Progress in Polymer Science xxx (xxxx) xxx

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Next-generation polymers: Isosorbide as a renewable alternative

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ARTICLE INFO

Article history:
Accepted 10 December 2019
Available online xxx

Keywords:
Sustainable polymers
Isosorbide
Renewable feedstock
Synthetic strategies

ABSTRACT

With increasing interest in developing sustainable polymers for a broad range of applications, isosorbide has emerged as an attractive renewable feedstock for high-performance materials. Developments in the production scale and cost of isosorbide have further stimulated research interest. Step-growth polymerization of isosorbide has yielded polymers with excellent properties and applications ranging from packaging to automobile parts to biomedical devices. However, challenges associated with direct use of isosorbide in step-growth polymerization remain, demanding new synthetic strategies for producing tailored polymers from this building block. In this trend article, recent advances in isosorbide production, polymerization, and applications will be highlighted with a focus on new step- and chain-growth strategies to synthesize isosorbide-based polymers.

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Abbreviation: ADMET, acyclic diene metathesis; AIBN, azobisisobutyronitrile; AMP, acetal metathesis polymerization; BPO, benzoyl peroxide; BTCBA, 3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy)benzoic acid; CoNap, cobalt naphthenate; CQ, camphorquinone; CuAAC, copper(I)-catalyzed azide-alkyne cycloaddition; DAB, ethyl-4-(dimethylamino)benzoate; DBTDL, dibutyltin dilaurate; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DMF, *N,N*-dimethylformamide; DMPA, 2,2-dimethoxy-2-phenylacetophenone; DMSO, dimethyl sulfoxide; DP, degree of polymerization; FRP, free-radical polymerization; hi-vac, high vacuum; HO-CPAD, hydroxyethyl 4-cyano-4-(phenylcarbonothioylthio)-pentanoate; IBET, *S*-1-isobutoxylethyl *S'*-ethyl trithiocarbonate; LED, light-emitting diode; MALDI-TOF MS, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry; M_n, number average molecular weight; MTBE, methyl tert-butyl ether; M_w, weight average molecular weight; OEPED, *O*-ethyl-*S*-(1-phenylethyl)dithiocarbonate; RAFT, reversible addition–fragmentation chain transfer; ROMP, ring-opening metathesis polymerization; ROP, ring-opening polymerization; rt, room temperature; TAAC, thermal alkyne-azide cycloaddition; TBDMS, *tert*-butyldimethylsilyl chloride; TBPB, *tert*-butyl peroxybenzoate; T_d, thermal degradation temperature; T_g, glass transition temperature; THF, tetrahydrofuran; T_m, melting temperature; TPO, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; TPP, 2,4,6-triphenylpyriylium; USD, United States dollar; UV, ultraviolet.

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https://doi.org/10.1016/j.progpolymsci.2019.101196
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Please cite this article as: D.J. Saxon, A.M. Luke, H. Sajjad et al., Next-generation polymers: Isosorbide as a renewable alternative, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2019.101196

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1. Introduction

Meeting the increasing needs of plastic production, while simultaneously enhancing sustainability, has been a significant goal of academic and industrial research. Creating a new generation of sustainable materials as competitive alternatives for petroleum-based plastics can be a challenge due to the need for these new materials to match both the performance and cost-effectiveness of commonly used petro-plastics [1,2]. Isosorbide is a commercially available sugar derivative that has drawn considerable interest as a monomer for high-performance materials (Fig. 1) [3–7].

Until recently, the high cost of isosorbide was a major hinderance for manufacturing commercial isosorbide-based polymers. In 2015, Roquette became the largest producer of isosorbide when it launched a new site with an annual production capacity of 20,000 tons [8]. In 2018, the global isosorbide market was 190 million USD and is projected to reach 350 million USD by 2023 [9]. Despite the high cost of isosorbide over time, it has been studied extensively in the polymer literature, as it is structurally robust and rich in functionality. Isosorbide-based polymers exhibit many excellent properties ranging from their optical clarity to their strong resistance to UV irradiation, heat, chemical degradation, impact, and abrasion [10]. Because of these properties, these materials have shown great promise as sustainable alternatives for commercial applications such as packaging and electronic displays as well as specialty materials for more niche areas, particularly in the biomedical field. Consequently, resins and polymers now account for the majority of the isosorbide market share, nearing 60% in 2014 with further growth anticipated [9].

The topic of isosorbide as a rigid, renewable building block for functional materials—primarily synthesized via step-growth polymerization—has been highlighted and reviewed in several publications since 2010 [4–7]. While step-growth polymerization has been used extensively for the production of isosorbide-based polymers, challenges encountered with this method, such as the low reactivity of the secondary hydroxyl groups, have led to the development of new synthetic strategies. In some cases, these strategies involve new step-growth chemistries using relatively mild conditions. In most cases, however, new approaches involve extending the reactivity away from the hydroxyl groups of isosorbide and incorporating chain-growth polymerization strategies. In this trend article, new advances for incorporating isosorbide into materials will be highlighted with a focus on the most recent advances in isosorbide production, polymerization, and utility. A special emphasis is placed on efforts to tailor polymer compositions and architectures through creative synthetic polymer chemistry, which will play an important role for future innovations and applications of sustainable polymers from isosorbide.

