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Journal:	*Polymer Chemistry*
Manuscript ID	PY-REV-08-2020-001222.R1
Article Type:	Review Article
Date Submitted by the Author:	12-Oct-2020
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Synthesis and polymerization of bio-based acrylates: a review

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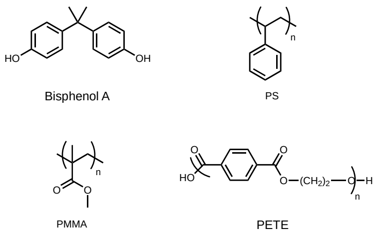
Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Abstract: Acrylates and polyacrylates have been produced massively due to their interesting application like Plexiglas. However, the contemporary issues of fossil depletion associated to climate change have raised serious concerns. As a result, utilization of renewable sources such as lignocellulosic material and the development of greener processes have been investigated intensively. Herein, we review the preparation of competitive (meth)acrylates and the corresponding polymers made from bio-renewable sources with a specific focus on lignocellulose. While covering a few family of biosynthon to produce acrylates through different synthetic pathways, we also approach the promising properties of the resulting materials.

Introduction

Over the last decades, polymer science has significantly developed, resulting in the design and synthesis of durable and versatile materials for daily-life applications[1] including textiles, electronics, toys, and packaging for food.[2] For instance, 45% of plastics used in the United states in 2010 were used as packaging, 35% for durable goods and 19% in nondurable goods like disposable diapers, cups, and plates.[3] In 2017, the polymer industry reached a production of approximatively 380 million tons with an annual growth rate of 8.4%.[4]



Scheme 1. Structures of some commodity plastics and additives

Commodity plastics such as poly(ethylene terephthalate) (PET), polystyrene (PS), and poly(methyl methacrylate) (PMMA) (**Scheme 1**) are mainly produced from fossil fuel-based resources and their monomers are often volatile and toxic.[1] For instance, polycarbonates and epoxy resins are produced from bisphenol A (BPA), an endocrine disruptor[5] while styrene required for the synthesis of polystyrene is a carcinogen.[6] Poly(meth)acrylates are high value daily-life polymers commonly prepared from acrylic and methacrylic acid (AA and MAA) and their corresponding esters[7] using non-sustainable strategies such as propylene oxidation[8] and the Acetone Cyanohydrin Process (ACH).[9] Acrylate polymers exhibit very interesting properties such as high T_g values,[10] attractive mechanical properties,[11,12] thermal stabilities,[10] and transparency[11,13] which allow their utilization for various applications. For instance, 55% AA production is being used for diapers SAP manufacturing, 30% for plastic, adhesives, and synthetic rubbers synthesis while the last 15% is used for coating and paint formulations[7,8] (**Figure 1**).

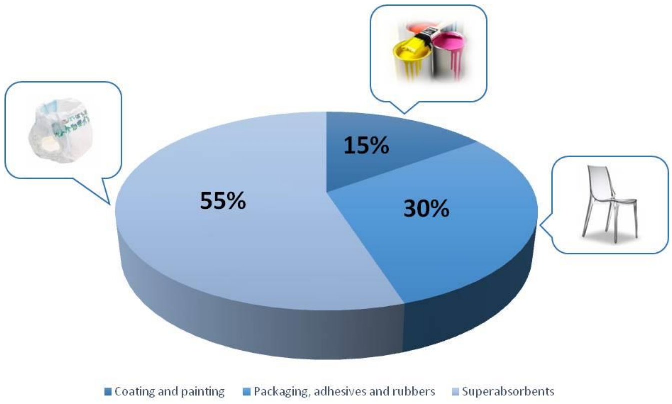


Figure 1. Commercially available applications of polyacrylic acid and its derivatives.

PMMA (Plexiglas®) is a transparent and resistant material[9] applied in various industrial and medical applications such as bone cement[14,15] and its annual production exceeded 2.8 million tons in 2011.[9] Due to the current non-sustainable pathways used to produce (meth)acrylate monomers and the resulting polymers, this industry largely contributes to the growing greenhouse gas emissions as well as fossil resource

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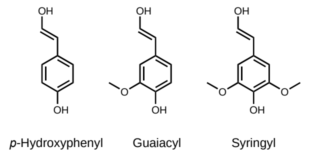
depletion.[16] Besides plastic pollution, producing bio-based polymers, and especially bio-based (poly)methacrylate, is an interesting approach to limit utilization of finite resources, and occasionally bio-based solutions contribute to decreasing CO_2 emissions.[17] Defined as polymers produced from renewable natural resources, bio-based polymers are an interesting alternative to traditional petroleum-based plastics, as they are often less toxic[2] and sometimes biodegradable.[18] In addition, as they can be derived from a large variety of feedstocks such as sugars, starch, corn, soybeans, algae, or food waste, their sourcing is considered, for now, bio-renewable.[19] Thus, over the last decades, a significant amount of research has been dedicated to the synthesis of bio-based polymers as an opportunity to reduce the utilization of fossil fuel-based resources.[2] Indeed, as reported by Geyer *et al.*[4] in 2015, 79% of plastic waste was accumulated in landfills or in nature. While bio-based polymer only shared 1% of the worldwide material production in 2015, studies showed that substituting 65.8% of the current polymers by bio-based solutions would save 241 to 316 million tons of CO_2-equivalent annually.[4]

Over the last decades, notable efforts have been dedicated to the search bio-based poly(meth)acrylates to, hopefully, reduce their impact on the environment. Preparation of new (meth)acrylate polymers from bio-based molecules obtained from either extraction or fermentation of biomass such as glucose, cellulose and lignin is an interesting strategy to synthetize bio-based poly (meth)acrylates. This review presents an outlook on the opportunities and challenges of the synthesis of bio-based (meth)acrylate polymers from renewable resources with a focus on lignocellulose while approaching vegetable oils.[20] For example, emphasis will be given to the utilization of readily available and sustainable resources such as lignin, terpenes and lactates to prepare competitive acrylate and methacrylate monomers and polymers with interesting properties for daily-life applications.

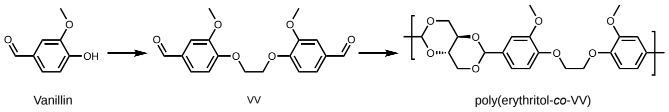
Bio-based acrylates from ligno-cellulosic-derived phenolic compounds

Obtained through the oxidative coupling of phenolic compounds—so called monolignols—*p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)[21], (**Scheme 2**) lignin is a three dimensional network that represents approximately 15-30% of the lignocellulosic biomass. Those phenolic compounds present interesting biological properties as they play a key role in the protection of the plant.[22,23] In addition, those building blocks have been used as starting materials for polymer production to take advantage of the aromatic ring rigidity. Originally extracted from vanilla and commonly used as food, perfumes, beverages, and pharmaceuticals flavoring,[24,25] vanillin is a versatile platform molecule that can be produced from Kraft lignin, the main by-product of the Kraft pulping process.[26]



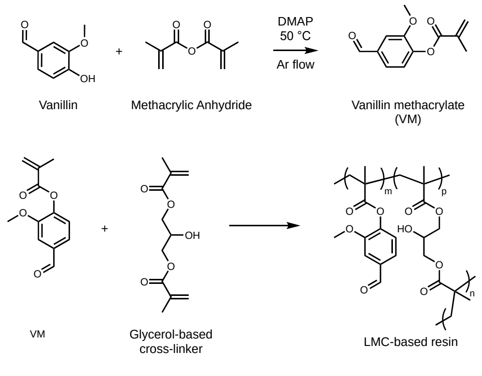
Scheme 2. Monolignol units composing lignin

For instance, steam explosion of hardwood lignin[27] allows access to both vanillin and syringaldehyde. The presence of the phenol functionality, which can act as a nucleophilic species once deprotonated, has been valuable for polymer preparation, such as polyacetals,[28] (**Scheme 3**) and even offer esterification possibilities to synthetize acrylates.



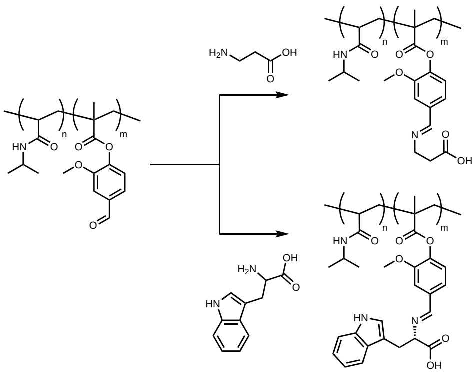
Scheme 3. Example of bio-based polyacetal incorporating vanillin.

