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RDRP (Meth)acrylic Homo and Block Polymers from Lignocellulosic Sugar Derivatives

Marc Palà, Sarah E. Woods, Fiona L. Hatton, and Gerard Lligadas**

Currently, most commodity chemicals and polymers are manufactured from nonrenewable petroleum-based resources. However, due to its finite nature and social claims about environment preservation, alternative sources of value-added and building block chemicals are being intensively studied. Renewable lignocellulosic biomass has offered an attractive replacement for fossil-based chemicals. Lignin and C5/C6 sugars obtained from lignocellulosic biomass through chemical and enzymatic methods can be further transformed to targeted chemical platforms. In the present review, synthetic pathways for well-defined poly(meth)acrylates obtained from C5/C6 sugar-derived platforms in which the sugar structure is not retained are discussed. While bio-based polymers from these monomers are investigated using a wide range of polymerization techniques, this study focuses on precise synthesis of macromolecular structures taking advantage of reversible-deactivation radical polymerization methods and their applications.

1. Introduction

Although the majority of commodity polymers are currently synthesized from fossil fuel-based resources, there is a shift in recent decades toward the development of eco-friendly polymeric materials.[1–4] Considering the inevitable exhaustion of fossil resources and the changing social perceptions concerning human-related activities, exploiting environmentally friendly resources is one of the current key challenges facing industrial and academic researchers. Lignocellulosic biomass (LB), which is present in a wide variety of agricultural, forestry, municipal, and industrial waste biomass sources, has attracted global interest as an alternative to fossil resources.[5–7] LB is considered as one of the most valuable types of biomass forms due to its inedibility, low cost, renewability, carbon neutrality, and wide distribution.[8] It consists of a complex assembly of three biopolymers, namely, cellulose, hemicellulose, and lignin (**Figure 1**A). The proportions of these three components depend on the types of plants as shown in Figure 1B; however, cellulose and hemicellulose typically form the bulk of biomass weight (about 30%–50%). Accordingly, the dominant sugar fraction of LB has been the main focus for targeting upgrading processes, with the final goal of producing second-generation sustainable fuels, chemicals, and materials without compromising global food security.[6,9–11]

Nowadays it is viable to convert polysaccharide fractions of LB into useful chemicals in biorefinery technologies.[26–29] Most of these upgrading routes involve treatments for reducing the structural complexity of LB, isolating the sugar-rich fractions (cellulose and hemicellulose), and finally conducting the depolymerization of polysaccharides into the respective monomeric fermentable C5/C6 sugars, i.e., glucose (from the degradation of cellulose) and xylose, arabinose, mannose, galactose, and rhamnose (from hemicellulose). Considering the well-known chemistry and biochemistry for upgrading carbohydrates, these monosaccharides are valuable substrates for the production of valuable bio-based chemicals. Accordingly, a plethora of platform chemicals such as sugar alcohols (e.g., xylitol and sorbitol), furanic compounds (5-hydroxymethyl furfural and furfural), carboxylic acids (e.g., succinic acid, lactic acid and itaconic acid), among others (e.g., levoglucosenone [LGO]) can be produced in pure form from the above-mentioned carbohydrate sources (see **Figure 2** for representative examples). Both production and conversion of these bio-based building blocks into a myriad of higher value-added carbon-based chemicals such as diphenolic acid (a levulinic acid derivative),[30] isosorbide (IS) (a sorbitol [SRB] derivative),[31] lactide (a lactic acid [LA] derivative),[32] and furfuryl alcohol (a furfural [FL] derivative)[33] have been intensively investigated and comprehensively reviewed elsewhere.[6,9–11]

This review provides an up-to-date overview on the opportunities to access new bio-based poly(meth)acrylates and analogs from LB using carbohydrate-derived products such as LA, SRB, itaconic acid (IA), LGO, FL, and α-unsaturated-γ-butyrolactones

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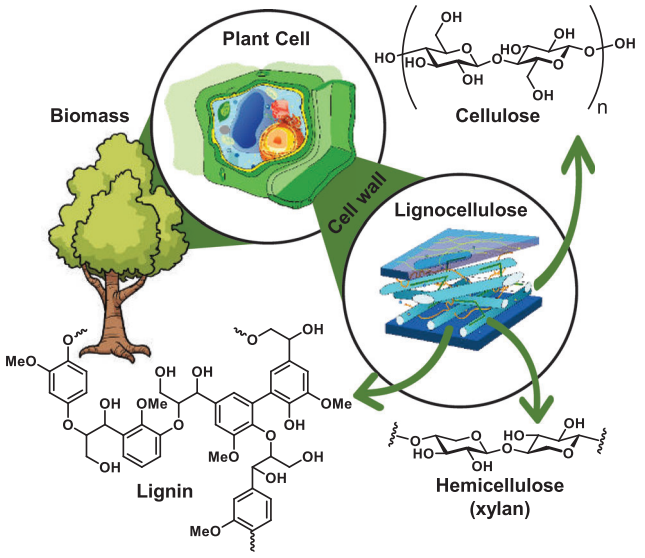

b) Composition of lignocellulosic biomass from different vegetal sources

Biomass	Composition (% dry wt)			Ref.
	Cellulose	Hemi-cellulose	Lignin	
Hardwood stem	40 – 55	24 – 40	18 – 25	[12]
Softwood stem	45 – 50	25 – 35	25 – 35	[12]
Bagasse	41 – 50	25 – 30	18 – 25	[13 - 16]
Wheat Straw	35 – 40	21 – 27	15 – 25	[14 - 16]
Oat straw	31 – 35	20 – 26	10 – 15	[17]
Cotton stalk	31	11	30	[18]
Rice Straw	35 – 38	25 – 26	13 – 25	[16, 19]
Barley Straw	31 – 45	27 – 38	14 – 19	[20]
Switchgrass	45	32	12 – 20	[21]
Silvergrass	37	29	19	[16]
Sawdust	31 – 64	71 – 89	14 – 34	[22]
Pine	42 – 49	13 – 25	23 – 29	[23]
Banana peels	12	10	2	[24]
Orange peels	14	6	2	[25]
Newspaper	40 – 55	24 – 39	18 – 30	[21]

Figure 1. A) Structure and B) composition of LB from different vegetal sources. Cellulose is the major component (typically about 35–50 wt%) and is composed of D-glucose subunits linked by β-1,4-glycosidic bonds. Hemicellulose, which is commonly the second most abundant polymer (typically about 20–35 wt%), is composed of several different polymers, such as xylan, galactomannan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan, built from various pentoses and hexoses connected by several forms of glycosidic bonds. Hemicelluloses are imbedded in the plant cell walls to form a complex network of bonds, which serve as a connection between the cellulose fibers and lignin. The latter (typically about 10–25 wt%) is an amorphous heteropolymer based on three different phenylpropane units (*p*-coumaryl, coniferyl, and sinapyl alcohol).

such as α-methylene-γ-butyrolactone (MBL) as platform chemicals. The subject of bio-based acrylates, with some focus on lignocellulosic sources has been recently reviewed.[34] Herein, special emphasis will be given to well-defined homo and block polymers based lignocellulosic sugar derivatives prepared by reversible-deactivation radical polymerization (RDRP) methods.[35,36] The various applications of the resulting polymers are described, and finally future opportunities for this area of research are also discussed.

2. RDRP Methods: Efficient Control of Radical Polymerization

Poly(meth)acrylates are a commercially successful class of commodity plastics exhibiting varied properties such as transparency, weather resistance, good adhesion to polar substrates, and biocompatibility.[37,38] Beyond the standard and cost-effective industrial approaches for producing these valuable materials using the free-radical polymerization (FRP) method, the use of RDRP methods is mandatory to develop well-defined materials with precisely controlled structures (i.e., predictable molecular weight, low dispersity, $Đ$, and high level of end group functionality). Macromolecular architecture control comes by a variety of techniques including the use of so-called nitroxide-mediated polymerization (NMP),[39] atom transfer radical polymerization (ATRP),[40,41] single-electron transfer living radical polymerization (SET-LRP),[42] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[43] The commonality among these techniques is that they all limit and control the number of radicals reacting at a particular time. Their fundamental aspects have been exhaustively discussed and reviewed previously.[44–46] Briefly, the key concept to moderate the kinetics of RDRP processes is to establish a fast and reversible activation of dormant polymer species. This significantly reduces the concentration of active radicals and thus the probability of the chains to undergo termination by recombination or disproportionation, since the kinetics of these reactions are second order with respect to the radical concentration, while the propagation step is first order. Accordingly, the degree of polymerization in RDRP increases linearly with conversion up to a programmed limit and the $Đ$ of the polymers obtained is significantly lower than in FRP. Additionally, a substantial amount of polymer chain end groups introduced by the RDRP agent is preserved. Hence, RDRP is the method of choice to develop well-defined poly(meth)acrylate homopolymers, block copolymers, and more advanced macromolecular architectures such as graft, cyclic, and star-shaped polymers.

In the following subsections, fundamental studies on the use of various RDRP techniques in the precise synthesis of poly(meth)acrylate polymers and analogues from various LB-derived carbohydrate sources in which the structure of the original sugar is not maintained are discussed. The chemical structure of the 28 vinylic monomers that will appear through this review, categorized according to the lignocellulosic sugar platform they can be sourced from, is presented in **Figure 3**. Most of these monomers are typically produced via chemical modification of alcohol-functional precursors with acryloyl chloride or methacrylic anhydride,[4] although alternative routes closer to ideal from a green chemistry point of view were recently explored (vide infra).