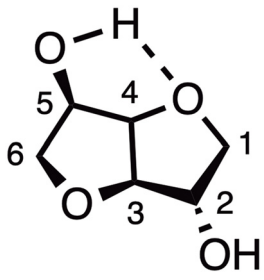

Fig. 1. Structure of isosorbide.

2. Isosorbide as a renewable building block

2.1. Structure and reactivity of isosorbide

Isosorbide is a rigid, bi-heterocyclic diol derived from glucose (Fig. 1). The two *cis*-fused tetrahydrofuran (THF) rings exhibit a puckered conformation (120°) with secondary alcohols at the 2- and 5-positions [4,5,11]. The C2 hydroxyl group extends outside the ring system (*exo*) and the C5 hydroxyl group sits inside the "V" shape of the rings (*endo*), with the latter participating in hydrogen bonding with the adjacent THF ring. This hydrogen bonding is thought to be at least partially responsible for higher reactivity typically observed for the *endo* hydroxyl group [4,6,12,13].

Due to the low overall reactivity of the alcohol groups in isosorbide, step-growth polymers of isosorbide are frequently restricted to lower molecular weights ($M_n \leq 10\,kg\,mol^{-1}$) and low isosorbide content (< 50 mol%). If larger amounts of isosorbide are to be incorporated into polymers, very high temperatures, long reaction times, and/or complex processes are necessary [4]. The limited thermal stability of isosorbide (T_d = 270 °C) can be problematic under the high-temperature conditions typically employed in polycondensation reactions [4]. Moreover, many methods of direct isosorbide polymerization require the use of toxic reagents (e.g. phosgene, isocyanates) that diminish their sustainability. Some of these issues may be addressed by use of derivatives of isosorbide that are amenable to controlled polymerization.

2.2. Advances in isosorbide production

The most common contemporary procedure for the production of isosorbide begins with the hydrogenation of glucose to sorbitol, which is well established and can be performed on large industrial scales [14–16]. Sorbitol is then subjected to acidic conditions, where a crucial, selective double-dehydration mechanism yields isosorbide. This dehydration reaction also produces several other singly-dehydrated side products, as well as unidentified oligomeric species. Consequently, yields of isosorbide through this process are typically less than 70%. A recent review article provides an overview of the various methods for producing isosorbide, covering homogenous and heterogenous acid catalysts for the dehydration of sorbitol in addition to methods for the production of isosorbide directly from biomass [17]. Here, we briefly highlight key efforts in recent years involving the direct conversion of glucose or cellulosic biomass to isosorbide (Fig. 2).

An attractive approach towards isosorbide production from glucose uses a dual-catalytic system that promotes the hydrogenation of glucose and the subsequent double-dehydration of sorbitol using the same catalytic bed. A heterogenous catalyst comprised of ruthenium metal sites and acidic sites immobilized on the same support

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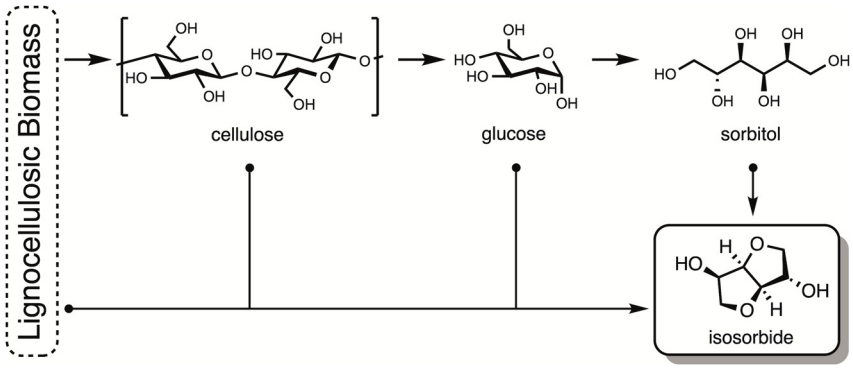

Fig. 2. Conversion of lignocellulosic biomass and downfield products to isosorbide [14–20].