To the best of our knowledge, utilization of vanillin in esterification to generate acrylate monomers is quite recent. Stanzione and co-workers[29] were among the first researchers to consider vanillin. They reacted this valuable synthon with methacrylic anhydride to create a novel acrylate monomer and employed it for the synthesis of resin (**Scheme 4**). To do that, they copolymerized the latter monomer with glycerol dimethacrylate, a cross-linking agent, and obtained a transparent thermoset with a high glass transition temperature of 155 °C. Zhang *et al.*[30] also proposed a vanillin-based polymer including cross-linking. Rather than using a bio-based cross-linker like glycerol dimethacrylate, they performed the reduction of vanillin into vanillyl alcohol which was then subjected to methacrylation. The resulting methacrylated vanillyl alcohol (MVA) was then polymerized to provide a material exhibiting improved properties versus poly(vanillin methacrylate) (PMV). For instance, PMV shows a storage modulus of 0.7 GPa at 80 °C vs 3.5 GPa at 80 °C for poly(MVA).



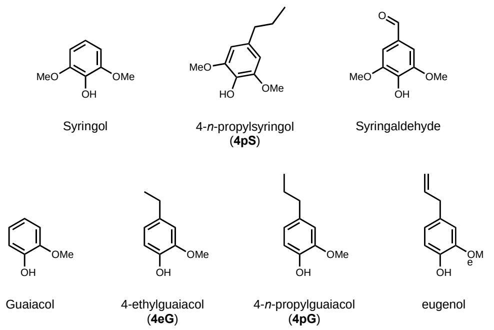
Scheme 4. Preparation of Vanillin methacrylate and the resulting LMC-based resin with a glycerol-based cross linker.

Several reports employed a similar process to use the corresponding vanillin-based polyacrylate to explore its potential. For instance Holmberg et al.[31] incorporated vanillin methacrylate into block copolymers with lauryl methacrylate to create a material that self-assembled. Zhou and co-workers[32] reported the synthesis of both syringaldehyde and vanillin acrylates as well as their methacrylate versions by using acryloyl or methacryloyl. They also applied free radical polymerization conditions in solution to obtain the targeted polymers with broad dispersity and M_n from 7.6 to 14.6 kDa. They showed that the extra methoxy group present in the syringaldehyde-based polyacrylates has an important impact on the thermal properties. Indeed, poly(vanillin methacrylate) has a T_g of 110 °C vs 180 °C for poly(syringaldehyde methacrylate). Abdelaty and Kuckling[33] described the copolymerization of vanillin acrylate with *N*-isopropylacrylamide to prepare thermo-responsive material. They took advantage of the aldehyde present in the polymer chain to perform post-polymerization click modifications aiming at Schiff's base formation with amino compound like tryptophan and β-alanine (**Scheme 5**).



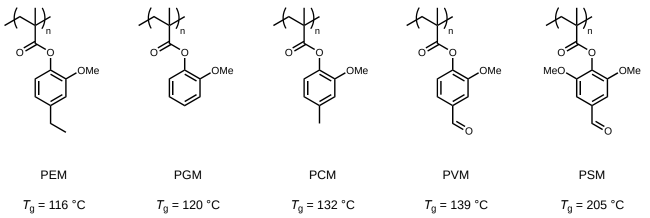
Scheme 5. Schiff's base formation after copolymerization of VM and *N*-isopropylacrylamide

Syringol, guaiacol, and their alkyl derivatives (**Scheme 6**) are phenolic compounds that can be obtained from lignin through different processes. For instance, Shen and co-workers succeeded in the development of a selective method to access only guaiacol and syringol[34] and Van den Bosch and co-workers[35] reported depolymerization of poplar wood by using a Ru/C catalyst that gave access to an oil mainly composed of 4-*n*-propylsyringol (**4pS**) and 4-*n*-propylguaiacol (**4pG**). After Ru/C catalyzed deconstruction of poplar wood to access **4pS** and **4pG**, Wang *et al.*[10] employed those building blocks as acrylate and methacrylate monomers for RAFT polymerization. While the targeted homopolymer proved to have high T_g values (up to 169 °C), copolymerization of **4pS** with butyl acrylate gave a pressure sensitive adhesive which exhibits 180° peel forces up to 4 Ncm^{-1} and tack forces up to 2.5 Ncm^{-1}.



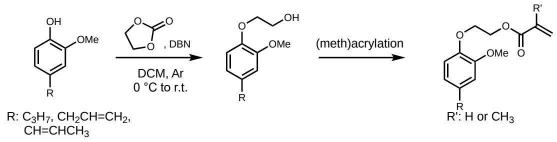
Scheme 6. Syringol and derivatives

In 2012, Stanzione and co-workers[36] subjected guaiacol and eugenol to DMAP-catalyzed esterification with methacrylic anhydride. Homopolymerization of the resulting guaiacol methacrylate (**GM**) and eugenol methacrylate (**EM**) gave polyacrylates with T_g of 92 and 103 °C, respectively. In addition, they performed blending of vinyl ester resins with the aforementioned monomers creating novel thermosets that compete with vinyl ester-styrene resins. Holmberg *et al.* focused a huge part of their work on the study bio-oil constituents, especially on guaiacol and its derivatives. First, they showed the reactivity of the acrylates from bio-oil was largely impacted by the nature of some pendant group. Indeed, removing a methoxy from a phenolic ring would influence the reactivity significantly. However, they observed the *p*-position substituent in the guaiacol motif did not seem to affect the acrylate's behavior during polymerization.[37] Secondly, they emphasized the high potential of polyacrylates from guaiacol and syringyl derivatives by describing T_g values above 100 °C up to 205 °C (**Scheme 7**).[38,39]



Scheme 7. Polyacrylate from bio-based phenolic compounds

Recently Molina-Gutiérrez and co-workers[40] explored the preparation of acrylates from eugenol. They extended the molecules by reacting the phenol function with ethylene carbonate prior to acrylation (**Scheme 8**). Interestingly, they used the inherent vinyl function of eugenol to perform epoxidation followed by carbonation and they applied the same procedure to isoeugenol. The series of acrylate monomers was polymerized to give bio-based materials with moderate T_g values from 10 to 40 °C. It is noteworthy to mention that both the unreacted carbonates and epoxide moieties offer post-polymerization cross-linking that broadens the scope the possibilities.



Scheme 8. Preparation of eugenol-based (meth)acrylates

Bio-based acrylates from terpenes

Terpenes and terpenoids are another type of natural molecule that can be used to prepare new acrylate monomers and polymers. Belonging to the *hydrocarbon-rich natural molecules class,*[41] they are produced by many plants and trees such as pine and conifer trees (**Figure 2**).[38]

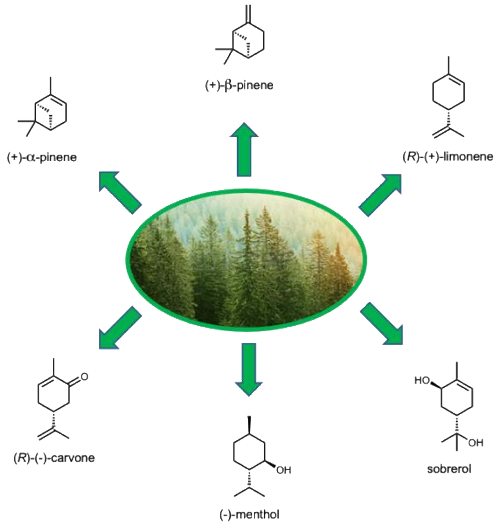
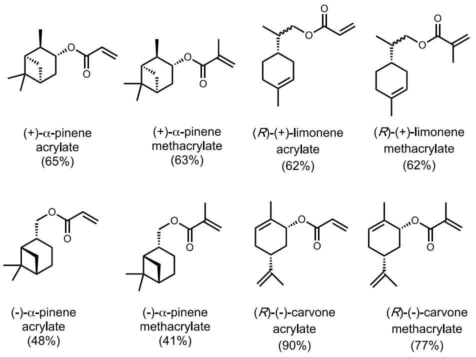


Figure 2. Examples of terpenes

Turpentine, a volatile fraction of resins industrially produced at 300,000 tons per year,[42] is the major precursor of terpenes mainly constituted of α-pinene and β-pinene.[42] Terpenes and terpenoids are used for various applications such as fragrances and flavors, fine chemical building blocks and as anticancer agents.[41,43,44] Because of the large variety of existing structures, terpenes can be interesting for the synthesis of new polymers.[42,45] Indeed, due to their isoprene fragment, free radical polymerization can easily be performed to create terpene-based polymers and modification of terpenes can also give access to polyacrylates.[46,47]

