this study were colorless when using AIBN alone or AIBN and DDM as the initiating system. As expected, the RAFT agents used to synthesize the block copolymers imparted their color to the final material (yellow to pale yellow for CPDTC or pink to slightly orange for CPDB at low loadings, see Figure 2). If necessary, color removal is in principle feasible, as Perrier et al. reported an efficient method for end-group modification and chain transfer agent recovery from polymethacrylates synthesized by the RAFT process.[30]

Finally, the environmental impact of our one-pot methodology was quickly assessed by determining the E-factor of the overall synthesis and comparing it to existing literature. For instance, Epps and co-workers reported an elegant synthesis of a block copolymer of lauryl methacrylate and vanillin methacrylate, by RAFT polymerization, via a stepwise method.[31] Their work was highlighted by the promising properties displayed by these new materials, but they also rightfully noted that the E-factor of their synthesis path could be improved (estimated at 500, which did not even include monomers synthesis). We could prepare a similar polymer (Table 5, entry 4) in one-pot fashion and estimated the E-factor of the overall process, including monomers synthesis, to approximately 150 (see Supporting information for detailed calculations). This dramatic decrease in mass intensity is due to the fact that workup solvents account for the major part of the total E-factor. Avoiding monomers and homopolymers isolation is therefore key for reducing the environmental impact of a synthesis path, a feature that is inherently accomplished by one-pot methodologies.

Conclusion

A new one-pot synthetic route for the production of (meth)acrylate monomers and the corresponding (co)polymers has been developed from renewable feedstocks. This approach makes it possible to directly obtain biobased materials in the form of homopolymers, or random or block copolymers, without needing to isolate and purify intermediates. In addition, these catalytic systems are remarkably robust, thus allowing the use of unpurified monomers and bench-top reaction setup. In this regard, the first steps can be performed under ambient air, although maintaining an inert atmosphere is essential for the control of the subsequent

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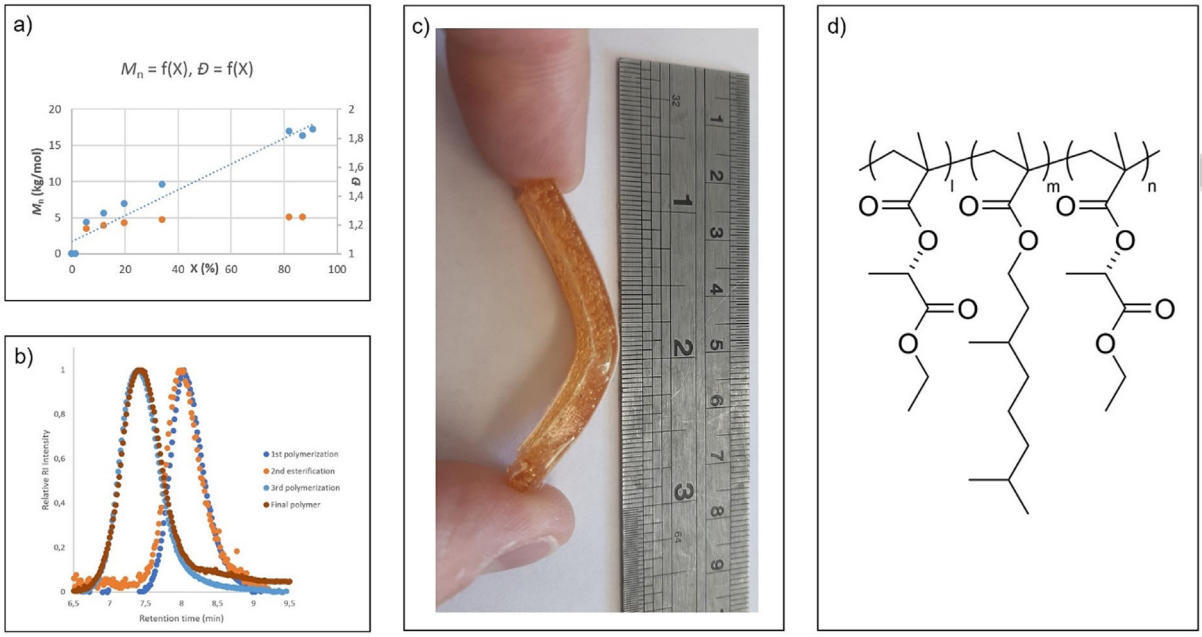

Figure 2. a) Evolution of M_n (blue dots) and $Đ$ (orange dots) versus the conversion of THGMA during its one-pot synthesis and polymerization using a RAFT agent. CPDB mol% = 0.9; AIBN mol% = 0.09. T = 70 °C, for 46 h. b) Evolution of the SEC-RI trace during the one-pot synthesis of the poly(ELMA-*b*-THGMA-*b*-ELMA) triblock copolymer (Table 6, entry 8), calibrated with polystyrene standards at 35 °C. c) Visual representation (photo) highlighting the elastomeric character of the poly(ELMA-*b*-THGMA-*b*-ELMA) triblock copolymer (Table 6, entry 8). Polymer sample manufactured by thermocompression using a hot press (see SI). d) Structure of the poly(ELMA-*b*-THGMA-*b*-ELMA) triblock copolymer (Table 6, entry 8).

polymerization step. Ultimately, the strategy provides easy access to a set of unique macromolecular structures that can be used to meet the growing demand for new applications for commercial polymers. Our future efforts are oriented towards further study of the reaction mechanism, as well as development of catalysts that exhibit higher reactivities for the whole process.

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Conflict of Interest

The authors declare no conflict of interest.

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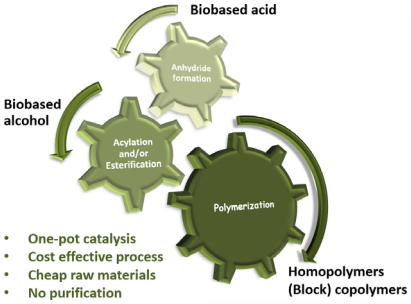

We have developed a multicatalytic approach for the one-pot production of (meth)acrylate monomers, allowing the formation of the corresponding (co)polymers from renewable feedstocks. This highly efficient strategy allowed us to perform multiple catalytic transformations in one pot, while bypassing several purification steps. This procedure can therefore minimize chemical waste, save time, and simplify practicalities.

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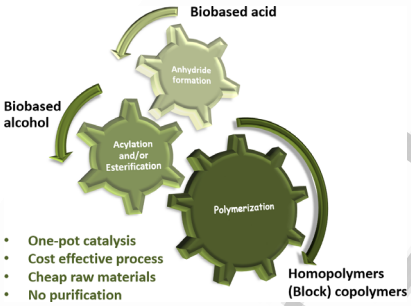

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