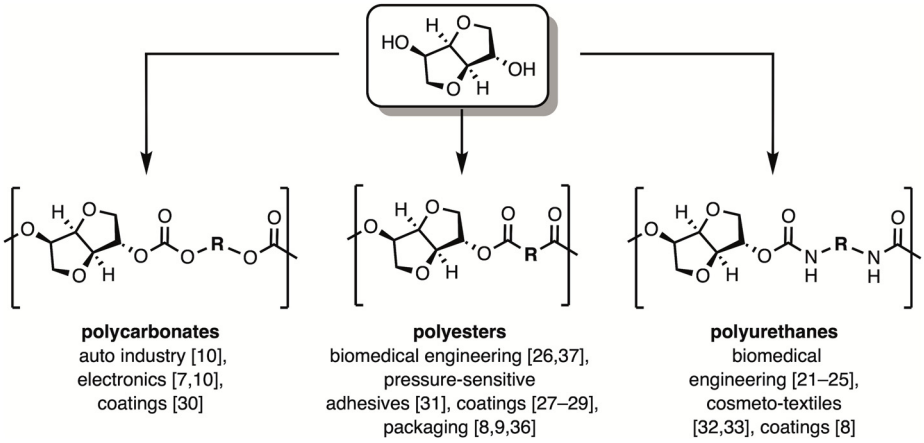

Fig. 3. Classes of polymers from isosorbide and their potential applications.

reportedly produces isosorbide through a one-pot, one-stage process from C_6 sugars in up to 86% yield [18]. The authors suggest that the high yield and selectivity for isosorbide stems, in part, from the low Lewis acidity of the catalyst which favors a sequential hydrogenation-dehydration pathway.

The direct conversion of cellulose to isosorbide was accomplished using mesoporous niobium phosphate-based heterogeneous catalysts [19]. The authors first depolymerized cellulose via hydrolysis to generate glucose, which was hydrogenated in the same step. In the next step, isosorbide was produced via the double-dehydration mechanism. By optimizing reaction conditions, the authors report obtaining isosorbide in up to 57% yield.

A unique example of the direct synthesis of isosorbide from lignocellulosic biomass uses Ru supported on carbon and ion-exchange resins for a one-pot conversion [20]. This process offers a direct advantage over similar methods as a "pretreatment" step to remove lignin and hemicellulose from the biomass is unnecessary. Using Ru/C and Amberlyst 70, the authors report a yield of 25.4% for isosorbide from Japanese cedar chips in the one-pot, one-step process. The authors propose that the choice of starting lignocellulosic biomass is important, as lower yields were obtained when using eucalyptus or bagasse chips due to higher content of other, unusable components (i.e. lignin and hemicellulose) that diminishes the activity of the catalysts.

3. Traditional step-growth polymers from isosorbide and their applications

The promise of isosorbide-based polymers has been realized through commercialization of several materials derived from step-growth processes. For example, 35% of the total isosorbide produced in 2014 was used to produce poly(ethylene-*co*-isosorbide) terephthalate [8,9]. Moreover, Mitsubishi Chemical has now implemented an isosorbide-based copolycarbonate (Durabio) for use in their automobile parts and electronic displays, which exhibits superior properties to its counterpart incorporating bisphenol A [7,10]. In this section, we will briefly highlight some of the polymers synthesized by traditional step-growth methods and their implications for a variety of applications (Fig. 3).

3.1. Biomedical applications

Polymers containing isosorbide are increasingly used as biomedical engineering materials because of their biodegradability and biocompatibility (e.g. cell adhesion, proliferation, and differentiation) [21–23]. For example, a series of polyurethanes containing isosorbide and polycaprolactone were synthesized (50–88%) in the presence of an aliphatic diisocyanate (**1**, Fig. 4) [21]. These polymers have molecular weights ranging from 17 to 51 kg mol^{-1}, T_g values ranging from 31 to 42 °C, and are degradable under physiological conditions. Cytotoxicity assays indicated that seeded cells (from rat bone marrow mesenchymal stroma) grew when cultured on the polyurethane samples. Similarly, a series of polyurethanes were synthesized with diol monomers [poly(propylene glycol) or isosorbide] and aliphatic diisocyanates (**2**–**3**, Fig. 4) [24]. These polymers exhibited lower molecular weights (3–4 kg mol^{-1}), but higher T_g values (55–70 °C). Again, high cell viability was observed when cultured on the films (> 70%, HaCaT human skin cells), indicating their biocompatibility.

Other authors reported a method to improve the mechanical properties of polyurethanes by incorporating isosorbide as a chain extender for a series of isocyanate-terminated poly(lactide)