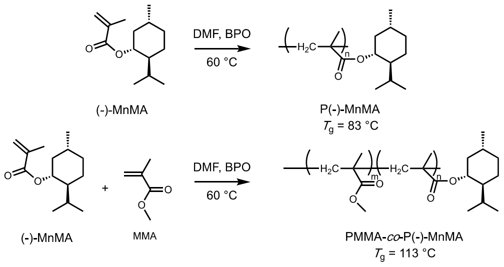
In 2016, Sainz *et al*. investigated the synthesis of new types of polyacrylates from terpenes, focusing on the four most commercially available terpenes: (+)-α-pinene, (−)-β-pinene, (*R*)-(+)-limonene, and (*R*)-(−)-carvone).[47] Their strategy was to functionalize those terpenes by adding acrylate and methacrylate groups to their chemical structure. (+)-α-pinene, (−)-β-pinene, and (*R*)-(+)-limonene were transformed into alcohols using a hydroboration/oxidation protocol[48,49] while the ketone functionality of (*R*)-(−)-carvone was reduced with lithium aluminum hydride conditions.[50] Then, the resulting alcohols were esterified with acryloyl or methacryloyl chloride to give eight acrylate monomers.[47] (**Scheme 9**)



Scheme 9. Terpene-based acrylate monomers

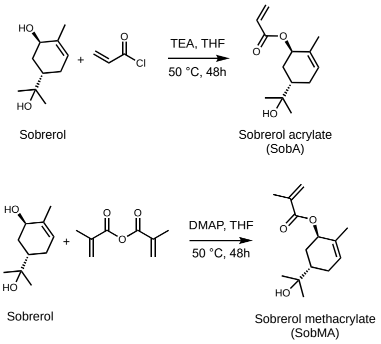
Another method using acrylic acid with propyl phosphonic anhydride (T3P®)[51] as a coupling agent was investigated to prevent the use of toxic acyl chlorides, and improved the yields of (+)-α-pinene acrylate, (−)-β-pinene acrylate, (*R*)-(+)-limonene acrylate, and (*R*)-(−)-carvone acrylate up to 98%, 86%, 78%, and 98%, respectively.[47] Sainz and co-workers also developed a catalytic one-pot pathway based on White's catalytic allylic oxidation[52] and incorporated methacrylate groups at the allylic position of β-pinene. They were able to reach 82% yield for the preparation of two new terpene-based methacrylate monomers using 2 mol% $Pd(OAc)_2$ with 2 equivalents of benzoquinone and methacrylic acid as solvent at 50 °C for 72h. The monomers were then polymerized using free radical polymerization with dodecanemercaptan (DDM) as a chain transfer agent to obtain new transparent materials with T_g values up to 142 °C.

Compared to other terpene molecules, menthol is a bio-synthon that already bears a hydroxyl moiety, therefore no modifications are needed prior to the esterification. Even though a few attempts to produced menthol-based acrylate through esterification of acrylic acid are described in the literature, the yields are rather low to moderate probably due to the lower reactivity of a secondary vs. primary alcohol.[53,54,55] As a result, the synthesis of menthyl acrylates (**MnA)** mainly goes through a more polluting process involving acryloyl chlorides and organic base.[56,57] For instance, Baek *et al.* achieved 73% yield of **MnA** in 30 min at 0 °C when using acryloyl chloride in the presence of Et_3N in DCM.[56]



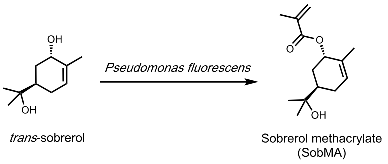
Scheme 10. Polymerization of menthyl acrylates

To the best of our knowledge, menthyl acrylate polymerization was first studied by Matsuzaki *et al.*[55] who subjected the monomer to an anionic polymerization processes in the presence of either BuLi or phenylmagnesium bromide but neither thermal nor mechanical properties were reported. In 2007, Liu and Mishra[58] investigated **MnA** polymerization by using an ATRP strategy. They were able to reach high a M_n of 14.0 kDa with a narrow dispersity of 1.11 and a conversion of 78% when tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was used as a ligand. Rather than using an ATRP process, Min and co-workers[57] focused on classic free radical polymerization in the presence of benzoyl peroxide as initiator to access both the homopolymer and a copolymer with MMA that exhibit T_g values of 83 °C and 113 °C, respectively (**Scheme 10**). They both investigated bulk and solution process to access their copolymer for optical fibre fabrication. However, the generation of air bubbles during the polymerization in solution made this approach unsuitable for the targeted application while the bulk process was more promising for optical fibre production.



Scheme 11. Acrylation and methacrylation of sobrerol

Discovered by Sobrero in 1851, Sobrerol is a monoterpene used in the pharmaceutical field as a microregulating agent for the treatment of respiratory diseases.[59] In 1909, Henderson *et al.* reported one of the first methods for the production of Sobrerol from α-pinene through the aqueous oxidation of this terpene with mercuric acetate.[60] From biotransformation involving *Armillaria Mella*[61] to epoxidation followed by dehydration,[62] several processes have been developed to produce Sobrerol from α-pinene. Offering a hydroxyl moiety, this bio-synthon was used in acrylate preparations. In 2018, Lima and co-workers accomplished the esterification of sobrerol in the presence of either acryloyl chloride and Et_3N or methacrylic anhydride and DMAP to access sobrerol acrylate (**SobA**) and sobrerol methacrylate (**SobMA**) in 72% and 84% yield, respectively (**Scheme 11**).[63] Aiming to repalce styrene in unsaturated polyester resins, they studied the thermomechanical properties of three unsaturated polyesters containing sobrerol-based acrylates. In 2019, Stamm *et al.* optimized sobrerol acrylate preparation (96% conversion) using an enzymatic method involving a lipase, *Pseudomonas fluorescens*, in the presence of vinyl methacrylate (**Scheme 12**).[64] In addition to exploring free radical polymerization methods such as ATRP and RAFT to reach narrow dispersity, they also proposed a horseradish peroxidase (HRP)-mediated polymerization[64,65] and were able to obtain high M_n values up to 48.2 kDa for the homopolymers and T_g values around 150 °C.



Scheme 12. Chemo-enzymatic methacrylation of Sobrerol

In 2019 Noppalit and co-workers[66] explored the potential of Tetrahydrogeraniol (THG) (**Figure 3**), a side product from the paper industry, as a possible precursor of bio-based acrylate to produce triblock copolymers. They took advantage of the low glass transition of poly(tetrahydrogeraniol acrylate) (-46 °C) to prepare the “soft” segment of their elastomers while styrene was chosen as the monomer for the “hard” segment. Polymerization of THGA was performed through either RAFT or free radical processes. While RAFT provided M_n up to 96.5 kDa with a narrow $Đ$ of 1.2 or lower, free radical processes resulted in higher M_n of 278.0 kDa and a broader dispersity of 2.4. The targeted elastomer was then prepared via RAFT process. First, they prepared poly(THGA)-based macro RAFT agent, then styrene blocks were added on both sides to give the desired triblock material with T_g values of -22 °C and 110 °C for the poly(THGA) segment and the poly(styrene) segment, respectively.

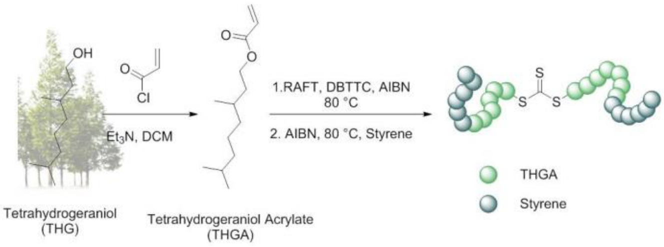
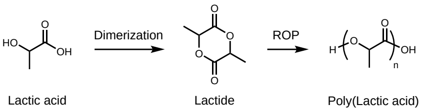


Figure 3. Preparation of THGA-based triblock

Recently, Droesbeke and co-workers[67] reported the synthesis of bio-based pressure-sensitive adhesives composed of terpenoids such as THGA, MnMA, and Citronellyl (meth)acrylate (CA & CMA). Most of the sustainable materials obtained through emulsion polymerization exhibit low T_g values around -40 °C due to the high content of THGA. Mechanical tests focusing on tack, peel, and shear resistance behavior were attempted on three different surfaces: steel, glass, and polyethylene. Peel resistance reached 7.7 N/25 mm and 6.5 N/25 mm on steel and glass, respectively, depending on the composition of the material.

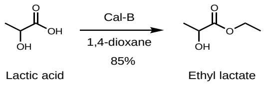
Bio-based acrylates from lactic acid

The Lactic acid, a top 30 molecule identified by the Department of Energy,[68] is probably one of the most known bio-synthons mainly because of polylactic acid (PLA) (**Scheme 13**), a commercially available bio-based plastic. Even though PLA has made lactic acid famous, this bio-based hydroxyacid is used as a building block in many industries other than plastics.