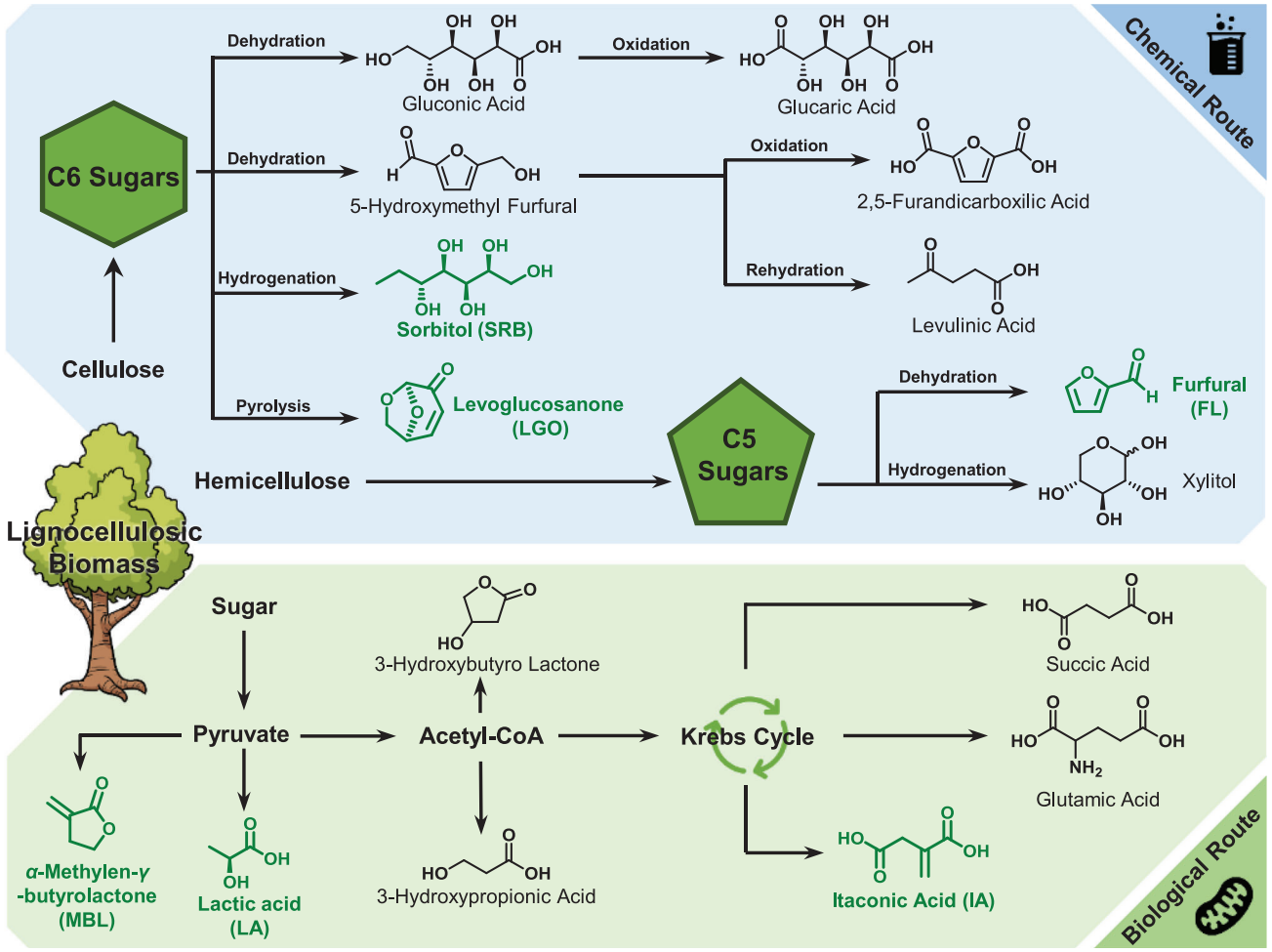

Figure 2. Platform chemicals obtained from lignocellulosic sugars through chemical and biological routes.[26–29] Note that this figure only depicts representative examples and is not meant to be exhaustive.

3. Well-Defined Poly(meth)acrylates Based on Lignocellulosic Sugars Derivatives

3.1. Lactic Acid Platform

LA is one of the C3 building blocks which can be produced from lignocellulosic sugars such as glucose, sucrose, or lactose by LA bacteria.[47,48] For example, Corbion manufactures L-LA through microbial fermentation of carbohydrates. Although the industrial application of LA is very broad, it is mainly known because of polylactic acid (PLA), one of the most important commercially available renewable and biodegradable polymers.[6,49] Esterification of the –COOH group in LA with linear alcohols affords the corresponding alkyl lactates (ALs), which are already used in several industries such as the pharmaceutical, food, agricultural and polymer industries and their use is expected to increase further in the near future.[50,51] Among them, one of the most remarkable is ethyl lactate (EtL),[52] which is produced from LA and ethanol. EtL is considered a prospective renewable substitute for some petroleum-derived solvents such as dimethylsulfoxide (DMSO) and *N*-methylpyrrolidone because of its combination of properties including high boiling point, high solvency power, and biodegradability.[53,54] Recently, the potential of EtL as a solvent for organic synthesis[55] and polymerization reaction media[56] has also been demonstrated. The secondary –OH group in ALs offers a straightforward access to the corresponding bio-based (meth)acrylic monomers (**Figure 4**). In this sense, acrylic derivatives of ALs such as EtL, methyl lactate, and butyl lactate are simply accessible in high yield through chemical functionalization of the corresponding alcohol precursor with acryloyl chloride in the presence of triethylamine (TEA) using dichloromethane (DCM) as solvent (Figure 4).[57]

This library of bio-based monomers is also accessible via alternative greener routes. For example, the direct esterification of ALs with acrylic acid, which is also a potentially bio-based molecule, avoids the use of toxic acyl chlorides. Puroshothamn and co-workers reported the preparation of AL acrylates with methyl, ethyl and propyl ester groups through an azeotropic distillation of the corresponding ester with acrylic acid under acidic catalysis (Figure 4).[58] The use of propylphosphonic anhydride (T3P) as an environmentally friendly ester coupler promoter in Me-THF at room temperature also afforded ethyl lactate acrylate (EtLA) in moderate yield (60%) (Figure 4).[57] Regarding methacrylate-type monomers, traditional esterification

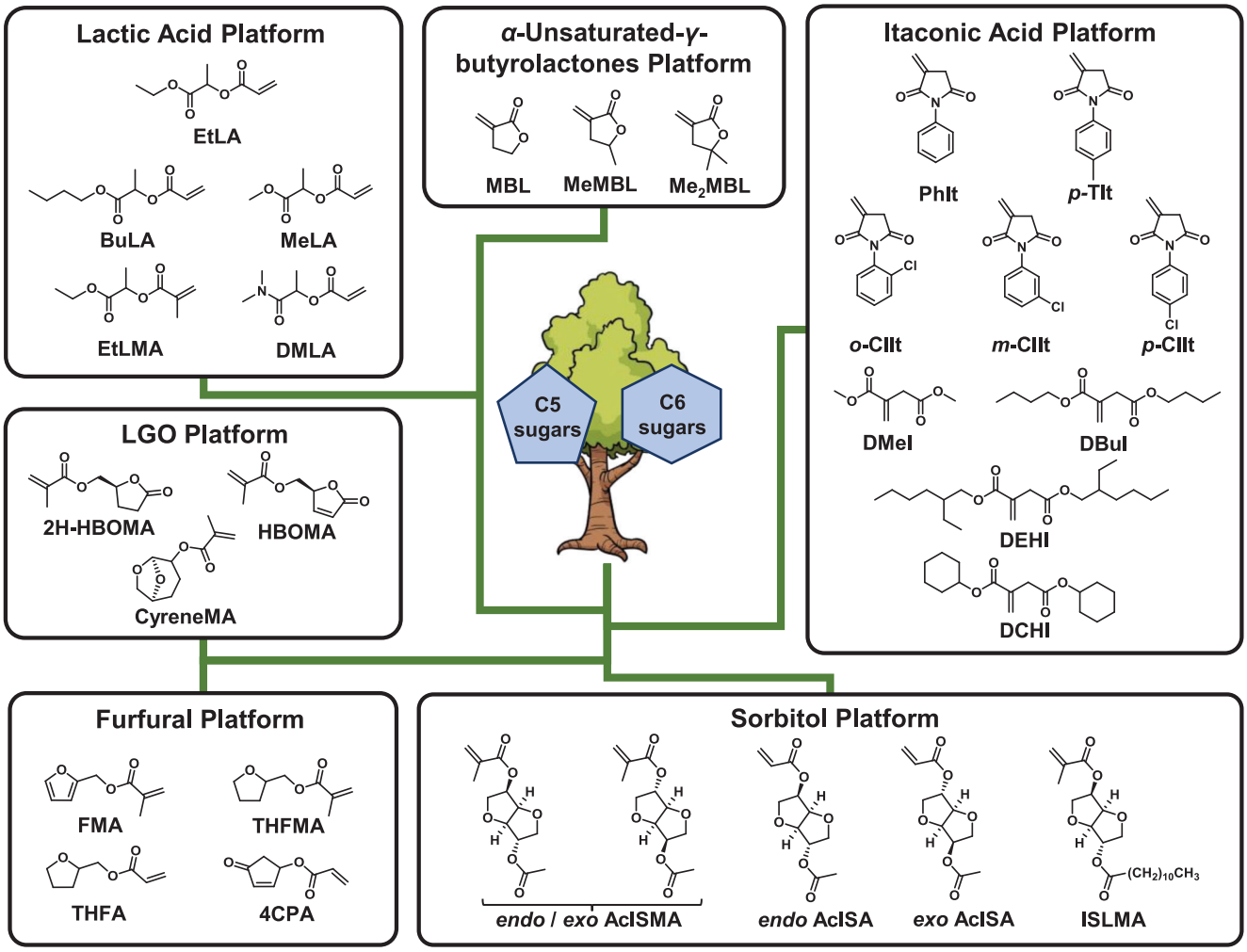

Figure 3. The (meth)acrylic monomers prepared from various lignocellulosic platform chemicals that will appear through this review.

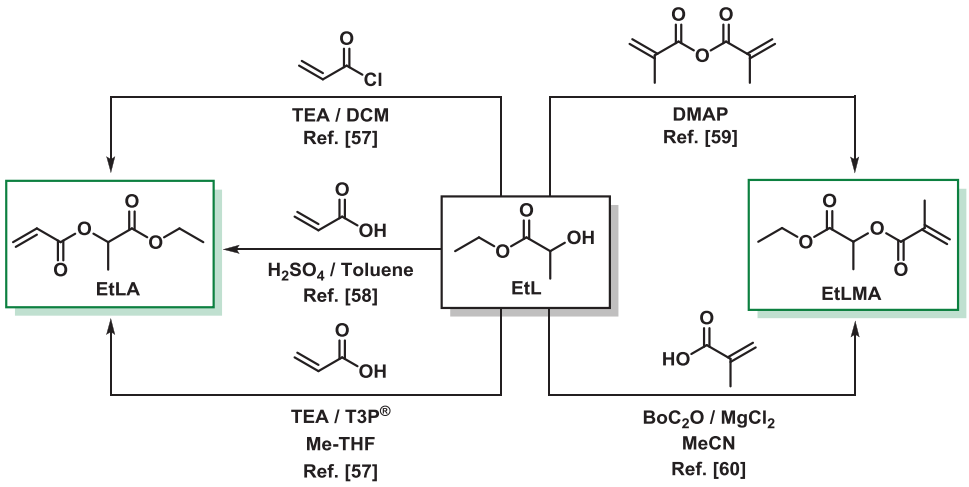

Figure 4. Synthetic routes to EtLA and EtLMA monomers from EtLa solvent.