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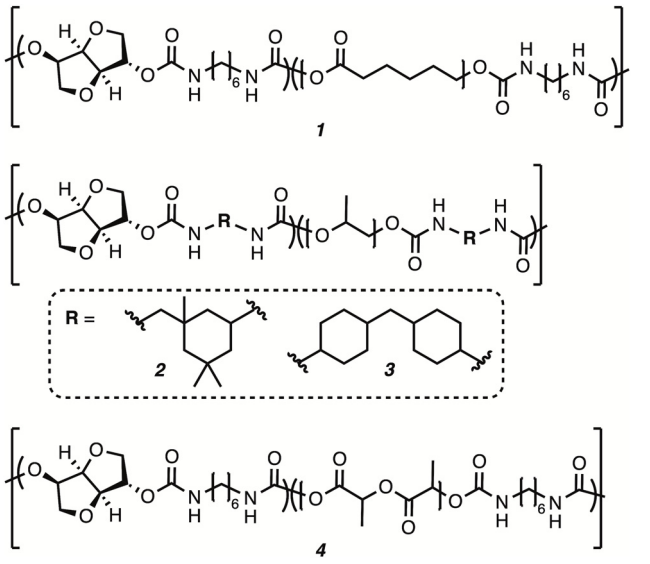


Fig. 4. Polyurethanes comprised of aliphatic diisocyanates, isosorbide, and other diols [21,24,25].

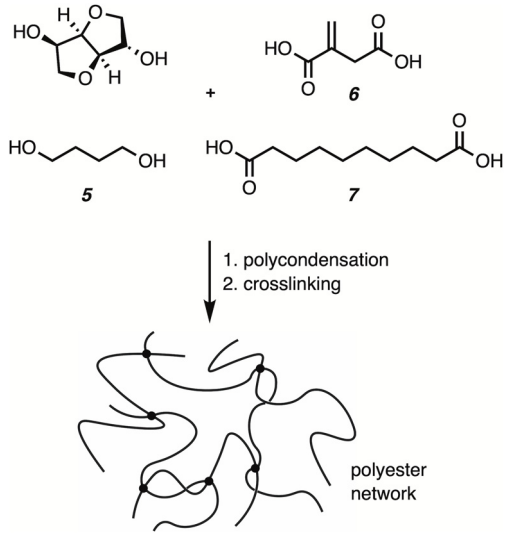
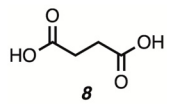
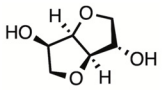
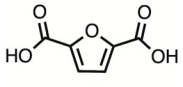
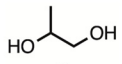
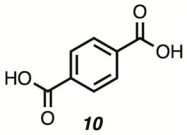
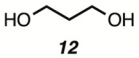
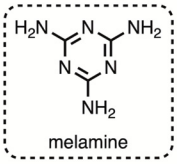
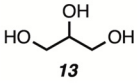


Fig. 5. Polyester networks derived from isosorbide, 1,4-butanediol (**5**), itaconic acid (**6**), and sebacic acid (**7**) [26].

(**4**, Fig. 4) [25]. The resulting polymers displayed higher tensile strength and moduli (43 MPa and 2.5 GPa, respectively) than the lactide-based polyurethanes used previously (36 MPa and 2.1 GPa, respectively). The mechanical properties, along with good cytocompatibility, demonstrate these materials as promising candidates for bone regeneration scaffolds.

Copolyesters containing isosorbide, 1,4-butanediol (**5**), itaconic acid (**6**), and sebacic acid (**7**) have also been synthesized (Fig. 5) [26]. Thermal characterization revealed low T_g values (–51 to –35 °C) and tunable T_m values (34–60 °C) based on the isosorbide content. The polyesters were then crosslinked in the presence of dicumyl peroxide; interestingly, these materials exhibited shape memory properties such as shape fixity and recovery rates near 100%, which can provide structural support for medical implants and devices. Biocompatibility of these materials was demonstrated through cytotoxicity studies examining cell adhesion and proliferation (CCK-8 assay of L929 mouse fibroblasts).

Table 1
Structures of diacids and diols used to prepare copolyesters [27–29].

diacids	diols
 **8**	 *isosorbide*
 **9**	 **11**
 **10**	 **12**
crosslinker [27]:  melamine	 **13**

3.2. Coatings

The coatings industry has also been increasingly employing isosorbide-based polyesters and polycarbonates. Recently, isosorbide-based polyesters of succinic acid (**8**, Table 1) were synthesized with varying amounts of isosorbide (12–30 wt%) and other biobased diols (**5**, **11**–**13**, Table 1), resulting in polymers with T_g values ranging from 3 to 30 °C ($M_n \approx 4$–5 kg mol^{-1}) [27]. The prepolymers were crosslinked with melamine and exhibited excellent chemical and photochemical durability even after 2,000 h of aging.

Others reported the synthesis of polyester coatings based on succinic acid, 2,5-furandicarbonxylic acid (**9**), isosorbide (10–70 mol%), and aliphatic diols (Table 1) [28]. The T_g of these coatings ranged from –46 to 35 ºC, increasing with greater isosorbide content. While the molecular weights suffered as the amount of isosorbide was increased, the inclusion of isosorbide led to enhanced thermomechanical properties of the coatings.