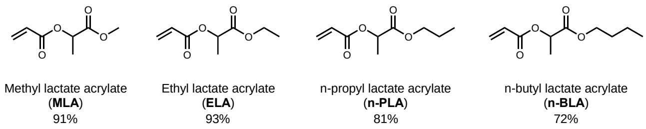
Scheme 13. Production of PLA

Indeed, lactate esters have proved to be good emulsifiers and are used for both cosmetic and food applications.[69, 70] For instance, Dupont has developed GRINDSTED® LACTEM,[71] a lactic acid-based emulsifier used in cream and topping powders. Several studied have even considered lactate esters as bio-degradable green solvents[72,73] to replace halogenated and petroleum-based ones.



Scheme 14. Chemo-enzymatic synthesis of ethyl lactate

Usually acid-catalyzed, lactic acid esterification often involves harsh conditions to prevent self-polymerization into PLA. In 2008, Hasegawa *et al.*[74] reported the chemo-enzymatic esterification of lactic acid in the presence of *Candida antarctica* lipase type B to green up the reaction (**Scheme 14**). They observed that ketone and ether solvents significantly impacted the conversion and the yield, reaching 85% when 1,4-dioxane was used. Taking advantage of the hydroxyl moiety of lactic acid, Yee and co-workers developed a Pd-catalyzed hydroesterification in the presence of CO and C_2H_4 at high temperature. The resulting methyl- and ethyl 2-(propionyloxy) propanoates, obtained in 79% and 99% yield, respectively, were then subjected to pyrolysis to form methyl acrylate in moderate yield.



Scheme 15. Preparation of alkyl lactate monomers

Lactate esters are commonly produced through the esterification of lactic acid with alcohols using anhydrous hydrogen chloride, sulfuric acid, or phosphoric acid as acid catalysts.[75] In 2014, Purushothaman *et al.*[76] reported the synthesis of four alkyl lactate acrylates through two sequential acid-catalyzed esterifications in toluene. First, they reacted lactic acid with methanol, ethanol, n-propanol or n-butanol and the targeted esters were subjected to a second esterification in the presence of acrylic acid to access the desired monomer in high yield (72% to 93%) (**Scheme 15**). Then, the lactate-based acrylates were polymerized through free radical processes with AIBN as initiator to produce the corresponding homopolymers with decent M_n values, 9.0 to 18.0 kDa, and $T_{d10\%}$ above 190 °C. They showed that the greater the alkyl chain length, the lower the T_g value. For instance, poly(methyl lactate acrylate) exhibits a T_g of -19 °C compared to -37 °C for poly(n-propyl lactate acrylate) (**Figure 4**).

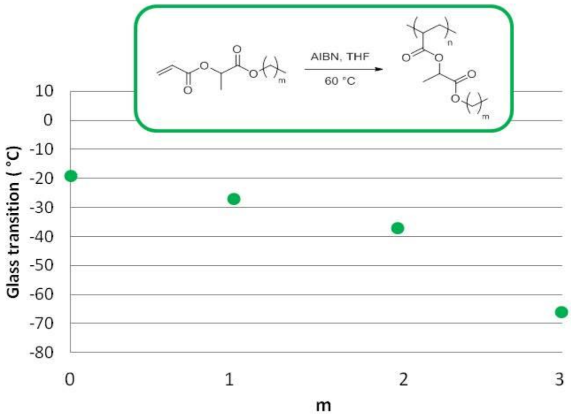
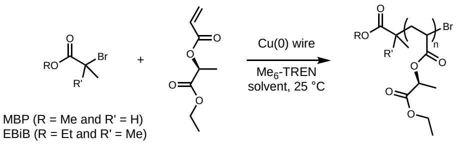


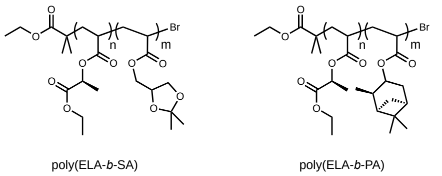
Figure 4. Impact of the alkyl chain on the lactate ester based polyacrylates

Finally, Purushothaman and co-workers focused their efforts on moisture absorption and hydrophilicity of those polymers. They observed that at equal relative humidity (RH), those materials have a higher tendency to absorb water compared to PMMA while remaining more hydrophobic than poly(acrylic acid) (PAA). Indeed, they mentioned that hydrogen bonds between water and the esters encouraged moisture uptake. While glass transition values follow a trend previously described, moisture absorption and hydrophilicity contradict the rule since poly(*n*-propyl lactate acrylate) happened to be the less hydrophilic with a contact angle of 62.2 ° compared to 37.8 ° for poly(*n*-butyl lactate acrylate).



Scheme 16. Single electron transfer-living radical polymerization of ethyl acrylate

In 2019, Bensabeh *et al*[77] proposed the Cu(0)-catalyzed single electron transfer-living radical polymerization (SET-LRP) of ethyl lactate acrylate at room temperature in the presence of Me_6-TREN, a ligand, and ethyl bromoisobutyrate (EBiB) to initiate the process (**Scheme 16**). Moderate M_n values were found between 8.0 and 10.0 kDa with lower dispersities from 1.17 to 1.30 compared to free radical processes, with an exception of 2.13. Higher M_n values reaching 64.0 kDa with a $Đ$ of 1.23 were obtained in ethanol when the molar amount of monomer was increased up to 400 vs. 1 and 0.5 for EBiB and Me_6-TREN, respectively. After expanding their procedure to homopolymerization of methyl lactate acrylate (MLA) and butyl lactate acrylate (BLA), they described block copolymer preparation involving either α-pinene acrylate (α-PA) or solketal acrylate (SA) (**Scheme 17**). Poly(ELA-*b*-α-PA) proved to exhibit two different T_g values of 7 and 65 °C, assigned to ELA and α-PA, respectively, resulting in a hard-soft material and a potential sustainable elastomer while poly(ELA-*b*-SA) was transformed into an amphiphilic block copolymer after hydrolysis of the acetal contained in the SA monomer.



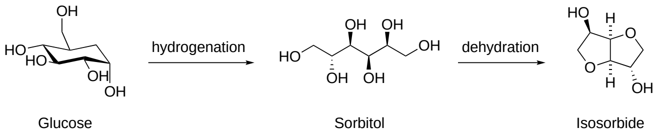
Scheme 17. Block co-polymers involving ethyl lactate ester acrylate and either solketal acrylate or α-pinene acrylate

Recently, Bensabeh and co-workers[78] used ELA again for the preparation of novel amphiphilic block copolymers involving *N*,*N*-dimethyl lactamide (DML acrylate) as a hydrophilic moiety. This new bio-based block copolymer produced through Cu(II)-mediated photoinduced LRP demonstrated its potential as surfactant for aqueous emulsion polymerization of PMMA and PS to form latexes.

main text of the article should appear here with headings as appropriate.

Bio-based acrylates from isosorbide

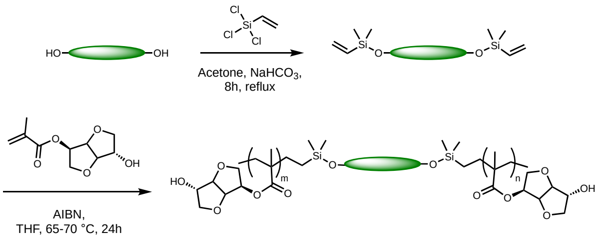
Isosorbide (1,4:3,6-dianhydro-D-glucitol) is a chiral bicyclic diol considered as one of the top 12 most renewable building blocks according to Liu and co-workers.[79] Presenting steric hindrance due to its bicyclic nature, isosorbide has been identified as a good candidate to improve thermomechanical resistance of polyesters such as PET and PBS.[80] This positive impact on polymer properties makes isosorbide a potential green alternative to the petroleum-based terephthalate and was even foreseen as substitute for bisphenol A.[81, 82] Therefore, isosorbide production has gained attention over the last few years. For example, in 2015 Roquette was producing 20 000 tons of high purity isosorbide.[83] Using D-glucose as feedstock, the production of isosorbide is a two-step process (**Scheme 18**) which starts by hydrogenation of D-glucose to access D-glucitol, commonly known as D-sorbitol, followed by its dehydration to obtain the desired diol. [81,84,85,86,87,88] The potential of isosorbide motivated explorations of new synthetic processes. For example, de Almeida and co-workers[86] reported a method involving a Ru/C catalyst in molten hydrated salt ($ZnCl_2$) to perform glucose hydrogenation into sorbitol while Sun *et al.*[87] developed tungstophosphoric acids (PW) supported on metal oxides to dehydrate sorbitol and access isosorbide.