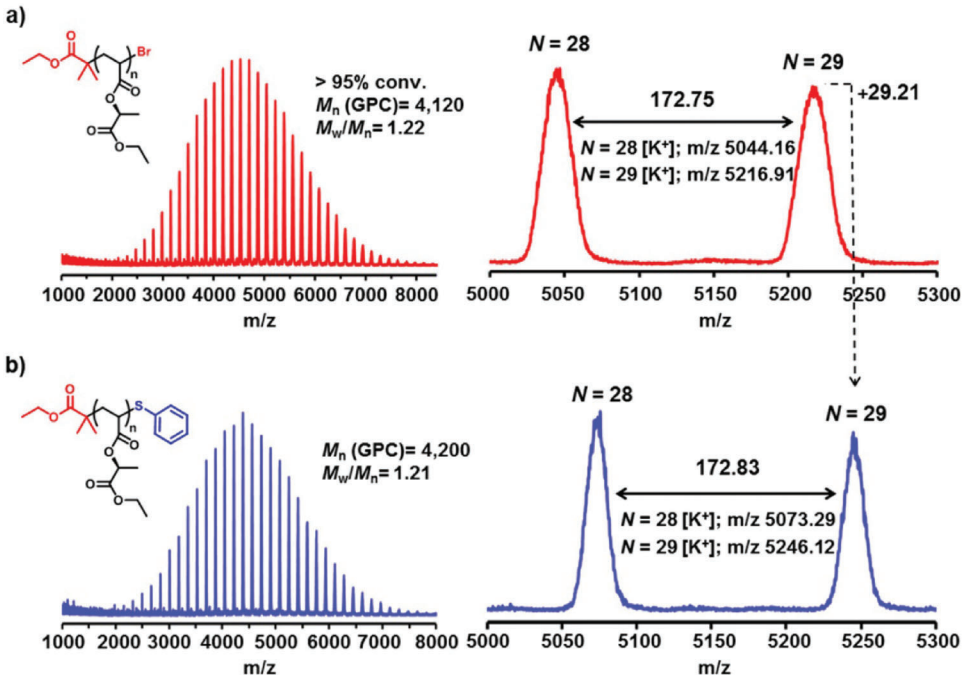

Figure 5. MALDI-TOF spectra of PEtLA obtained by SET-LRP at 97% conversion before and after thio-bromo "click" modification at ω-bromo chain end with thiophenol. Magnified regions confirm the expected peak-to-peak spacing and the near-perfect bromine chain-end functionality for the synthesized polymer. Reproduced with permission.[57] Copyright 2019 American Chemical Society.

methods using (meth)acrylic acid in the presence of a dehydrating agent, for example by the Steglich method using dicyclohexylcarbodiimide (DCC), or by treatment of the corresponding alcohols with (meth)acrylic anhydride in the presence of a base and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (Figure 4) have been reported.[59] Recently, the Thomas Laboratory reported an alternative efficient route to EtL methacrylate (EtLMA) via the esterification of the corresponding alcohol with methacrylic acid, di-*tert*-butyl dicarbonate (Boc_2O), and catalytic amounts of $MgCl_2$ (Figure 4).[60]

The controlled radical polymerization (CRP) of this forgotten class of vinylic monomers was first attempted in our laboratory in 2019 using Cu(0)-catalyzed SET-LRP as a RDRP method.[57] It was demonstrated that alcohols are excellent solvents to deliver well-defined poly(AL acrylate)s (PALAs) at 25 °C using Cu(0) wire. Methyl, ethyl, and butyl lactate acrylate monomers (MeLA, EtLA, and BuLA, respectively) could be polymerized in a controlled fashion using tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) and ethyl α-bromoisobutyrate (EBiB) as ligand and monofunctional initiator, respectively. Different alcohols including ethanol and EtL, as well as EtL-water mixtures, were used to mediate an efficient SET-LRP process. This methodology produced well-defined ω-bromo-terminated PALAs with high monomer conversions (>90%) while retaining high control over molecular weight up to 65 000 g mol^{-1} and low $Đ$. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis was used to demonstrate high levels of chain-end functionality for some of the produced polymers (**Figure 5**).

AL methacrylate-type monomers such as EtLMA could also be polymerized in a controlled fashion under SET-LRP conditions.[59] However, in this case, the use of sulfonyl halide initiators such as *p*-toluenesulfonyl chloride (Ts-Cl) was mandatory to achieve a controlled polymerization. EtLMA was polymerized at 50 °C in a mixture of EtOH/H_2O (8/2 v/v), with a molar ratio of [EtLMA:Ts-Cl] = 200:1. After 4 h, a monomer conversion of 85% was determined to produce a PEtLMA with molecular weights 32 000 g mol^{-1} and $Đ = 1.20$.

Similarly, other RDRP methods have also been efficient in controlling the polymerization of AL acrylic monomers. For example, BuLA proved to be well-behaved under RAFT polymerization conditions.[61] Using 2-(dodecylthiocarbonothioylthio)propionic acid (DTPA) as the RAFT agent and 2,2′-azobis(2-methylpropionitrile) (AIBN) as the initiator, BuLA was polymerized in bulk using different $[BuLA]_0/[DTPA]_0$ ratios (50:400). PBuLA homopolymers with molecular weight up 80 300 g mol^{-1} and $Đ$ ranging from 1.22 to 1.27 were obtained. Also remarkable is the one-pot methodology to deliver PEtLMAs from EtL using an ultimate RAFT polymerization step.[60] Last but not least, the precise synthesis of PEtLA was also achieved using Cu(II)Br_2-catalyzed photoinduced radical polymerization.[62] The combination of Cu(II)Br_2, Me_6-TREN and DMSO under UV light ($\lambda_{max} \approx 365$ nm) irradiation, enabled the fast and CRP of EtLA up to 75 000 g mol^{-1} with near quantitative monomer conversion.[63]

Beyond homopolymers, RDRP methods are also capable of producing block copolymer architectures based on AL-derived monomers. The block copolymerization of EtLA and EtLMA with other bio-based monomers such as α-pinene acrylate (αPA),[64] solketal acrylate (SA),[65] tetrahydrofurfuryl methacrylate (THFMA), and N,N-dimethyl lactamide acrylate (DMLA)

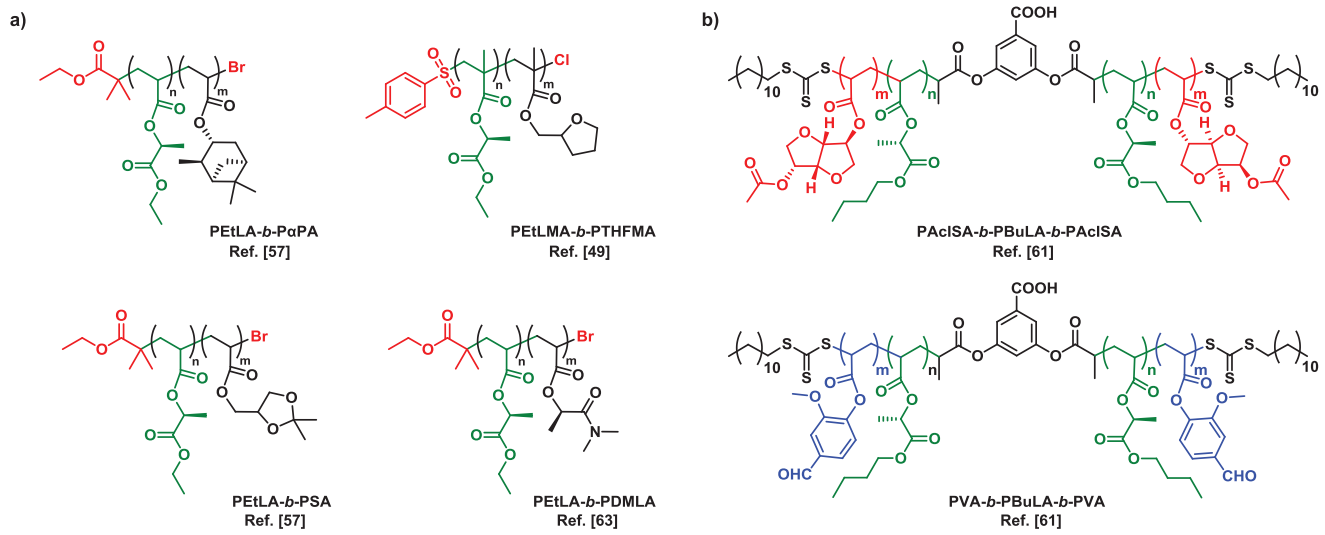

Figure 6. Structure of various a) AB and b) ABA block copolymers based on AL-derived (meth)acrylic monomers and other bio-based monomers.

was successfully performed by chain-extension of a PEtLA and PEtLMA macroinitiators produced at high conversion (>95%). Following this approach, it was possible to deliver various AB block copolymers such as PEtLA-*b*-P*α*PA, PEtLMA-*b*-PTHFMA, PEtLA-*b*-PDMLA, and PEtLA-*b*-PSA designed to accomplish different properties (**Figure 6**a).

For example, PEtLA-*b*-PDMLA prepared by Cu-catalyzed photoinduced radical polymerization could self-assemble in water to generate nanoaggregates with different morphologies such as large compound micelles, worm-like micelles, and vesicles (**Figure 7**a).[63] Note that, DMLA was produced from *N*,*N*-dimethyl lactamide which is also a LA derivative with excellent solvating properties.[63] These copolymers were successfully used as macromolecular surfactants in emulsion polymerization. On the other hand, differential scanning calorimetry (DSC) analysis of PEtLA-*b*-P*α*PA revealed immiscibility between both blocks (i.e., two different T_g values for PEtLA at 7 °C and P*α*PA at 65 °C), thus pointing toward promising applications for the development of bio-based thermoplastic elastomers (TPEs) based on well-defined ABA triblock copolymers having an elastomeric middle block (B) and glassy end blocks (A). In that sense, ABA copolymers with butyl lactate-derived soft middle block for high-performance pressure-sensitive adhesives (PSAs) were also developed by means of RAFT polymerization (Figure 6b).[61] First, a telechelic PBuLA macroinitiator (M_n = 78 150 g mol^{-1} and $Đ$ = 1.18) with a relative low T_g (−20 °C), good thermal stability (5% wt. loss at 340 °C), and low toxicity was prepared in bulk using a bifunctional trithiocarbonate-type RAFT agent (3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy)benzoic acid). Next, the synthesis of triblock copolymers was accomplished by chain extension with IS and vanillin-derived acrylic monomers (exo-AcISA and VA, respectively) using Rhodiasolv PolarClean as a green solvent. The resulting ABA copolymers containing ≈20 wt% of hard block exhibited competitive 180° peel adhesion properties when compared with commercial PSA tapes (Figure 7b).

3.2. Itaconic Acid Platform

IA, also known as 2-methylene butane-1,4-dicarboxylic acid or 2-methylenesuccinic acid, can be produced by pyrolysis of natural citric acid or the bacterial fermentation of biomass feedstocks such as glucose, molasses, starch, and glycreol by *Aspergillus terreus*.[66] For example, Beech wood biomass was used for the production of IA, whereby glucose was generated by the enzymatic hydrolysis of cellulose.[67] Although, there is evidence of direct polymerization of IA using RDRP in the fields of mesoporous silica nanoparticles[68–71] and molecularly imprinted polymers[72,73] these surface-initiated techniques are beyond the scope of this review. Importantly, these studies illustrated that complexation of IA with metallic catalysts could be the main limitation to accomplish an efficient polymerization when using metal-catalyzed RDRP techniques such as ATRP. Moreover, the authors did not find any publications showing RAFT polymerization of IA directly. However, there are many examples of well-defined bio-based polymethacrylate analogues from IA derivatives. The FRP and RDRP of several cyclic, monosubstituted and disubstituted IA derivatives have been recently exhaustively reviewed by Sollka and Lienkamp.[74] Recent examples on the RDRP of dialkyl itaconate and *N*-aryl itaconimide monomers to deliver block copolymers are primarily discussed here.