Poly(ethylene terephthalate) was shown to be chemically recycled through depolymerization with isosorbide to give oligomers that were subsequently subjected to polycondensation with succinic acid to make new polyesters (Table 1) [29]. The resulting polymers have similar properties to a commercial polyester commonly used in coating applications (Crylcoat 1771-3), including melt viscosity (5500 mPa s vs 4900 mPa s at 200 °C) and T_g (60 °C vs 56 °C).

Copolycarbonates based on isosorbide have also been studied for coating applications. For example, polycarbonates were prepared via melt polycondensation of isosorbide and 1,3-propanediol or 1,4-butanediol with either triphosgene or diphenyl carbonate (**14**, Fig. 6) [30]. The resulting materials had modest molecular weights ranging from 1.3 to 7.2 kg mol^{-1} and exhibited T_g values ranging from 43 to 138 °C. Moreover, the polycarbonates were cured with conventional polyisocyanate crosslinkers, which

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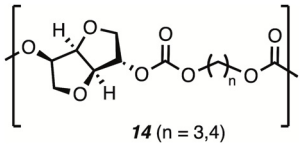

Fig. 6. Copolycarbonate of isosorbide and 1,3-propanediol or 1,4-butanediol [30].

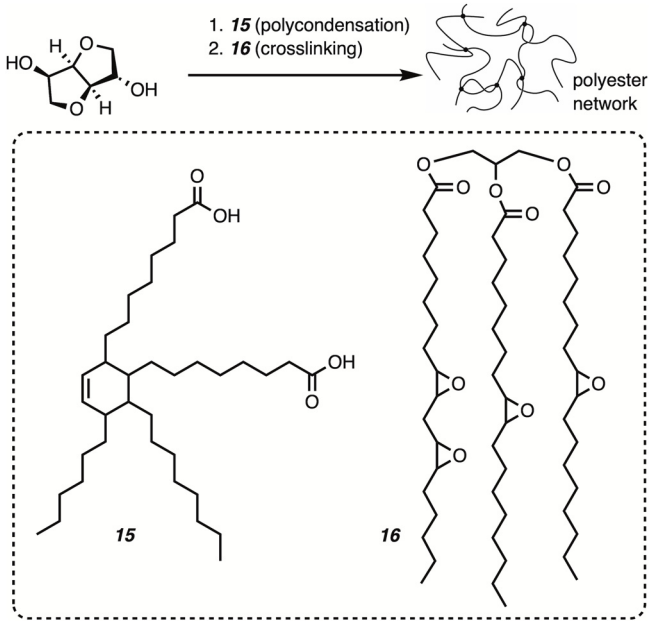

Fig. 7. Isosorbide-containing polyester networks for pressure-sensitive adhesives [31].

resulted in coatings with excellent chemical and mechanical resistance.

3.3. Other applications

The pressure sensitive adhesive industry has also benefitted from isosorbide-based polymers. For example, self-adhesive gel materials were prepared via bulk polycondensation of a dimerized fatty acid (**15**) and isosorbide (M_n = 14–27 kg mol^{-1}; Fig. 7) [31]. The linear polyesters were then crosslinked with epoxidized plant oils (e.g. **16**), forming elastomers with higher T_g values than non-isosorbide analogues (−18 °C as compared to −46 °C) with the ability to modulate other properties such as viscoelasticity and interfacial adhesion.

Additionally, the cosmeto-textile industry has benefitted by employing isosorbide-derived polymers for microcapsule walls. Microencapsulation of materials is a useful technique for controlled delivery of substances [32,33]. New microcapsules were reported that contain a polyurethane copolymer wall made by interfacial polycondensation of isosorbide and bis-isocyanates (Fig. 8). The original materials (**17**) exhibited encapsulation of a perfume, which could then be impregnated on fibers [32]. Modification of the polyurethane backbone (**18**) and the formulation process (i.e. adding in a cationic surfactant) resulted in better adhesion to fibers and a slower perfume release over 40 washing cycles [33].

While isosorbide-based polymers have been used in a variety of applications as mentioned above, many other examples exist that are beyond the scope of this trend article, including use as anti-fogging materials [34], flame retardants [35], aerosol containers [36], and polyester nanofibers [37].

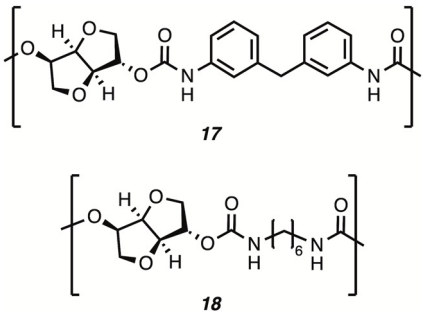

Fig. 8. Polyurethane copolymers for microencapsulation [32,33].

4. Novel step-growth approaches towards isosorbide-based polymers

A particular challenge to overcome in efforts to incorporate isosorbide via step-growth polymerization is the relatively low and disparate reactivity between the secondary alcohols of isosorbide. This section will highlight new step-growth chemistries that generally involve derivatizing isosorbide to extend the reactivity away from the alcohols.