Scheme 18. Production of Isosorbide from Glucose

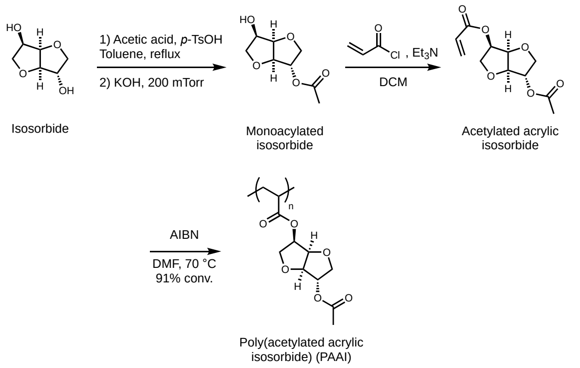
he growing interest in isosorbide has motivated various efforts on its use as a building block for new monomers and polymers. In 2012, Mansoori and co-workers[89] proposed the synthesis of a new isosorbide-based acrylate in five steps in an overall yield of 23%. First, they prepared an organophilic clay by reacting Cloisite 20A with vinyltrichlorosilane. The modified clay was then grafted with isosorbide methacrylate through a free radical process (**Scheme 19**) to improve the thermal properties of the polymer. For instance, the T_g was increased from 74 °C for a pure homopolymer to 92 °C when the polymer was grafted onto the clay.

In 2015, Gallagher *et al.*[90] reported the two-step preparation of acetylated methacrylic isosorbide (AMI) in the presence of scandium (III) triflate ($Sc(OTf)_3$) a catalyst that does not require inert and anhydrous conditions due to its surprising stability toward oxygen and water. ($Sc(OTf)_3$)-mediated acetylation of isosorbide proved to be extremely rapid and was completed in less than 10 min with a low catalyst loading of 0.05%. After a second step of methacrylation involving methacrylic anhydride and the same catalyst, they obtained the targeted product in an overall yield of 44%. The homopolymer was obtained either by a free radical process or RAFT-CTA method to improve the polymerization control. Poly(AMI) demonstrated thermal stability comparable to PMMA and a T_g value of 130 °C for M_n higher than 55.0 kDa, providing a good and low cost candidate for the hard component of bio-based elastomer thermoplastics



Scheme 19. Preparation of grafted Cloisite 20A[89]

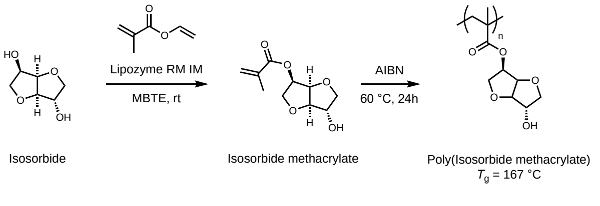
Later on, Gallagher and co-workers prepared Acetylated acrylic isosorbide (AAI) in two steps[91, 92] targeting block copolymers with adhesive properties. First, isosorbide reacted with acetic acid in toluene using *p*-toluene sulfonic acid as a catalyst to form the *exo* monoacetylated isosorbide form in 38% yield after distillation. The resulting product was then acrylated with acryloyl chloride in the presence of Et_3N to give acetylated acrylic isosorbide (AAI) in 58% yield. Free radical process with AIBN as initiator was then performed in DMF to access PAAI with 91% monomer conversion after 2h of reaction (**Scheme 20**). The resulting material not only presents high thermal resistance but also interesting T_g value of 95 °C. The isosorbide acrylate was also engaged in copolymerization using RAFT polymerization to form tri-block copolymers. While PAAI-PEHA-PAAI exhibits limited adhesive properties, PAAI-PnBA-PAAI offer more attractive results with peel forces and tack forces up to 2.9 $N.cm^{-1}$ and 3.2 $N.cm^{-1}$, respectively. This showed the usefulness of the low-cost isosorbide for elastomers thermoplastics.



Scheme 20. Polymerization of AAI into PAAI

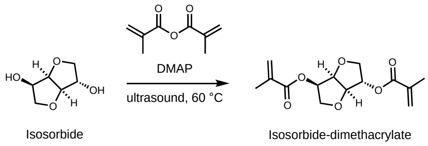
In 2017, Baek and co-workers[93] reported the utilization of Isosorbide acrylate (ISA), prepared with acryloyl chloride, as co-monomer with 2-ethyhexyl acrylate and 2-hydroxyethyl acrylate in pressure-sensitive adhesive preparation. They showed ISA content enhanced adhesion properties of the material without altering its transparency.

Recently, Matt *et al.*[94] reported on the lipase-catalyzed synthesis of Isosorbide methacrylate in the presence of either vinyl methacrylate or methacrylic anhydride. They investigated the efficiency of three enzymes including the well-known Novozyme 435 (*Candida antarctica* lipase B) and Lipozyme RM IM (*Rhizomucor miehei* lipase (RML)), and were able to reach 87% yield using Lipozyme RM IM (**Scheme 21**). Not to mention this method prevents utilization of methacryloyl species, a simple extraction workup with ethyl acetate is needed to isolate the targeted monomer in purity higher than 99%. The associated homopolymer demonstrated a high T_g value of 167 °C but solubility issues hindered SEC analysis. However, acetylation of the monomer allowed soluble materials with M_n higher than 26.0 kDa and offered tunable T_g. For instance, poly(acetylated isosorbide methacrylate) exhibited a glass transition of 130 °C while poly(dodecanoated isosorbide methacrylate) with the *endo* position tethered has a lower T_g of 54 °C. Surprisingly, they observed that poly(dodecanoated isosorbide methacrylate) with the *exo* position tethered showed an unforeseen melting temperature of 83 °C.



Scheme 21. Chemo-enzymatic synthesis of Isosorbide methacrylate and thus polymerization

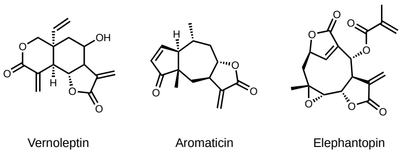
Liu *et al.*[79] reported the production of Isosorbide dimethacrylate (IdM) (**Scheme 22**) to prepare bio-based thermosetting resins. They used an ultrasonic bath at 60 °C to react isosorbide with methacrylic anhydride in the presence of DMAP and obtained the dimethacrylated product in 92% yield. The latter monomer was then involved in copolymerization with acrylated epoxidized soybean oil (AESO) to access adhesive materials with promising properties such as a high flexural modulus of 2060 MPa and a T_g value of 142°C.



Scheme 22. Preparation of isosorbide-dimethacrylate for thermosetting resins synthesis

Bio-based acrylates from lactone-based acrylate

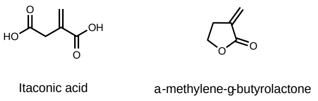
In addition of their cytotoxic, antitumoral and bactericidal properties,[95] bio-based lactones are interesting compounds for new (meth)acrylate monomer and polymer production. In 1988, Park and co-workers[96] also developed Methylenolactocin, an exomethylene lactone, which showed antitumoral properties against *Erhlich carcinoma*. In addition, α-methylene lactones take part in natural sesquiterpene lactone structure (**Scheme 23**).[95]



Scheme 23. Examples of sesquiterpene lactones

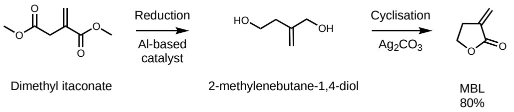
Finally, poly(α-methylene-lactone)s possess high glass transition temperatures which allow their utilization as thermoplastic materials such as dental resins.[97] Thus, due to their high potential, α-methylene-γ-butyrolactone (MBL), α-methylene-γ-valerolactone (MGVL), and their derivatives have been intensively used in bio-based polyacrylate synthesis.

MBL, α-methylene-γ-butyrolactone, is a lactone commonly found in tulips[98] and produced at large scale through chemical processes involving petroleum-based starting materials such as acrylates[99] or (para)formaldehyde.[100] Thus, different strategies have been considered to prepare MBL and its derivatives from renewable resources such as itaconic acid. (**Scheme 24**). [68,101,102,103]



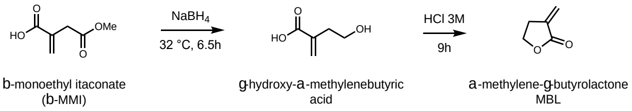
Scheme 24. Structure of Itaconic acid and MBL

Identified as a “top 12 value added chemical from biomass” by the Department of Energy in 2004,[68] itaconic acid has gained attention over the last few years and is now currently produced at large scale from the fermentation of corn or rice.[103] For instance, in 2001, Wilke and co-workers developed a method for itaconic acid production from fermentation of carbohydrates using the fungus *Aspergillus terreus.*[104] Due to its renewability, itaconic acid has been used as a bio-based building block for various chemicals synthesis. Thus, various processes have been imagined for MBL production from itaconic acid and derivatives. For example, in 1975, dimethyl itaconate was reduced to 2-methylenebutane-1,4-diol followed by oxidative cyclization in the presence of a Ag_2CO_3 to give MBL in 80% yield (**Scheme 25**).[101]



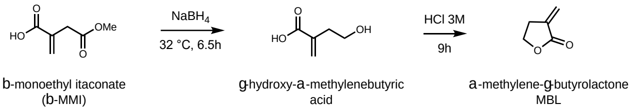
Scheme 25. α-methylene-γ-butyrolactone (MBL) synthesis from itaconic acid derivatives

Recently, Trotta and co-workers[103] obtained MBL in overall yield of 52% in two steps. First, they reduced β-monomethyl itaconate (β-MMI) using $NaBH_4$ at 32 °C for 6.5h, then lactonization was performed under acidic conditions for 9 hours. **(Scheme 26)**. In addition, they proposed Me_2MBL synthesis in 55% yield from the reaction of β-MMI with methyl magnesium chloride in dichloromethane.