Initial studies on the CRP of sterically hindered dialkyl itaconate-type monomers date back to 2001. Fernández-García and co-workers reported kinetic studies on the ATRP of dimethyl itaconate (DMeI) to prepare the corresponding homopolymer PDMeI.[75] Reactions were carried out in bulk (100 and 120 °C) using various combinations of ATRP complexes and initiators, i.e., Cu(I)X/2,2′-bipyridine (bpy) or N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) (X = Cl, Br) and methyl 2-bromopropionate or Ts-Cl as initiators. Their best results with Cu(I)Cl/bpy/Ts-Cl system showed a monomer conversion plateau at around 50%. Although molecular weight control was achieved, the polymer distribution broadened with

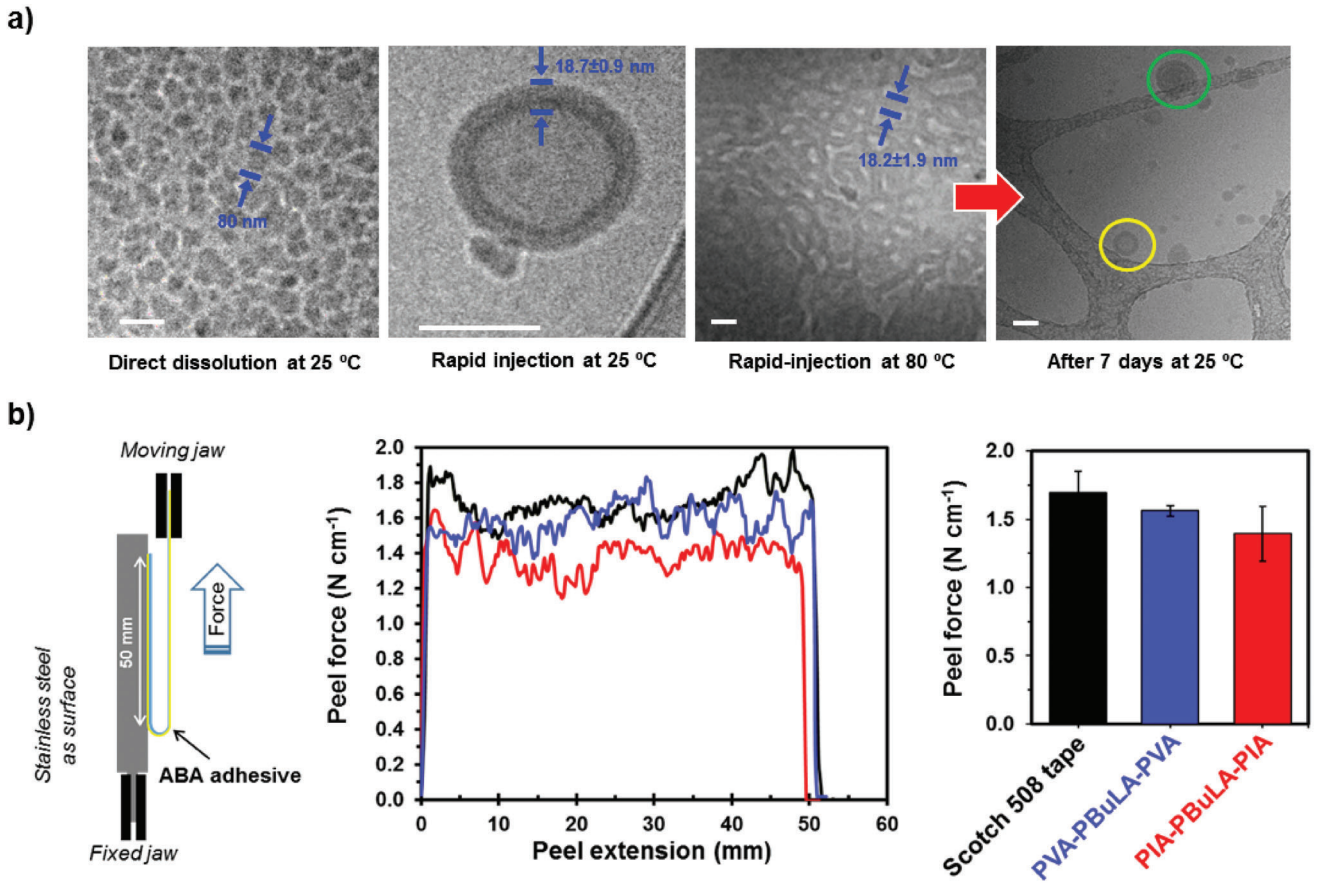

Figure 7. a) Representative cryo-TEM images of the various nanostructures formed from a fully bio-based amphiphilic for PEtLA-*b*-PDMLA. Scale bars are 100 nm. Adapted with permission.[63] Copyright 2020, American Chemical Society. b) Schematic design of a 180° peel test and 180° peel force data of PexoAcISA-*b*-PBuLA-*b*-PexoAcISA, PVA-*b*-PBuLA-*b*-PVA, and Scotch 508 tape. Adapted with permission.[61] Copyright 2020, MDPI.

conversion, and this resulted in polymers reaching $Đ \approx 1.4$. Later on, the ATRP of dibutyl itaconate (DBuI) and dicyclohexyl itaconate (DCHI) was also attempted with limited success, i.e., monomer conversion < 30%, due to the steric hindrance to the growing polymer chain offered by the two unaligned substituents.[76,77]

The ATRP of *N*-aryl itaconimides, offering less steric hindrance, has also been reported. Anand et al. synthesized five *N*-aryl itaconimide monomers by reacting itaconic anhydride with the appropriate primary amine.[78] Next, they used the classic ATRP system to form random and block copolymers. To prepare block copolymers, firstly, an *α*-chloropoly(methylmethacrylate) (PMMA-Cl) macroinitiator was formed by bulk polymerization using AIBN as the initiator and a $FeCl_3 \cdot 6H_2O/PPh_3$ catalytic system. This macroinitiator, was then used to polymerize *N*-aryl itaconimides such as *N*-(phenyl)itaconimide (PhIt), *N*-(*o*-chlorophenyl)itaconimide (*o*-ClIt), *N*-(*m*-chlorophenyl)itaconimide (*m*-ClIt), *N*-(*p*-chlorophenyl)itaconimide (*p*-ClIt), and *N*-(*p*-tolyl)itaconimide (*p*-TIt) using Cu(I)Br/bpy catalytic system in toluene to furnish block copolymers with *Đ*, from 1.19 to 1.39. However, this approach only enabled the incorporation of oligomeric P(*N*-aryl itaconimide) blocks due to isomerization and chain-transfer reactions. IA was also used to synthesize ATRP initiators such as *N*-phenyl(3-bromo-3-methyl)succinimide, *N*-phenyl(3-bromo-4-methyl)succinimide, and *N*-phenyl(3-bromomethyl)succinimide, that are optimized for the polymerization of cyclic itaconimides.[79] More recently, improved results on the CRP of PhIt were reported by the Matyjaszewski laboratory using initiators for continuous activator regeneration ATRP (ICAR-ATRP) with $FeBr_3$(IDipp) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) as catalyst complex and ethyl *α*-bromophenylacetate and AIBN as initiation system.[80] This gave an almost linear PPhIt molecular weight increase with conversion, although the *Đ* increased over time. At 69% conversion, PPhIt homopolymer with molecular weight of 11 900 g mol^{-1} and $Đ = 1.52$ was obtained. The use of ICAR-ATRP also enabled the successful copolymerizations of PhIt with styrene (St) at various molar ratios providing a range of alternating copolymers P(St-*alt*-PhIt). Interesting, when the copolymerization was carried out with high $[St]_0 > [PhIt]_0$ ratio, a one-pot synthesis of a block copolymer P(St-*alt*-PhIt)-*b*-PSt was achieved. The thermal analysis of the alternating block copolymer by DSC revealed a T_g at 162 and 104 °C, corresponding to a P(St-*alt*-PhIt) and PSt segments, respectively.

Barner Kowollik and later Kamigaito laboratories demonstrated that the application of RAFT polymerization to dialkyl itaconate and *N*-aryl itaconimide monomers significantly

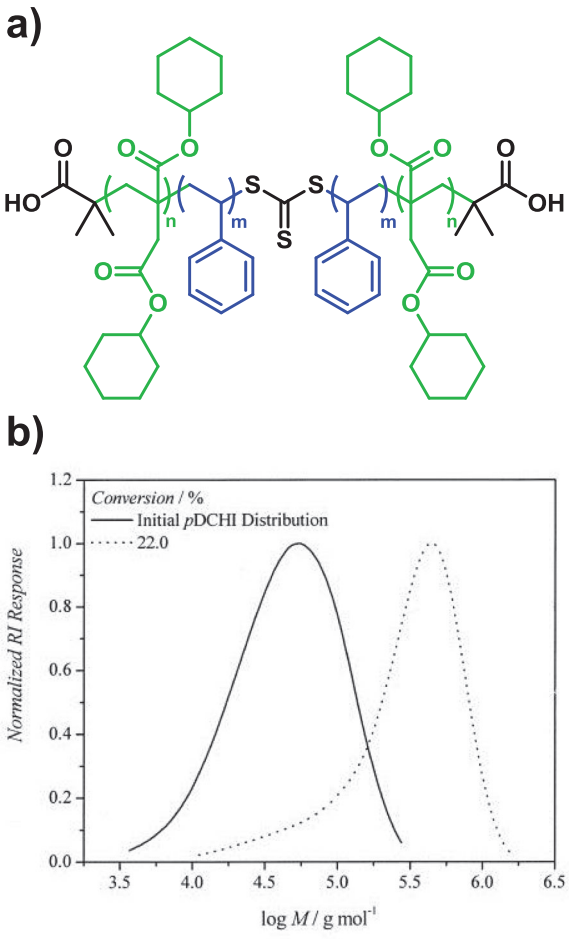

Figure 8. a) Schematic representation of a PDCHI-*rod*-PSt-*coil* block copolymer generated via the RAFT polymerization process of DCHI and St. b) Size-exclusion chromatography (SEC) traces of the chain extension with the initial PDCHI distribution shifting from 35 600 to 164 000 g mol^{-1} (at 22% St conversion). Reproduced with permission.[81] Copyright 2004, Wiley Periodicals.

improved the reaction control of these polymerizations. After a series of optimizing studies focused on various RAFT agents; cumyl dithiobenzoate (CDB), cumyl phenyldithioacetate (CPDA), and *S*,*S*′-bis(*α*,*α*′-dimethyl-*α*″-acetic acid) trithiocarbonate (TRIT), solvent concentration and polymerization temperature, the RAFT polymerization of DMeI, DBuI, and DCHI provided the corresponding homopolymers with monomodal molar mass distribution curves and $Đ$ values below 2.[77,81,82] More interestingly, RAFT polymerization also enabled the preparation of complex macromolecular architectures such as rod/coil block copolymers by first synthesizing a PDCHI macromolecular chain transfer agent (macroCTA) (using trithiocarbonate as the RAFT agent) which was subsequently chain extended with St to give PDCHI-*rod*-PSt-*coil* block copolymers (**Figure 8**).[81]

These fundamental studies served as a basis for the incorporation of various IA derivatives into TPEs based on ABA block copolymers. Liu and co-workers designed ABA copolymers with inner soft segments from lysine-based *O*-carboxyanhydride monomer and outer hard segments based on

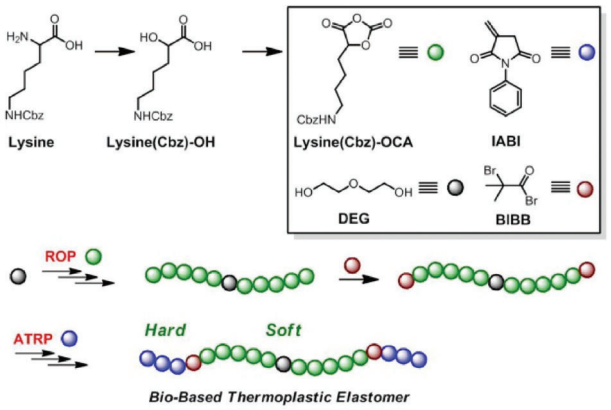

Figure 9. ABA thermoplastic elastomers from lysine and IA by the combination of ROP and ATRP. Reproduced with permission.[83] Copyright 2017, Wiley Periodicals.