4.1. Cyclic anhydride functionalization

A common method to enhance the reactivity of isosorbide in step-growth polymerizations has been to first functionalize the alcohols to make a diacid (**19**), which can be accomplished by heating with a cyclic anhydride (e.g. succinic, maleic) to >100 °C (Fig. 9). The resulting molecules are typically used in thermosetting materials, which have numerous applications. In one example, a bis-maleic acid ester of isosorbide was crosslinked with epoxidized sucrose soyate, resulting in materials with high moduli (0.5–1 GPa). [38]. Similarly, a bis-succinic acid ester of isosorbide was prepared under microwave conditions, significantly reducing the reaction time [39]. This monomer was crosslinked with glycerol (**13**) in the absence of solvent, resulting in a rigid polyester network with a high plateau modulus (7.9 MPa at 100 °C), $T_d \approx 300$ °C, and T_g = 55 °C. The properties were tuned to create more flexible thermosets by inclusion of a small percentage of oligomeric poly(ethylene oxide) (M_n = 300 g mol^{-1}).

The cyclic anhydride functionalization approach has also been extended to the synthesis of linear polyurethanes by transforming the α,ω-acids to isocyanates (Fig. 9) [40,41]. Polymerization of isosorbide diisocyanate **20** with virgin isosorbide led to polyurethane **21** with M_n = 14.3 kg mol^{-1} and T_g = 78 °C [40]. Copolymerization of diisocyanate **20** with bis-hydroxymethylfuran (**22**) afforded stiff polyurethane **23** (E = 2.30 GPa) with M_n = 11.7 kg mol^{-1} and T_g = 52 °C [41]. Because of the wide range of uses of polyurethanes, this strategy has potential for myriad applications (e.g. elastomers, adhesives, coatings, foams, and fibers) and for tuning existing polyurethane properties with isosorbide as a rigid, renewable feedstock.

4.2. Polycarbonate condensation catalysts

Polycarbonates from isosorbide are also of great interest, as these materials have a high T_g (~170 °C) and may serve as a replacement for polymers that incorporate bisphenol A. Among the many catalysts probed, lithium acetylacetonate and cesium carbonate are the most successful for preparing high molecular weight polycarbonates with minimal coloration [42–44]. Recently, metal-free catalysts including quaternary ammonium- or imidazolium-based ionic liquids that are able to overcome the low reactivity for melt polycondensation of isosorbide and diphenyl carbonate (**24**)

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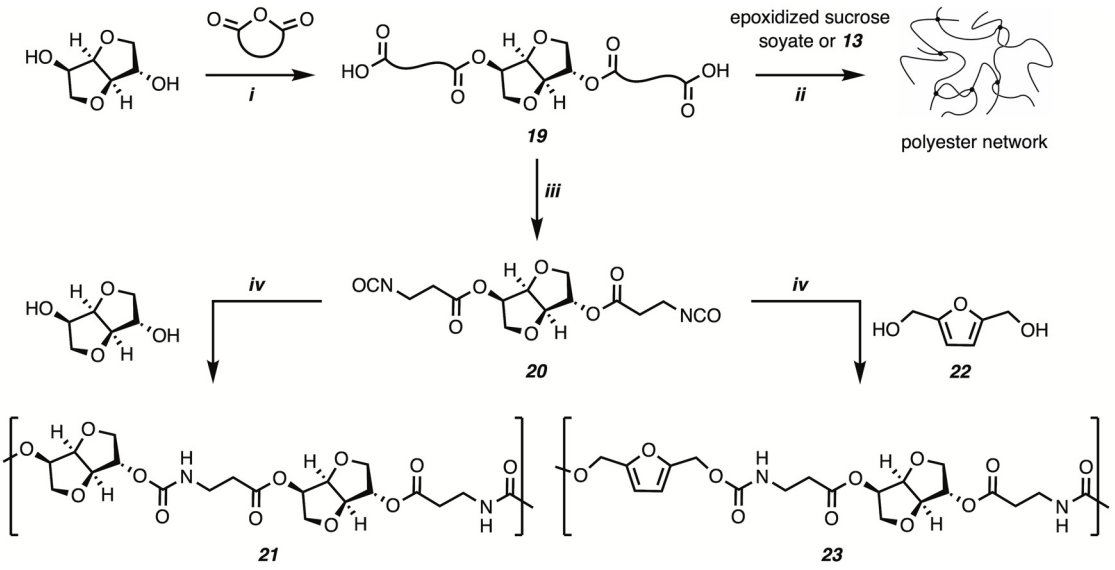

Fig. 9. Cyclic anhydride functionalization of isosorbide to yield either polyester networks (via **19**) [38,39] or linear polyurethanes (via **20**) [40,41]. *Reagents and conditions*: (*i*) >100 °C, neat or $Sn(Oct)_2$, microwave; (*ii*) 50–80 °C; post-cure 75–150 °C; (*iii*) a) $SOCl_2$, 75 °C; b) NaN_3, 0 °C; c) toluene, 110 °C; (*iv*) DBTDL, DMF, 30–120 °C.