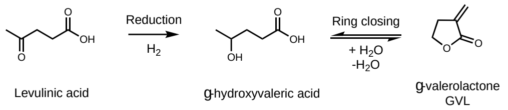
Scheme 26. Preparation of MBL via β-MMI reduction and γ-hydroxy-α-methylenebutyric acid cyclisation

Polymerizations of MBL and its derivatives were performed using various techniques to reach high value acrylate polymers with interesting properties.[103,105,106,107] **(Scheme 27)** For instance, Trotta and co-workers[103] performed reversible addition-fragmentation-chain-transfer (RAFT) polymerization and obtained P(MBL) with a *Đ* value of 1.22 for a 14.8 kDa polymer. Poly(MBL) was also prepared by Mosnáček *et al.*[108] with 95% MBL conversion using Atom Transfer Radical Polymerization (ATRP) with CuBr and 2,2’-bipyridine (bpy) as a catalyst complex and bromopropionitrile (BPN) as a radical initiator in DMF; this polymer exhibited an M_n value of 34.6 kDa. Zhang and co-workers[106] obtained poly(MBL) in 91% yield and reached M_n values of 44.8 kDa by using $Al(C_6F_5)_3$ based-catalysts. They also proposed coordination-addition polymerization[107] of MBL using neutral lanthanocene (II), non-lanthanocene silylamides, and cationic group 4 metallocene catalysts and they were able to produce poly(PBL) with a high M_n of 58 kDa and a high T_g value of 194 °C. Me_2MBL was also subjected to polymerization. For instance, the RAFT process[103] was performed to produce poly(Me_2MBL) with M_n between 8.8 and 61.1 kDa and a T_g value of 210 °.



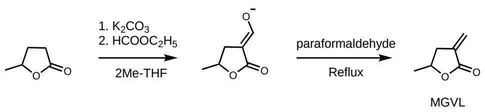
Scheme 27. Structure of poly(MBL) and Poly(Me_2MBL)

α-methylene-γ-valerolactone (MGVL) is another interesting acrylate monomer produced from GVL (γ-valerolactone) which can be used as a comonomer for bio-based polymer synthesis thanks to its non-toxicity,[109] sustainable origin, and conformational rigidity.[110] It is commonly produced from Levulinic acid (LA), considered as one of the “top 12 value added chemicals from biomass” by the Department of Energy,[68] through carbonyl reduction followed by lactonization (**Scheme 28**).[111]



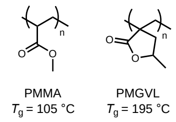
Scheme 28. Preparation of γ-valerolactone from levulinic acid

Levulinic acid, a promising bio-synthon,[112] can be produced from glucose. For instance, in 1990, Biofine produced Levulinic acid in 75% yield from C_6 sugars from wood, corn and paper waste using sulfuric acid as a catalyst.[113] Subsequent hydrogenation of levulinic acid by using, for example, metal-based catalyst such as Pt oxide or a Ru-based compound,[114,115] gave GVL, a colorless and odorant liquid often used for fragrance and food additives production[109] as well as a bio-based solvent or green solvent precursor. For instance, Galletti *et al.* reached 100% GVL yield using Ru/C and Amberlyst-70 catalysts in H_2O at 70 °C. Other pathways such as ring closing of 4-pentenoic acid[116] or LA dehydration to angelica lactone can also lead to this compound of interest.[117] α-methylene-γ-valerolactone (MGVL) is a very interesting acrylic monomer due to its similar properties to methyl methacrylate (MMA).[118] Initially produced in 2 steps, MGVL synthesis has been subjected to several optimizations. One of the first preparations of this lactone acrylate involved NaH and ethyl formate to form an enolate which was then condensed with cracked paraformaldehyde.[119] Liquid and gas phase methylenations were also investigated by using homo- or heterogeneous basic catalysts.[120] For instance, K_2CO_3 was used as a catalyst for the reaction of GVL with paraformaldehyde in 2-methyl-THF at 180 °C (**Scheme 29**) while in 2004, Manzer and co-workers[118] converted GVL into MGVL with selectivity up to 95% of GVL by using barium-base catalyst.



Scheme 29. Methylenation of GVL into MGVL

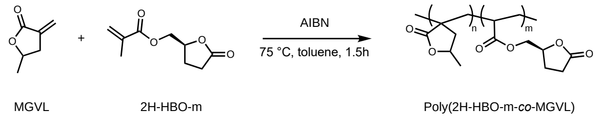
Homopolymerized and copolymerized through either radical or anionic methods,[121] MGVL demonstrated its potential to afford high T_g polymers. Indeed, polyMGVL exhibits a glass transition temperature of approximately 195 °C while PMMA has a T_g around 105 °C (**Scheme 30**).[122]



Scheme 30. Poly(Methyl methacrylate) & Poly(Methylene-γ-valerolactone) and their corresponding T_g values

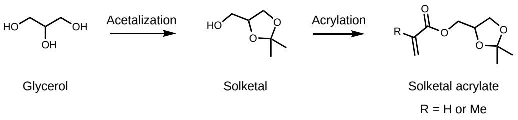
For instance, Stille *et al.* [121] reported the anionic and radical polymerization of MGVL using benzoyl peroxide (BPO) as a radical initiator in benzene and butyllithium as an anionic catalyst in THF, and obtained rigid polymers exhibiting interesting solubility and thermal properties. The racemic poly(MGVL), soluble in many organic solvents such as acetone, chloroform, dimethylformamide, and propylene carbonate, exhibited high T_g values ranging from 211 to 220 °C.

In addition, incorporation of MGVL helped to tune T_g values of the resulting materials. For instance, co-polymerization with the bio-based 2H-HBO methacrylate or other methacrylate derivatives allowed glass transition temperatures between 98 and 200 °C depending on the percentage of MGVL incorporated into the polymer chains—the higher the MGVL content, the higher the T_g (**Scheme 31**).[110]



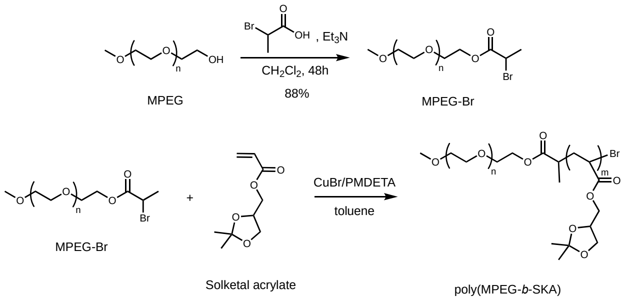
Scheme 31. Copolymerization of MGVL with 2H-HBO-m

Bio-based acrylates from Glycerol



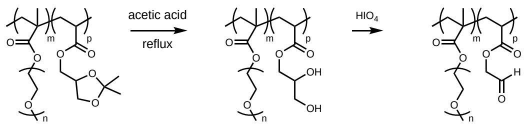
Scheme 32. Formation of Solketal acrylate from glycerol

Obtained from the condensation of glycerol onto acetone followed by acrylation (**Scheme 32**), solketal acrylate (SKA) is an attractive monomer due to the ketal functional group which allows post-polymerization hydrolysis. Several papers have reported either RAFT or ATRP processes to copolymerize SKA with co-monomers such as styrene or *N*-isopropyl acrylamide. For instance, Man Yu and co-workers applied ATRP method using CuBr, *N,N,N′,N′,N″*-Pentamethyldiethylenetriamine (PMDETA) to first polymerize styrene and then SKA.[123] Post-polymerization hydrolysis of the SKA ketal moiety gave an amphiphilic block copolymer. Kuckling *et al.* used both ATRP[88] and RAFT[124] strategies but chose *N*-isopropyl acrylamide to build their hydrophobic block. In 2014 Anastasaki and co-workers proposed a photoinduced ATRP in the presence of Me_6-Tren ligand and $CuBr_2$ to prepare poly(SKA-*co*-methyl acrylate) that was hydrolyzed to access a self-assembling material containing glycerol acrylate and methyl acrylate as hydrophilic and hydrophobic blocks, respectively.[125] Rather than using conventional co-monomers to build a block copolymer, Zhang *et al.*[126] built their hydrophilic block from monomethoxy-poly(ethylene glycol) (MPEG). They subjected MPEG to esterification with 2-bromopropionyl bromide to prepare MPEG-Br which was used as a macroinitiator in the ATRP of SKA (**Scheme 33**). While most of the strategies effect the hydrolysis of the SKA block, Zhang and co-workers retained it as a hydrophobic moiety for encapsulation that would allow the release of the encapsulated chemical in acidic media.