PhIt (**Figure 9**).[83] The synthetic approach combined ROP and ATRP. Hence, the itaconamide monomer was polymerized from a polyester macroinitiator functionalized with *α*-haloester end groups to form triblock copolymers with varying amounts of PPhIt (12–25 mol%). Block copolymerization was conducted with Cu(I)Cl/Cu(II)Cl$_2$/bpy system in *N*,*N*-dimethylformamide (DMF) at 100 °C. All triblock copolymers were obtained with molecular weight below 50 000 g mol^{-1} ($Đ < 1.3$) and acted as TPEs with moderate tensile stress (10–15 MPa) and high tensile strain (500%–700%).

In an independent study, Satoh and co-workers replaced the inner polyester block by a methacrylic polymer based on an IA diester to prepare all acrylic TPEs with enhanced hydrolytic stability (**Figure 10**).[82] The combination of DBuI and bis(2-ethylhexyl) itaconate (DEHI) and IA imides, such as PhIt and *p*-TIt, succeeded in achieving sequential block RAFT copolymerizations using a difunctional RAFT agent. Narrow molecular weight distributions ($1.1 < Đ < 1.6$) were achieved for all of the copolymers synthesized, i.e., PPhIt-*b*-PDBI-*b*-PPhIt and PPhIt-*b*-PDEHI-*b*-PPhIt. These materials could be used as TPEs with high service temperature because of the low T_g (DEHI at −28 °C and DBI at 12 °C) of the P(dialkyl itaconate) block and the higher T_g (>230 °C) of the PPhIt block.

3.3. *α*-Unsaturated-*γ*-butyrolactones Platform

Biomass-derived monomers based on five-membered *γ*-butyrolactone rings bearing an exocyclic double bond are valuable platform chemicals for functional polymers. Among them, the natural *α*-methylene butyrolactone (MBL) monomer which is found in tulips called as tulipalin A has recently received increasing attention as an MMA-mimicking bio-based monomer. Recent developments at Arzeda on the scalable fermentative production of MBL from LB-derived sugars encouraged us to include this biomass-derived building block in this review.[85] MBL has been homopolymerized via radical, anionic, group transfer and coordination polymerizations in a similar manner to methacrylates.[86] The FRP of MBL produced polymers with a higher service temperature ($T_g \approx 190$ °C) than those from PMMA (≈110 °C) due to the rigid lactone ring, which also

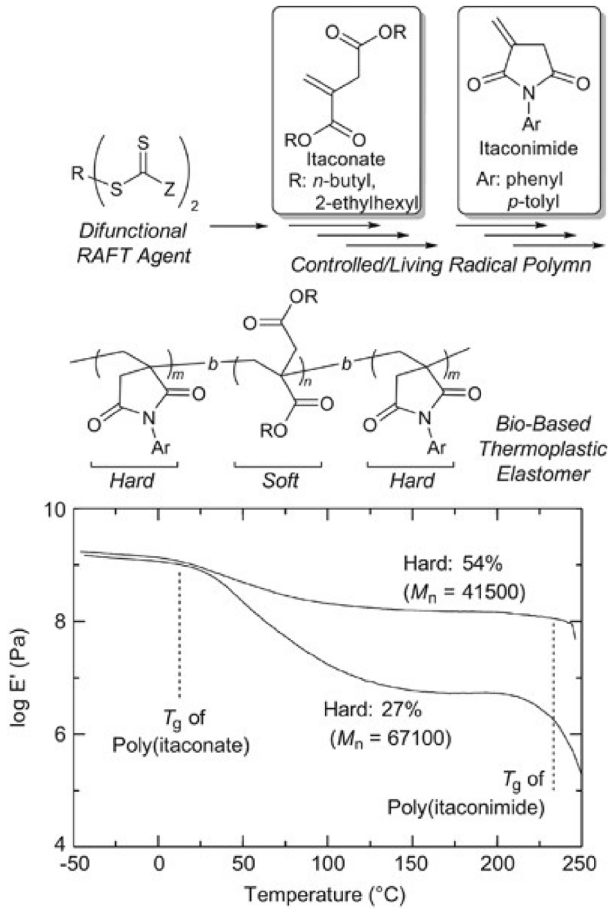

Figure 10. Schematic synthetic approach and dynamic tensile storage (E') as a function of temperature of bio-based triblock copolymer as an acrylic TPE prepared by RAFT polymerization of dialkyl itaconates and itaconimides. Reproduced with permission.[84] Copyright 2015, Springer Nature Limited.

provides the polymer with a good durability and a good refractive index.

First precise polymerization of MBL with control over molecular characteristics was performed by Mosnácek and Matyjaszewski in 2008.[87] PMBL homopolymers were prepared using Cu(I)Br/bpy catalyst complex, bromopropionitrile (BPN) initiator in DMF at 50 °C. The ATRP process reached 90% monomer conversion in 100 min with a dispersity, $Đ$, of 1.09. More recently, the polymerization of MBL was optimized under more environmentally friendly conditions using photochemically-induced ATRP.[88] In this case, the polymerization was performed at room temperature with only ppm amounts of $Cu(II)Br_2$/tris(2-pyridylmethyl)amine catalyst without necessity to remove oxygen from the polymerization mixture. Kinetic studies demonstrated that photo ATRP led to the formation of PMBL with molar masses well fitted to the theoretical ones and $Đ$ values at about 1.3 (**Figure 11**). This method was also successful in the preparation of well-defined block-random copolymers from MBL, MMA, and St by chain extension of macroinitiators. These works proved that PMBL with narrow molecular weight distribution (MWD) can be obtained when synthesizing homopolymers and block copolymers.

Taking advantage of RDRP methods, MBL has been exploited as a rigid segment in TPEs with high service temperature based on ABA triblock copolymers. For example, Mosnácek and Matyjaszewski formed triblock copolymers with butyl acrylate (BA) PMBL-*b*-PBA-*b*-PMBL using a difunctional Br-PBA-Br macroinitiator prepared using dimethyl 2,6-dibromoheptanedionate as a difunctional initiator (**Figure 12**a). Again, a low dispersity copolymer was obtained ($Đ$ = 1.11), with a monomodal distribution as observed by SEC analysis. Physical properties of these triblock copolymers were subsequently investigated. Solution cast films of PMBL-*b*-PBA-*b*-PMBL triblock copolymers exhibited microphase separation as observed by atomic force microscopy (AFM) (see Figure 12b) and small angle X-ray scattering (SAXS), while thermo-mechanical properties elucidated by dynamic mechanical analysis (DMA) showed distinct T_g for each block (PBA $T_g \approx 50$ °C, PMBL $T_g \approx 195$ °C).[89] The tensile strength of the material increased with increasing PMBL content, and incorporation of P(MBL-*r*-MMA) "hard" blocks increased the elongation at break. The resulting thermoplastic material could be suitable for high-temperature applications. The low solubility, quite low elongation at break and tensile strength of the triblock copolymers were significantly improved by preparation of star-like block polymers with PBA-*b*-PMBL arms.[90]

MBL has also been used to prepare polyester acrylic block copolymers using the renewable lactones as comonomer.[91] For example, Hillmyer and coworkers used the terpene-derived lactone menthide (M) to introduce a degradable block. A telechelic α,ω-dihydroxy poly(menthide) (PM) was first synthesized by ring opening polymerization (ROP) and subsequently reacted with 2-bromoisobutyryl bromide to furnish a difunctional ATRP macroinitiator, Br-PM-Br. MBL was then polymerized by ATRP from both ends to give the corresponding ABA copolymer PMBL-*b*-PM-*b*-PMBL. Fully renewable TPEs were targeted owing to the differing T_g of each block; PM exhibited a T_g around −21 °C, and measured T_g for PMBL blocks were 170–190 °C, by DSC. Microphase separation was observed by AFM and SAXS analyses, while mechanical testing in a tensile mode showed promise for these renewable TPEs, with elongations up to 1800% and good recovery properties. More recently, Verdugo and co-workers, also investigated the synthesis of ABA triblock copolymers with poly(δ-decalactone) (PDL) middle block and PMBL end blocks with enhanced recycling properties.[92] In this case, middle-chain cleavable groups were incorporated in the core of the copolymers by using diols containing disulfide, acetal or thioacetal groups as ROP initiators (**Figure 13**). With analogy to the Hillmyer work, a polyester ATRP macroinitiator was first prepared through ROP of DL and subsequently functionalized with 2-bromoisobutyryl groups. Next, the prepared macroinitiators were chain extended with MBL by ATRP ($Cu(I)Cl/Cu(II)Cl_2$/bpy in DMF) to afford stimuli-cleavable PMBL-*b*-PDL-I-PDL-*b*-PMBL triblocks with molecular weight up to 22 000 g mol^{-1} and $Đ$ between 1.17 and 1.27. The cleavage behavior of the ABA copolymers under reductive, acidic and photooxidative conditions was systematically studied by SEC and the resulting AB copolymers structurally characterized.

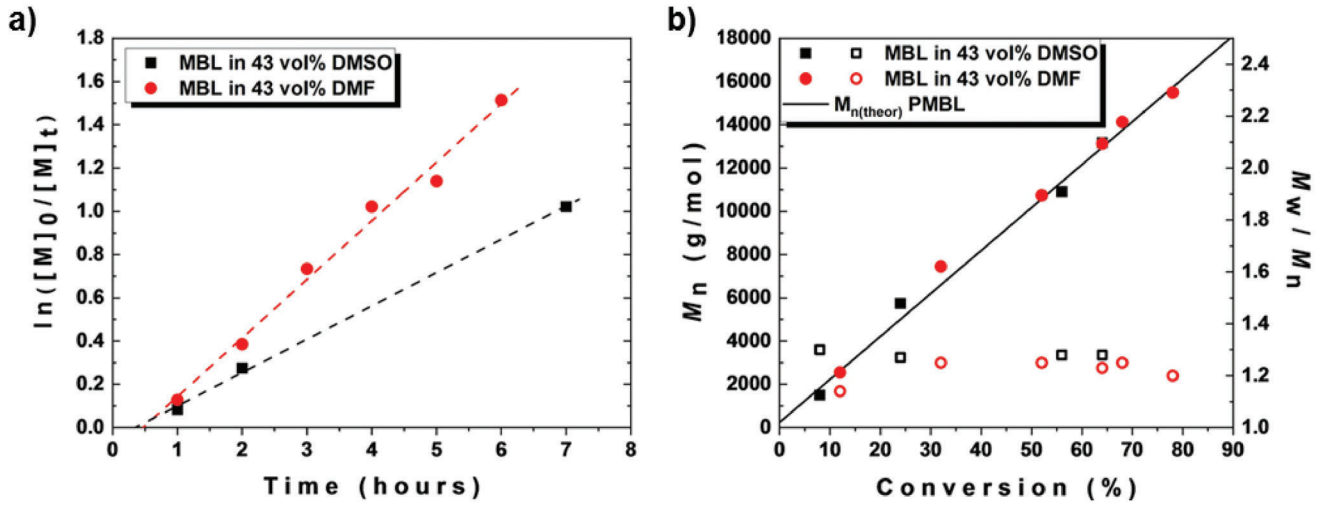

Figure 11. a) Kinetic plots and b) evolution of the molar mass and $Đ$ with the conversion of MBL during photo-ATRP in 43 vol % of either DMF or DMSO. Experimental conditions: [MBL]/[EBPA]/[Cu(II)Br_2]/[TPMA] = 200/1/0.04/0.16; [MBL] = 6.5 M, T = 28 °C, light intensity of 9 mW cm^{-2} (λ = 365 nm). Reproduced with permission.[88] Copyright 2019, Wiley-VCH.