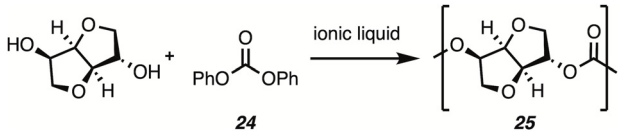

Fig. 10. Polycondensation of isosorbide and diphenyl carbonate (**24**) in the presence of ionic liquids [45,46]. *Conditions*: 100 °C; then 100–240 °C, hi-vac.

have been reported (Fig. 10) [45,46]. For example, imidazolium-based ionic liquids (0.05 mol%) yielded homopolycarbonate **25** with M_n = 61.7 kg mol^{-1} and excellent thermal properties (T_g = 174 °C, T_d = 342 °C) [46]. Ionic liquids with more electronegative anions and hydrogen bonding ability were found to be most effective. Additionally, copolycarbonates with other aliphatic diols were synthesized in efforts aimed at tuning the thermal properties [45,46]. The high molecular weights achieved are atypical with isosorbide, but necessary for materials with useful mechanical properties (M_w > 70 kg mol^{-1} are ideal) [46,47].

Others have recently pioneered a mild step-growth polymerization method employing bis-carbonylimidazolide and diol monomers [48,49]. Since the parent compounds are diols, this is a versatile strategy allowing for a variety of polycarbonate backbones to be developed exclusively from commercially available diols. Using CsF as a catalyst, homopolycarbonates of isosorbide (**25**, Fig. 11) with M_n = 20.4 kg mol^{-1} and T_g = 169 °C were synthesized, producing only imidazole as a byproduct [48]. Additionally, copolymers with other 1,3- or 1,6-diols (**26**–**28**) were synthesized in good yield with T_g values ranging from 31 to 113 °C. In an extension of this work, an organocatalytic approach was employed (DBU catalyst) to synthesize copolymers with acetal-protected dihydroxyacetone, affording copolycarbonate **29** (M_n = 4.5–9.5 kg mol^{-1}) with tunable thermal and degradation properties [49]. In contrast to their aromatic counterparts, aliphatic polycarbonates are appealing for certain biomedical applications, such as drug delivery vehicles and tissue engineering scaffolds, as they do not affect local pH and they exhibit low T_g and slow degradation (surface erosion of the polymers rather than bulk degradation) [48–50].

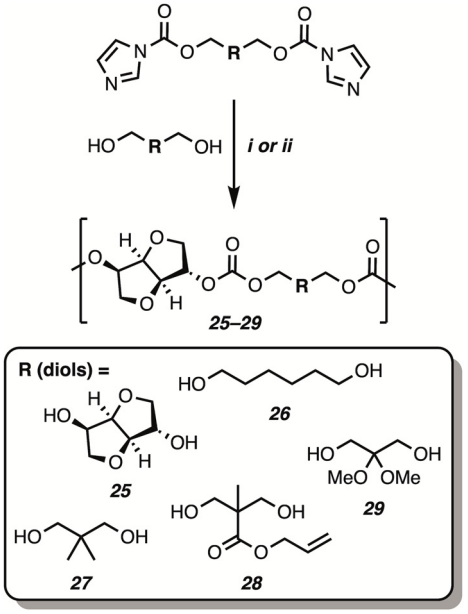

Fig. 11. Polycarbonates synthesized from bis-carbonylimidazolide and diol comonomers [48,49]. *Reagents and conditions*: (*i*) CsF, EtOAc, 60 °C *or* (*ii*) DBU, neat or $CHCl_3$/MeCN, rt–120 °C.

4.3. Azide–alkyne click

The development of highly efficient and orthogonal chemistries, such as azide–alkyne "click" reactions, has also been valuable for creating materials with high isosorbide content. For example, a series of azide- and alkyne-functionalized monomers of isosorbide have been designed for step-growth polymerization employing either Cu(I)-catalyzed or thermal azide–alkyne cycloaddition (CuAAC and TAAC, respectively) (Fig. 12) [51–54]. AB monomers (**30a–b**) with α-azide–ω-alkyne structures originating from isosorbide were polymerized to molecular weights of ~10 kg mol^{-1} (**31**) [52]. Installation of the azide, which requires a substitution reaction, causes inversion of the stereochemistry of either the 2- or 5-position in these monomers and results in either *endo-endo* (**30a**) or *exo-exo* (**30b**) products. The corresponding monomers with *endo-exo*/*exo-endo* (**30c**/**30d**) functionality could also be synthesized from the corresponding isohexide (isomannide and isoidide, respectively) to yield polymers with an isosorbide repeat unit, revealing no marked differences in the resulting molecular weights or thermal properties. Bulk TAAC was preferred due to the phys-