Scheme 33. Preparation of poly(MPEG-*b*-SKA) from MPEG-Br initiator and Solketal acrylate through an ATRP process

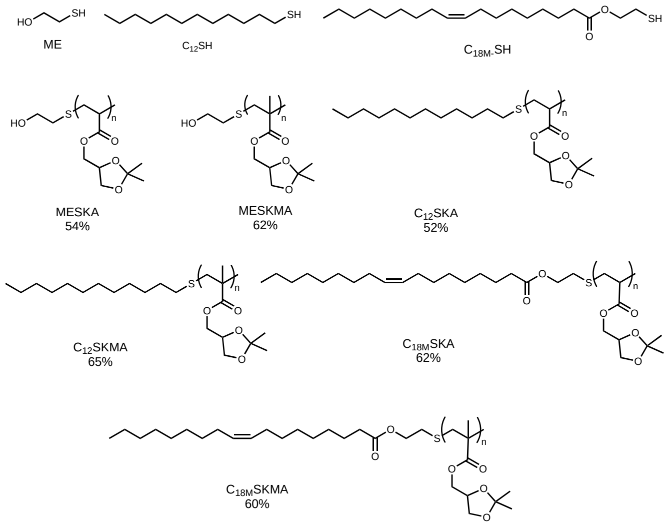
The hydrolysis of SKA block frees two hydroxyl functions that can be involved in post-polymerization modifications. For instance, after RAFT co-polymerization of SKA with poly(ethylene glycol) methyl ether methacrylate (PEGMA), Rossi and co-workers performed hydrolysis of the ketal and the resulting 1,2-diols were oxidized in the presence of HIO_4 (**Scheme 34**). The resulting aldehydes could then be reacted with molecules bearing amine functional groups, for example.



Scheme 34. Hydrolysis of poly(PEGMA-co-SKA) followed by oxidation of the resulting pendent diols

Beyaz and co-workers[127] reported one of the first grafts of SKA onto cellulose derived from palm tree leaves. The developed method involving potassium persulfate as initiator of polymerization allowed a maximum grafting weight gain of 27%

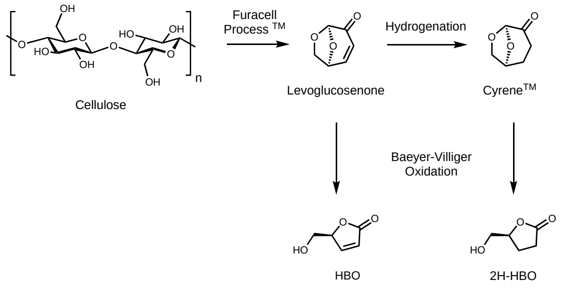
in approximately 1.5h. Even though the resulting grafted cellulose did not demonstrate improved thermal properties, the mechanical properties were substantially enhanced. For example, the Young's modulus of the grafted cellulose proved to be 5 times higher than the Palm cellulose, 48.3 vs. 256.8 MPa. Recently, they applied a similar procedure to hydroxyethyl cellulose (HEC) to prepare a material with moisture absorption properties.[128] The co-polymerization of SKA and Solketal methacrylate (SKMA) with various transfer agents derived from fatty chains such as 2-mercaptoethanol (ME), dodecanethiol (C_{12}SH), and thiols prepared from lauric acid (C_{12M}-SH) and oleic acid (C_{18M}-SH) was performed by Robin *et al.*[129] in 2016 to prepare water–soluble glycerin-based polymers **(Scheme 35)**.



Scheme 35. Solketal-based polymers from various transfer agents

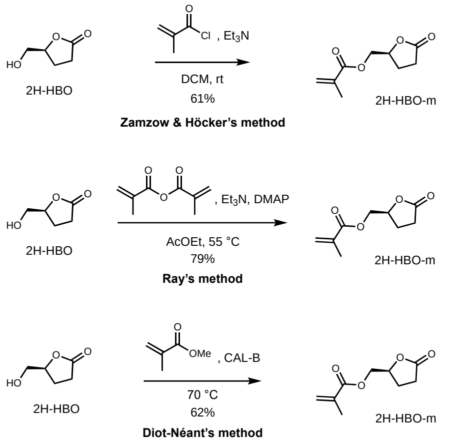
For instance, MESKMA and C_{12}SKMA were synthetized in 62% and 65% yields, respectively. Polymers made using AIBN as a radical initiator exhibited interesting properties such as respective M_n values of 6.7 kDa and 6.2 kDa and Đ values of 2.2 and 2.3.

Bio-based acrylates from Levoglucosenone (LGO)



Scheme 36. Preparation of HBO and 2H-HBO from cellulose-based levoglucosenone (LGO)

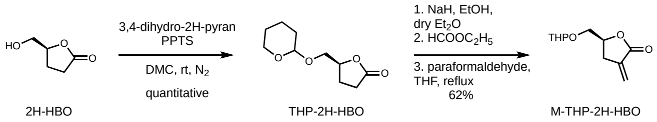
Levoglucosenone (LGO) is a bio-based cyclic α,β-unsaturated ketone that has been widely used as a versatile building block for the synthesis of potential medecines[130] and flavour molecules.[131] Produced through flash catalytic pyrolysis of cellulose-based feedstocks such as sawdust, Circa has developed the Furacell™ technology,[132] an eco-friendly process that allows high scale production of LGO. The reduced form of LGO, known as Cyrene,[133,134] is now considered as a promising solvent aiming at replacing petroleum-based polar solvents such as DMF. The Baeyer-Villiger oxidation (BVO) of LGO and Cyrene was investigated to access HBO and 2H-HBO, respectively, two valuable chiral synthons (**Scheme 36**). For instance, in 2016 Allais and co-workers greened up the aforementioned BVO by replacing peracetic acid[135] with hydrogen peroxide in aqueous media.[136]



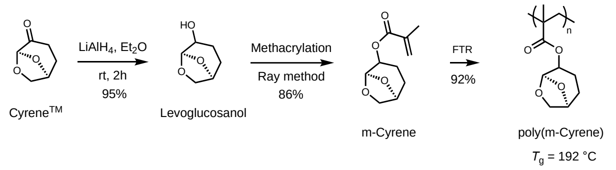
Scheme 37. Synthesis of 2H-HBO-m via 3 different methods

2H-HBO was the first LGO-derived molecule to be engaged in acrylate monomer synthesis and thus polymerization. In 1994, Zamzow and Hocker[137] reported the methacrylation of 2H-HBO in the presence of methacryloyl chloride and Et_3N (**Scheme 37**). The desired acrylate (2H-HBO-m) obtained in 61% yield was then homopolymerized through a free radical process using AIBN as the free radical initiator. Recently, Saito and co-workers[138] proposed an optimization to prevent utilization of the toxic halogenated methacryloyl chloride by replacing it by methacrylic anhydride. Even though this procedure uses 1.5 equiv. of Et_3N, it employs ethyl acetate a greener solvent (**Scheme 37**) compared to dichloromethane, and column chromatography is not needed for the purification. 2H-HBO-m was then subjected to three different polymerization methods: 1) bulk polymerization, 2) solution polymerization, and 3) emulsion polymerization. In addition to homopolymerization of 2H-HBO-m, they targeted styrene and methyl methacrylate as monomers for copolymerization. Although the incorporation of co-monomers remains far from the feed fraction, except for the co-monomer BMA, the resulting set of materials exhibit high M_n values up to 46.0 kDa as well as T_g values between 71 °C and 118 °C. Based on the work of Warwel and co-workers,[139] we developed a chemo-enzymatic procedure involving *Candida antarctica* lipase type B to perform the methacrylation of HBO or 2H-HBO (**Scheme 37**).[110] In that method, all the unreacted reagent can be easily isolated and the biocatalyst can be reused without significant loss of activity. For instance, methyl methacrylate used in excess can be distilled and recycled during the concentration step while HBO or 2H-HBO can be recovered in the aqueous layer in the extraction process. The α–proton of the lactone in 2H-HBO then offered methylenation possibilities after protection of the hydroxyl. This two-step protocol to prepare MGVL and MBL from the corresponding lactones involves the synthesis of an intermediate obtained by reaction between ethyl formate and the lactone in the presence of a strong base, typically NaH, followed by reaction between the resulting salt and paraformaldehyde (**Scheme 38**). This highly reactive lactone acrylate M-THP-2H-HBO was homopolymerized and copolymerized with MMA through a free radical process. In addition to a high M_n of 44.0 kDa, poly(M-THP-2H-HBO) exhibits a high T_g value of 148 °C.