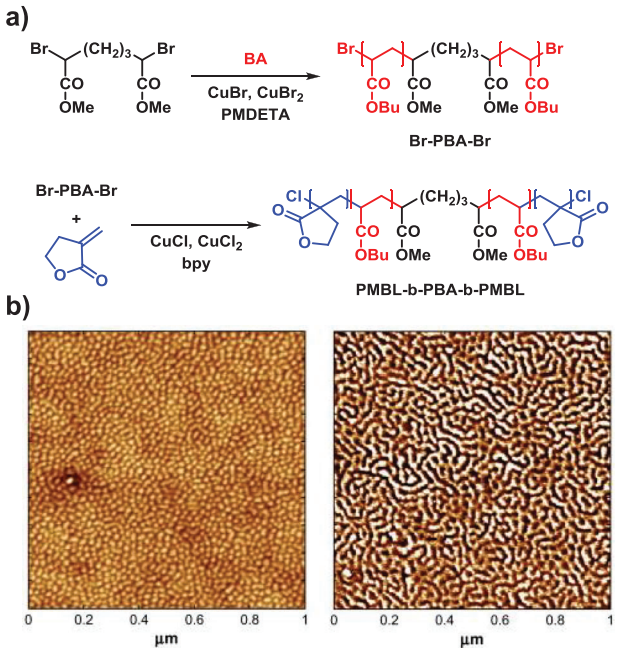

Figure 12. a) Preparation and b) representative AFM high images of PMBL-*b*-PBA-*b*-PMBL triblock copolymers, (left) BA_{375}-MBL_{60} (10.9 wt% PMBL) and (right) BA_{375}-MBL_{144} (22.7 wt% PMBL), prepared by ATRP. Reproduced with permission.[89] Copyright 2009, Elsevier.

Other bio-based α-unsaturated-γ-butyrolactones such as γ-methyl-α-methylene-γ-butyrolactone (MeMBL) and α-methylene-γ, γ-dimethyl-γ-butyrolactone (Me_2MBL) also proved to be well-behaved under RDRP conditions. Qi et al. conducted an assortment of RAFT miniemulsion and bulk polymerizations to investigate in detail the MeMBL polymerization.[93] Note that DuPont has developed a process for MeMBL synthesis from levulinic acid, a chemical intermediate derived from LB.[94] The RAFT polymerizations were conducted using 1-phenylethyl phenyldithioacetate (PEPDTA) as the RAFT agent and AIBN as the initiator. However, to achieve a well-controlled polymerization, styrene (St) with molar ratios of [MeMBL:St] = 1:4 and 1:1 was used as a comonomer. All four copolymers obtained a final dispersity, $Đ$, below 1.50 with both the bulk and miniemulsion polymerization of [MeMBL:St] = 1:4 achieving higher monomer conversions. This work was further reinvestigated in 2013 by Xu et al. who conducted RAFT bulk and emulsion copolymerization of MeMBL and St, again, with various molar ratios of MeMBL:St at 0:1, 1:1, 1:2, 1:4, and 2:1. They used the RAFT agent 2-(((dodecylsulfanyl) carbonothioyl)sulfanyl)propanoic acid, and acrylic acid and St as comonomers to make a macroCTA PAA_{20}-*b*-PS_5 which was then used to make the linear gradient P(MeMBL-*co*-St) in both bulk and emulsion.[95] Monomer conversions of >90% were calculated for all emulsion-polymerized gradient copolymers with reaction times between 50 and 100 min. When [MeMBL:St] was ≤1:2 the dispersites, $Đ$, were <1.20 but at [MeMBL:St] = 1:1 the control was lost, and gelation occurred. They also note that gelation occurred when conducting reactions with [MeMBL:St] = 1:4, and that an "incomplete conversion" was obtained. They state that gelation may have occurred due to the MeMBL which caused a diffusion-controlled reaction. In an independent study, Trotta et al. synthesized Me_2MBL monomer from IA before using RAFT polymerization to study its polymerization in benzene at 80 °C.[96] Using 2-cyano-2-propyl benzodithioate (CPDB) as the RAFT agent and AIBN as the initiator, they produced the corresponding homopolymer (PMe_2MBL) with relatively low dispersity ($Đ$ = 1.07-1.41). Modulating the ratio of CPDB to monomer enabled the synthesis of polymers with controlled molecular weight values ranging from 8800 to 61 100 g mol^{-1}. However, authors noted that at 50% monomer conversion the reaction solutions had "gelled", so the reaction was stopped at this point. Interestingly, PMe_2MBL shows improved solubility over PMBL (PMe_2MBL is soluble in tetrahydrofuran while PMBL is not), making it a potentially more processable polymer. All acrylic diblock copolymers were also prepared by chain extending a PMMA macroCTA with

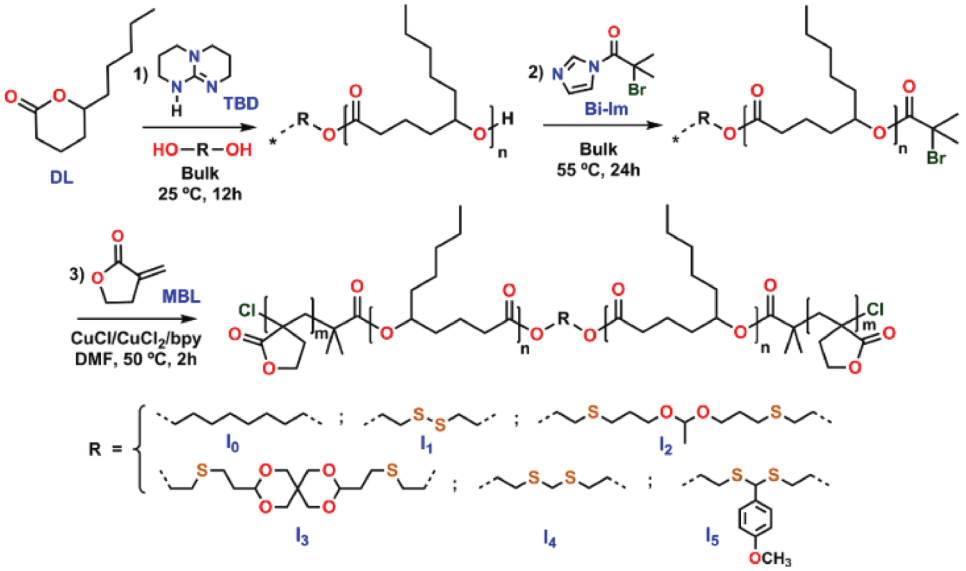

Figure 13. Synthesis PMBL-*b*-PDL-*b*-PMBL triblock copolymers by ROP and ATRP. Reproduced with permission.[92] Copyright 2021, Elsevier.

Me_2MBL to form PMMA-*b*-PMe_2MBL with a dispersity, *Đ*, of 1.11.

3.4. Levoglucosenone Platform

LGO is an α,β-unsaturated cyclic ketone, isolated during the acid-catalyzed pyrolysis of cellulose.[97] While LGO can be directly polymerized by ring opening metathesis polymerization[98] and cationic ring opening polymerization,[99] the structure of LGO does not lend itself to be directly polymerized by radical polymerization techniques. However, the LGO synthon can be revalorized into various (meth)acrylic monomers compatible with RDRP methods (**Figure 14**).

For example, the (*S*)-γ-hydroxymethyl-α,β-butenolide methacrylate (HBOMA) was produced by the Allais laboratory from LGO in two steps. First, LGO was transformed into HBO via lipase mediated oxidation[100] or alternatively through a solvent/catalyst-free H_2O_2-mediated process.[101] Next,

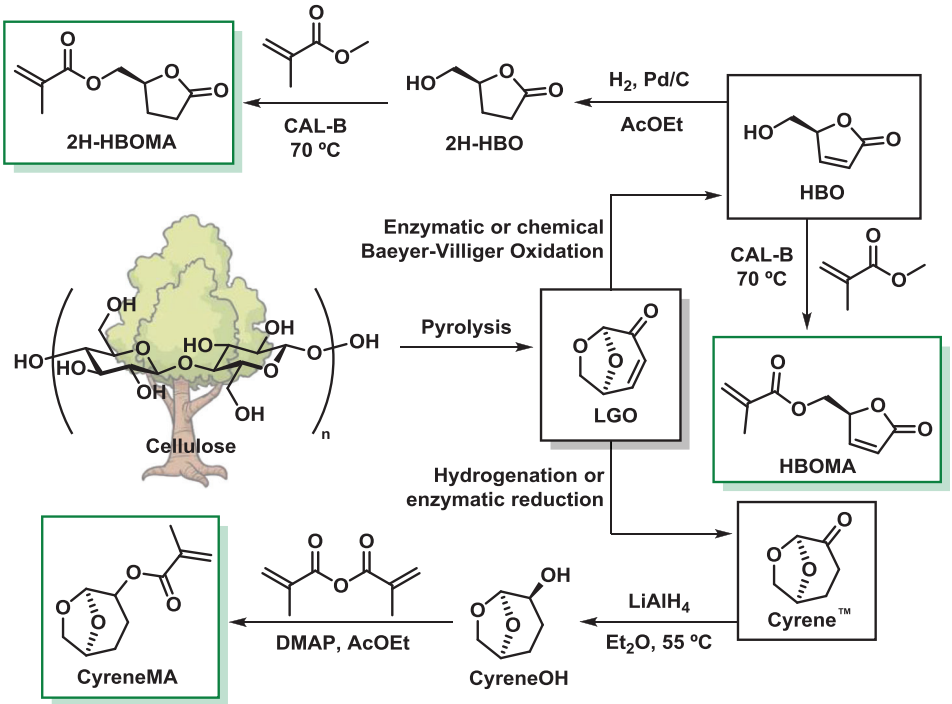

Figure 14. Synthetic routes to convert LGO into various monomers compatible with RDRP methods.

the produced hydroxyl-functional derivative was functionalized with a methacrylate moiety through a chemo-enzymatic transesterification of methyl methacrylate using *Candida antarctica* type B lipase. The hydrogenated version of HBO, named (*S*)-γ-hydroxymethyl-γ-butyrolactone (2H-HBO), was also transformed into the corresponding methacrylate monomer (2H-HBOMA).[102] In 2019, Ray and co-workers[103] reported the preparation of another methacrylate monomer (CyreneMA) derived from the LGO-derivative dihydrolevoglucosenone (CyreneTM) which is a well-recognized green solvent.[104] CyreneMA was prepared in two steps: reduction of CyreneTM with $LiAlH_4$ in Et_2O followed by functionalization of levoglucosanol product with methacrylic anhydride in ethyl acetate in the presence of a catalytic amount of DMAP and TEA.