Scheme 38. Synthesis of the cellulose-based lactone acrylate M-THP-2H-HBO



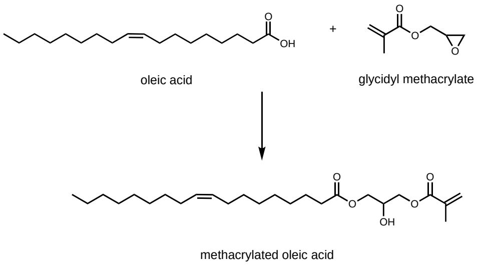
Recently, Saito and co-workers[140] proposed the reduction of Cyrene™ in the presence of lithium aluminum hydride to access levoglucosanol (**Scheme 39**). This Cyrene-based alcohol was then methacrylated by applying their strategy involving methacrylic anhydride in ethyl acetate; subsequent emulsion homopolymerization of levoglucosanol methacrylate afforded a high M_n polyacrylate in 92% yield with promising thermal properties such as a $T_{d10\%}$ of 287 °C and a glass transition of 192 °C.



Scheme 39. Synthesis of m-Cyrene and its polymerization

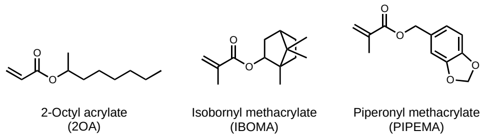
Bio-based acrylates from vegetable oils and fatty acid

Vegetable oils and fatty acids have been a significant source of promising bio-based molecules for material science. For instance, well-known companies like Arkema[141] have commercialized products involving molecules from castor oils for shoe production. In addition to being used for polyesters and polyamides, some molecules derived from vegetable oils have been identified as good candidates to produce polyacrylates. Recently, Lomège and co-workers[142] reviewed fatty acid-based acrylate synthesis and the resulting radical polymerizations such as ATRP or macroemulsion process. Covering fatty alcohols as well as fatty acids, they reported that acrylation often involves a 2-step process when the presence of hydroxyl functions is missing. For instance, oleic acid undergoes hydrobromination to install a secondary alcohol that is then subjected to acrylation.



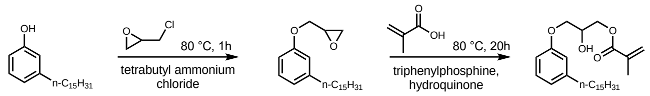
Scheme 40. Preparation of methacrylated oleic acid (MOA)

In 2012, Moreno *et al.*[143] reported the preparation of an oleic acid acrylate by reacting oleic acid with glycidyl methacrylate to preserve the unsaturation (**Scheme 40**). Homopolymerization of the desired acrylate via mini-emulsion gave latexes. Gel formation due to crosslinking via the unsaturation was observed. In 2014,[144] they explored the copolymerization of the aforementioned monomer with MBL to tune the glass transition of the latexes. They showed that an incorporation of 15% of MBL resulted in a T_g value of 39 °C compared to -2 °C for the poly(oleic acid acrylate). They noticed that increasing the MBL proportion improved the Young's modulus but decreased the strain at break due to the lactone steric hindrance.



Scheme 41. Examples of acrylates derived from vegetable oil, terpenes and bioaromatics

In 2018, Badia and co-workers[145] reported the copolymerization of 2-octyl acrylate (2OA) with isobornyl methacrylate (IBOMA), two bio-based acrylates obtained from castor oil and pine resin, respectively, in the presence of 1% MAA comonomer for the preparation of Pressure Sensitive Adhesives (PSAs) (**Scheme 41**). 2OA was used to build the "soft" segment due to the flexibility of the side chain while the steric hindrance in IBOMA was used to prepare the "hard" segment. The mechanical properties of the resulting set of copolymers with various IBOMA and 2OA compositions were then studied and compared to those of poly(2EHA-*co*-MMA-*co*-AA) (2EHA: 84%, MMA: 15%, AA: 1%). For instance, poly(2OA-*co*-IBOMA-co-MAA) (2OA: 84%, IBOMA: 15%, MAA: 1%) had a better shear strength (greater by 45) and a better Shear Adhesion Fail Temperature (SAFT, 133 °C vs 70 °C) than poly(2EHA-*co*-MMA-*co*-AA). Recently, Badia *et al.*[146] explored the copolymerization of piperonyl methacrylate (PIPEMA) with 2OA to create UV-sensitive PSAs thanks to the photo-crosslinkable benzodioxole moiety in PIPEMA (**Scheme 9.2**). The copolymer with 84/15 of 2OA/PIPEMA content was irradiated to study the influence of UV exposure. As the irradiation was performed for longer periods, decreases in mechanical properties - such as loop tack and work adhesion - were noticed while the shear resistance and the SAFT increased. For instance, 30 min of UV irradiation resulted in a shear resistance of 29 000 min vs 90 min and a SAFT of 136 °C compared to 64 °C for the unaltered material.



Scheme 42. Preparation of cardanol methacrylate

In addition to PSAs, acrylates derived from fatty acids are also used to replace petroleum-based compounds such as styrene used as diluents in resins.[147] In 2017, Ladmiral *et al.*[148] proposed the preparation of a cardanol derivative, a bio-based molecule obtained from cashew nut shell liquid (CNSL), to address both the issue of styrene and the resulting necessity to access low T_g aromatic latex for coatings. Their synthetic pathway starts by reacting cardanol with epichlorohydrin followed by methacrylation of the resulting intermediate (**Scheme 42**). The targeted acrylate was then copolymerized with MMA through free radical processes to give latexes with sizes between 25 and 75 nm.

Conclusion

Several bio-renewable synthons have been engaged in acrylate preparations and subsequent polymerizations, thus offering a wide range of properties such as high glass transitions and adhesive behaviors. Most of those monomers are synthetized through two main processes: 1) esterification of the hydroxyl moiety, commonly called acrylation or methacrylation, in the presence of acrylic acid or its derivatives; or 2) α-methylenation of esters or lactones. Esterification of alcohol to form new acrylates is, for now, the most common method because of its simple implementation. Initially performed with acryloyl species in halogenated solvent, several optimizations have been reported to green up the process such as the utilization of acrylic anhydride. While a wide variety of bio-based monomers has been synthesized through this method, α-methylenation has been used more rarely. First performed in 2 steps involving the formation of an enolate intermediate then condensed onto cracked paraformaldehyde, several optimizations have been explored to shorten the pathway. Even if the monomers synthesized *via* those two well-developed strategies are bio-based, the synthetic routes almost always imply utilization of petroleum-based reagents such as methacrylic anhydride and formaldehyde. In addition to the toxicity of acryloyl species, solvents and bases used in the processes are generally far from being green and sometimes present hazards for both human health and the environment. A few exceptions exist such as the use of ethyl acetate rather than dichloromethane, or lipase-mediated chemo-enzymatic methods, even though viability and costs of bio-catalytic process should be investigated. In addition, a few molecules have been transformed into acrylates through greener procedures that use neither conventional acrylation conditions nor α-methylenation. For instance, itaconic acid, a top 12 bio-renewable synthon can be selectively reduced. The resulting hydroxy acid can be subjected to ring-closing lactonization to access MGVL a valuable monomer used for preparation of high glass transition polyacrylate. Those promising strategies that use naturally occurring α,β-unsaturated esters or acids encourage us to rethink and simplify our approach to propose and share greener pathways. Finally, in the context of climate change and resource depletion, bio-based polyacrylates take on their full meaning when considered as substitutes for petroleum-based polymer.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the National Science Foundation (CHE-1607263), and a joint collaboration between URD Agro-Biotechnologies Industrielles (ABI) and the University of Florida. The authors are grateful to the Circa Group for providing industrial grade levoglucosenone. The authors are also grateful to Grand Reims, Département de la Marne, Grand Est and Fondation du Site Paris-Reims for financial support.

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FA, CV and FD-N: wrote and drafted the article. FA and SAM: reviewed and approved the article.

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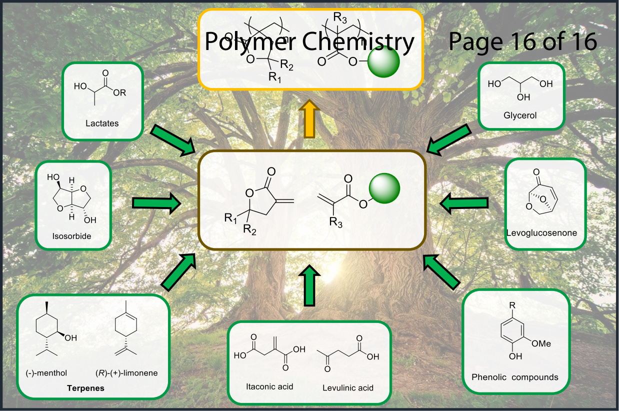
Lactates
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Levulinic acid
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