Although a range of experiments demonstrated the ability of the three LGO-derived monomers to polymerize under FRP conditions, RDRP methods were only applied to 2H-HBOMA. Saito, Simon, and co-workers prepared well-defined bioacrylic polymers based on 2H-HBOMA using RAFT-mediated emulsion polymerization.[102] 4-Cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoic acid was used as the chain transfer agent (CTA) while sodium dodecyl sulfate (SDS), and poly(vinyl alcohol) (PVA) were used as surfactant and costabilizer, respectively. Targeting a degree of polymerization of 100, after 5 h reaction time a conversion of 60% was reached, giving a final stable latex with molecular weight of 9200 g mol^{-1} and $Đ$ of 1.06. The "living" character of the RAFT polymerization was demonstrated by chain-extension experiments with MMA. Thermal analysis of P2H-HBOMA ($T_g \approx 100$ °C) revealed the potential of this bioacrylic polymer as a replacement of PMMA and PSt in different areas of application.

3.5. Sorbitol Platform

SRB is a C6 building block industrially produced by hydrogenation of D-glucose and commonly used as sugar substitute in food, cosmetics, beverage and other fields.[105] Intensive scientific efforts are also being made to achieve the one-pot production of SRB from biomass, focusing on the design of cheap and efficient catalytic systems.[106,107] The use of SRB as a platform chemical to produce derivatives such as IS and glycols is a well-consolidated technology. For example, the French company Roquette is currently producing annually over 20 000 tons of polymer-grade IS in the world's largest production plant. This chiral bicyclic sugar which is obtained by the dehydration of D-SRB, is considered one of the top 12 key chemical building blocks that can be obtained from biomass.[108,109] Due to its bicyclic structure and the resultant steric hindrance, IS is an excellent candidate for the production of polymers with high T_g and outstanding thermal stability.

Because it has a rigid V-shaped structure (two fused tetrahydrofuran rings), bearing two secondary OH groups in *endo* and *exo* configurations, its application in the field of step-growth polymers such as polyesters, polyurethanes and polycarbonates has been extensively investigated.[110] Conversely, only a few studies have been devoted to IS derivatives containing a single polymerizable moiety. Recent examples on the CRP of mono(meth)acrylate monomers are discussed here. As the two OH groups in IS are located in different molecular environments, the *endo* hydroxyl group in IS is a stronger nucleophile due to intramolecular hydrogen bonding. Accordingly, the preparation of mono(meth)acrylates bearing a free hydroxyl or acetate groups as regioisomeric mixtures in varying proportions of *endo*/*exo* products have been reported when using either acids or other coupling agents such as $Sc(OTf)_3$, $ZnCl_2$, or PbO. For example, Gallagher et al.[111] used a tandem esterification of IS with acetic anhydride and methacrylic anhydride using $Sc(OTf)_3$ as a catalyst to produce the acetylated IS monomethacrylate (AcISMA) with a methacrylate moiety (*endo*-methacrylate:*exo*-methacrylate = 4:1) with a final overall yield of 44% on a 20 g scale reaction. The proportion of the *endo*-functionalized product was also higher when IS was directly functionalized with methacrylic anhydride[112] or acrylic acid[111] in the presence of $Sc(OTf)_3$ to produce the corresponding mono(meth)acrylate monomers bearing a free hydroxyl groups. On the other hand, Reineke and Hillmyer laboratories reported the preparation of the pure *exo*-acetyl-*endo*-acryloyl regioisomer using common and metal-free catalysts without the need for column chromatography (38% yield).[113] In this study, the esterification of IS with acetic acid was followed by a tandem transesterification-distillation step, and a final esterification with acryloyl chloride. In this line, a regioselective, biocatalytic approach was recently demonstrated to synthesize IS *endo*-/*exo*-monomethacrylates in high yield and purity using Lipozyme RM IM (*Rhizomucor miehei* lipase).[114] A library of high purity (<99%) methacrylate monomers was synthesized with different substituents, i.e., acetate, dodecanoate, cyclohexanoate, and hydroxyl functionalities, achieving yields up to 87% to demonstrate that the process is straightforward and easily scalable.

Beyond the thermal- and photo-initiated FRP of monofunctional (meth)acrylated isosorbides, RDRP methods have been used to incorporate these monomers into well-defined homopolymers and block copolymers. For example, AcISMA, as a mixture of *endo*/*exo* diastereoisomers, was polymerized in a controlled manner by RAFT polymerization in DMF (**Figure 15**a).[111] The use of hydroxyethyl 4-cyano-4-(phenylcarbonothioylthio)pentanoate (HO-CPAD) as a monofunctional CTA and AIBN as a radical initiator yielded PAcISMA with controlled molar masses up to 30 000 g mol^{-1} and narrow molar mass distribution ($Đ \leq 1.09$). Kinetic experiments were used to demonstrate that RAFT polymerization of AcISMA was well-controlled as molecular weight increased linearly with conversion and molecular weight distribution remained narrow through the entire process (Figure 15b). Also the use of Cu(0) wire-catalyzed SET-LRP resulted in a well-defined homopolymer when applied to IS 2-laurate-5-methacrylate (ISLMA). In this case, the polymerization of this bulky IS derivative was conducted at $[M]_0/[I]_0 = 50$ to target a polymer of molar mass just below 20 000 g mol^{-1} ($Đ = 1.22$) in 8 h. A mixture of 2,2,2-trifluoroethanol/water (9/1, v/v) was chosen as a reaction media to perform SET-LRP at 50 °C using Ts-Cl as an initiator.

Control over the radical polymerization of mono(meth)acrylate IS derivatives enabled the incorporation of rigid IS vinylic segments as end blocks in ABA block copolymer elastomers.A series of triblocks with either PBA or poly(2-ethylhexyl acrylate) as a low T_g midblocks were prepared using RAFT polymerization.[113] Note that in this case, the pure isosorbide 5-acrylate-2-acetate monomer (endo-AcISA) was used. The symmetrical archi-

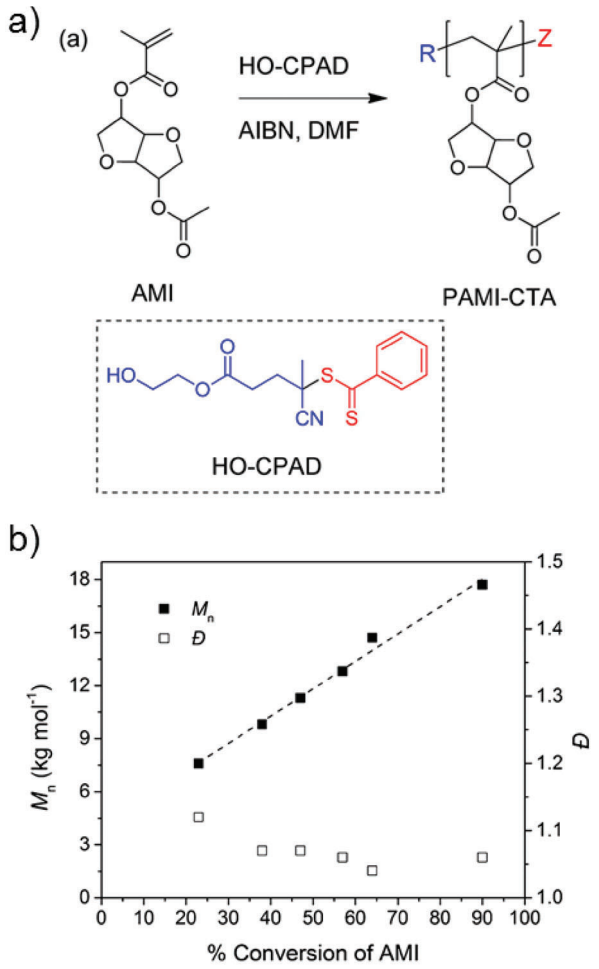

Figure 15. Molar mass and Đ evolution as a function of conversion for RAFT polymerization of AcISMA ([AcISMA]/[HO-CPAD]/[AIBN] = 60/1/0.1). Reproduced with permission.[111] Copyright 2015 American Chemical Society.

tecture of the pursued ABA copolymers required the use of a difunctional CTA, 3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy)benzoic acid (BTCBA). RAFT polymerization successfully produced triblock copolymers ranging from 8 to 24 wt% hard segment content which were evaluated as PSAs. The materials with PBA middle block showed better adhesive qualities with peel forces up to 2.9 N cm^{-1} and tack forces up to 3.2 N cm^{-1}. Moreover, they also exhibited a dynamic mechanical response similar of some available high performing pressure sensitive adhesives. The use of a mixture of isosorbide acrylate isomers was also reported with no significant differences in polymer properties.[115] The same approach was used in our laboratory to incorporate the isosorbide 2-acrylate-5-acetate monomer (exo-AcISA)[114] at the end blocks of all-acrylic ABA block copolymers with LA-based soft phase.[61]

3.6. Furfural Platform

The aldehyde containing a furan heterocycle aromatic ring named furfural (FL) is a promising precursor for the synthesis of numerous bio-based functional polymers.[6,116,117,118] Bio-based FL is obtained from polymeric pentoses present in the biomass, that are hydrolyzed to the corresponding monosaccharides, dehydrated, and finally cyclized.[119,120] FL can be reduced to furfuryl alcohol, a functional alcohol with a growing number of potential applications, including an industrial solvent, plastisizer, in fine chemicals, adhesives, and as a fuel precursor.[121,122] The primary OH group in furfuryl alcohol offers a straightforward pathway to prepare the corresponding methacrylate monomer (FLMA) which is commercially available (see Figure 3).[123]

The CRP of FLMA has been in the spotlight of RDRP methods because the furfuryl units can be involved in Diels-Alder (DA) and retro Diels-Alder (rDA) reactions after polymerization. Pioneering studies on the RDRP of FMA were reported by Singha and co-workers.[124] The Cu(I)Br/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) ATRP catalytic system enabled the preparation of well-defined PFMA with molecular weight at around 10 000 g mol^{-1}. The polymerization occurred with a linear increase of molecular weight and narrow dispersity (Đ ≈ 1.50), thus supporting the controlled character of the reaction. More recently, the Tang laboratory used metal-free photo-ATRP with similar results.[125] In this case, authors reported the preparation of PFMA with molecular weight of 6100 g mol^{-1} and Đ of 1.41. Interestingly, photo-ATRP enabled to switch on and off the polymer formation by simply alternating on/off UV light periods during polymerization. The metal-free CRP of FMA was also investigated using a conventional RAFT polymerization system using toluene as solvent.[126] However, from a sustainable viewpoint, it is more appealing to prepare PFMA via RAFT polymerization in an ionic liquid (IL) as a nonvolatile solvent.[127] Specifically, the ionic liquid 1-butyl-3-methylimidazoliumhexafluoro phosphate (BMIHFP) was successfully used to polymerize FMA up to ≈10 000 g mol^{-1} and Đ ≈ 1.30. The rate of polymerization of FMA in BMIHFP was much faster than in different organic solvents such as toluene, DMF, etc. Moreover, after the polymerization, the IL could be separated easily from the polymer mixture and reused for further polymerizations.

Importantly, the furan ring of FMA remained unaltered after both ATRP and RAFT polymerization processes. It is well-known that polymers bearing reactive furfuryl functionality can undergo DA reactions with suitable dienophiles like bismaleimides to form DA crosslinked polymers.[128] Moreover, these polymers undergo rDA reactions under suitable reaction conditions. Hence, they can lead to thermoreversible crosslinked materials, which can be used as thermoresponsive materials. Accordingly, RDRP copolymers containing FMA repeat units have been widely investigated for applications such as self-healing materials,[129–132] responsive nanoparticles,[133] smart hydrogels,[134] and surfaces.[135] Representative examples are self-healable materials based on well-defined ABA triblock copolymers containing reactive PFMA end blocks. Singha and co-workers used ATRP and RAFT polymerization to prepare triblocks in combination with poly(ethyl hexylacrylate) (PEHA) and poly(dimethylsiloxane) (PDMS) as soft blocks (PFMA-*b*-PEHA-*b*-PFMA with M_n < 55 000 g mol^{-1} and Đ ≈ 1.30, and PFMA-*b*-PDMS-*b*-PFMA with M_n < 15 000 g mol^{-1} and Đ ≈ 1.41, respectively).[136,137] More recently, our laboratory combined ROP and ATRP to prepare reactive PFMA-*b*-PTMC-*b*-PFMA copolymers (M_n < 25 000 g mol^{-1} and Đ ≈ 1.40) with a biodegradable

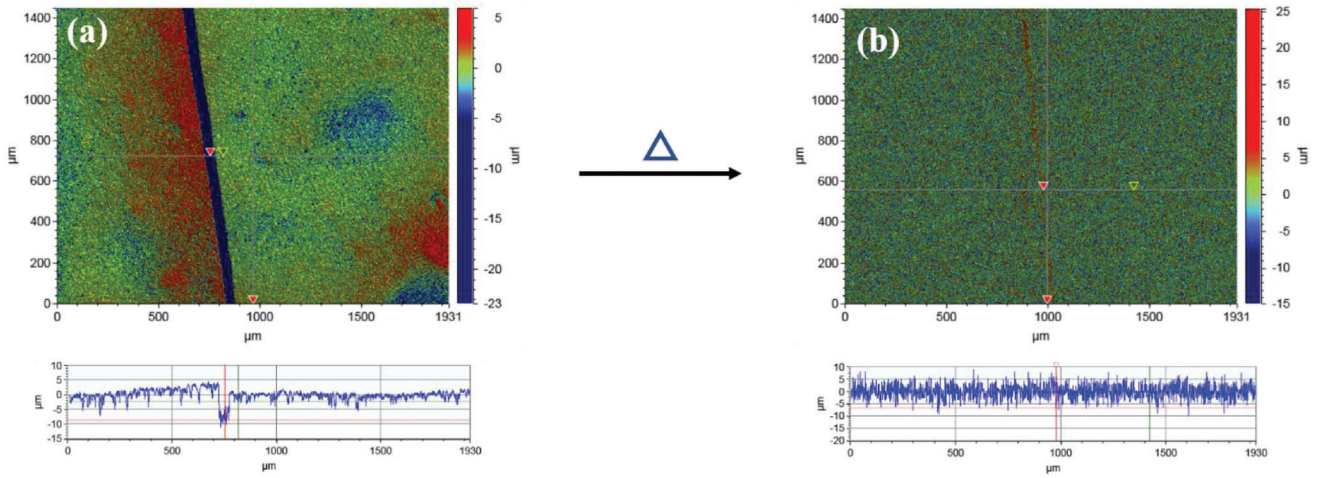

Figure 16. Scratch profilometer healing analysis of a PFMA-*b*-PDMS-*b*-PFMA (M_n = 14 200 g mol^{-1}, $Đ \approx 1.41$) crosslinked with 1,1-(methylene di-4,1-phenylene)bismaleimide via DA reaction: a) after scratching and b) after healing. Reproduced with permission.[136] Copyright 2017 Elsevier.

middle block based on trimethylene carbonate (TMC).[138] All these triblock copolymers were capable of undergoing reversible crosslinking and de-crosslinking via DA and rDA reaction respectively by the use of bismaleimide dienophiles which reacted with reactive furfuryl groups. The Singha laboratory exploited the reversibility of the DA reaction at the end block of these copolymers to prepare thin films with self-healing capabilities (**Figure 16**).

Tetrahydrofurfuryl acrylate (THFA) and the corresponding methacrylate (THFMA) are also FL-derived monomers that are well behaved under CRP conditions (see Figure 3). The former was used by Lu and co-workers for the preparation of all acrylic-based ABA TPEs.[139] In this case, PTHFA was used as elastomeric domain with T_g of around −13 °C. First, macroCTAs with molecular weights up to 28 600 g mol^{-1} and $Đ$ 1.08–1.21 were prepared from 1-adamatyl acrylate (AdA) using dibenzyl trithiocarbonate (DBTTC) initiator. Next, THFA was incorporated by RAFT polymerization to prepare a series of PAdA-*b*-PTHFA-*b*-PAdA triblock copolymers, with molecular weights up to 200 000 g mol^{-1} and broad $Đ$ (1.66–3.03). Thermal analysis, AFM, and SAXS measurements confirmed microphase separation between the soft (PTHFA) and hard blocks (PAdA segment, T_g = 118 °C), and the resulting cast films exhibited mechanical strength and elongation properties comparable to commercial TPEs. In an independent study, Moreno and co-workers demonstrated that a mixture of EtL/water (9/1 v/v) is an efficient and green reaction media to deliver PTHFMA homopolymers in a controlled manner by SET-LRP.[59] Taking advantage of the high chain end functionality of the SET-LRP polymers, the possibility to prepare well-defined AB block copolymers with microphase separation (PMMA-*b*-PTHFMA) was also investigated.

Last, but not least, FA can also be converted to 4-hydroxyciclopentenone (4HCP) via furfuryl alcohol through the Piancatelli rearrangement (**Figure 17**).[140]

4HCP is a recognized platform for complex natural products, however its use as monomer was not reported until Stouten and co-workers publication.[141] Authors functionalized 4HCP with acryloyl chloride to afford 4-oxocyclopent-2-en-1-yl acrylate (4CPA) with high yield. Homopolymerization of 4CPA was investigated by RAFT polymerization using 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) and cyanomethyl dodecyl trithiocarbonate (CDT) as RAFT agents. Better results were reported with DDMAT, although to obtain polymers with degree of polymerization at around 100, copolymerization with a comonomer was mandatory. Interestingly, well-defined random copolymers containing 4CPA were cross-linkable by UV irradiation via [2 + 2] photocyclodimerization to obtain thin films with high gel content.

4. Conclusion

The studies highlighted here present a broad range of monomeric building blocks derived from biomass, specifically C5/C6 sugar-derived platforms in which the sugar structure is not retained, and their corresponding (meth)acrylate homo- and copolymers. Various synthetic methodologies have been used to prepare such bio-based monomers, the more common being those using traditional esterification chemistries to functionalize bio-derived small molecules with a polymerizable functional group. However, more recently emphasis on the "greenification" of such syntheses has intensified, for example, by using greener solvents. Subsequent RDRP, including ATRP, SET-LRP and RAFT polymerization have demonstrated the ability to prepare well-defined poly(meth)acrylate homopolymers as well as, in some examples, poly(meth)acrylate AB diblock and ABA triblock copolymers. Moreover, the use of functional bio-based monomers which allow for post-polymerization modifications (i.e., crosslinking) demonstrates the versatility of building blocks derived from biomass. Investigated applications of these bio-based poly(meth)acrylates have ranged from thermoplastic elastomers, pressure sensitive adhesives and coatings to materials for self-healing applications. The precise synthesis of bio-based poly(meth)acrylates derived from lignocellulosic sugar derivatives is constantly developing and has seen increased interest in recent years as environmental concerns grow. In the same line, RDRP methods have been recently applied also to the synthesis of well-defined (meth)acrylic polymers from lignin fractions

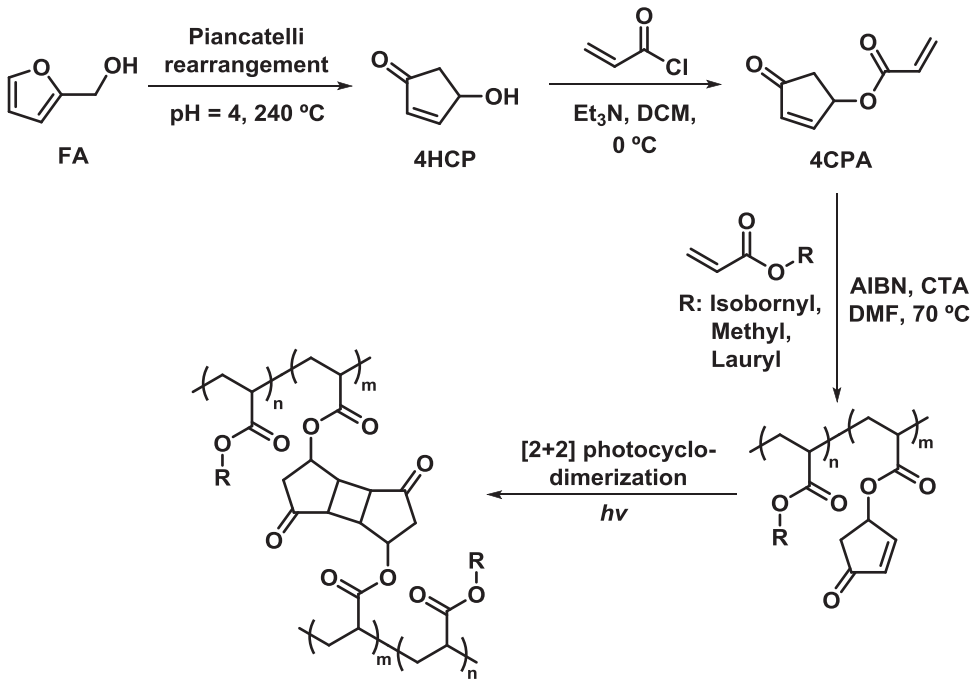

Figure 17. Procedure for the synthesis of 4-oxocyclopent-2-en-1-yl Acrylate (4CPA) and subsequent RAFT copolymerization and photo-crosslinking.

of lignocellulosic materials.[142–144] Future opportunities we envision in this area include the synthesis of more complex polymeric architectures, scale up of both monomer syntheses and polymerizations, as well as bio-based poly(meth)acrylate designed for currently unexplored applications. Block copolymers give interesting opportunities due to their ability to phase separate and form self-assembled nanostructures, which could be exploited further. Ultimately, the bio-derived monomer and polymer syntheses must be scalable to demonstrate industrial potential, which has been demonstrated for some syntheses, but efforts are still required overcome this hurdle. Finally, value added applications are typically targeted for the well-defined poly(meth)acrylates produced by RDRP techniques, as such we expect that to be no different for bio-based poly(meth)acrylates. Further investigations should expand this field to a range of new and exciting application areas.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

block polymers, controlled radical polymerization, lignocellulose, renewable resources

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