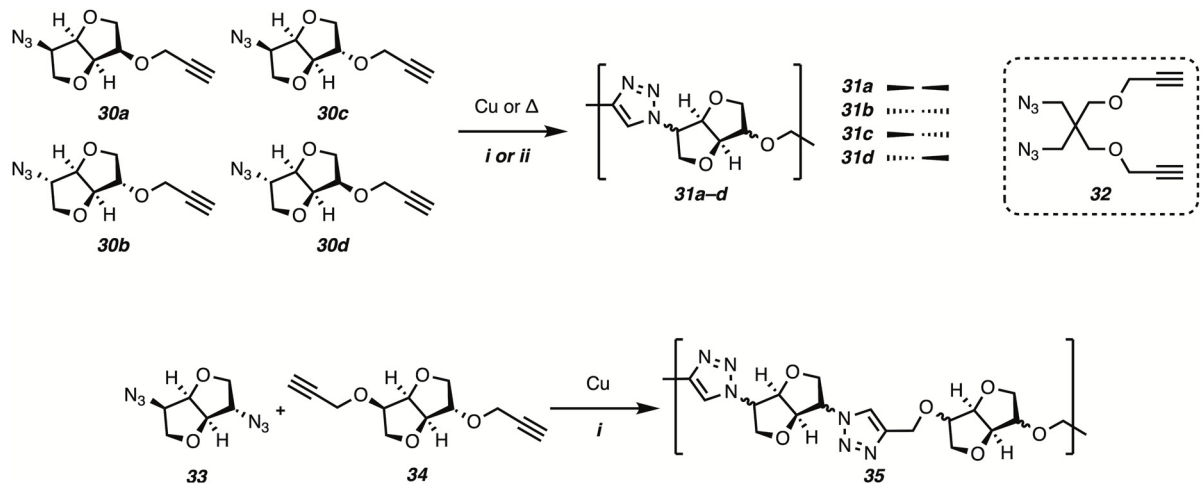

Fig. 12. Azide–alkyne "click" polymerization of AB (**30**) and $A_2 + B_2$ (**33**, **34**) monomers [51–54]. *Reagents and conditions*: (*i*) $CuIP(OEt)_3$, DMSO, 60 °C *or* (*ii*) bulk, 0–200 °C.

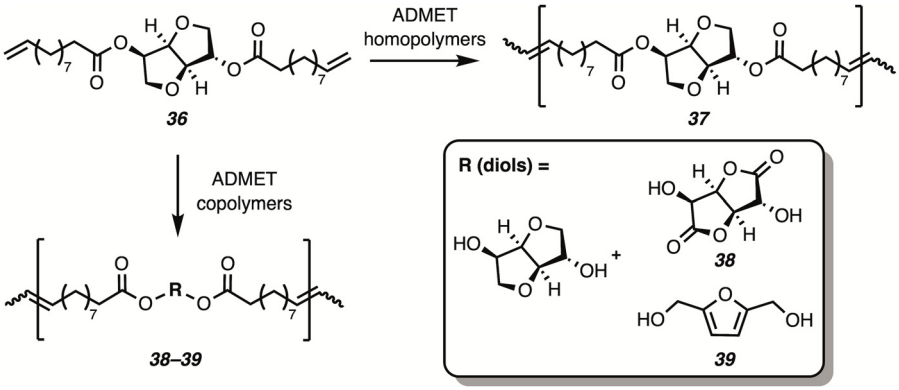

Fig. 13. Acyclic diene metathesis (ADMET) polymerization of α,ω-dienes derived from renewable diols and castor oil [55–57]. *Reagents and conditions*: Grubbs G2, 80 °C, hi-vac.

ical gelation of the polymerization mixture with CuAAC. This was attributed to the much higher regioselectivity of 1,4-disubstituted 1,2,3-triazoles with CuAAC than TAAC (100 % and 50 %, respectively). Furthermore, the *exo*-azide–*endo*-alkyne isosorbide was used to synthesize high T_g networks with A_2B_2 crosslinker **32** in the bulk [53]. Analogous $A_2 + B_2$ monomers **33** and **34** were also prepared and polymerized [54]. Interestingly, solution polymerization with CuAAC was unimpeded by gelation as previously seen with the AB system. Although only 1,4-disubstituted 1,2,3-triazole linkages were observed, the authors note that the $A_2 + B_2$ system leads to stereo-irregularity in the polymer backbone. Molecular weights of 12.1 kg mol^{-1} were achieved, affording polytriazoles with T_g = 126 °C and T_d = 342 °C. The authors observed higher molecular weights with these AB monomers using TAAC than with CuAAC, likely due to the insolubility of the materials at higher degree of polymerization for CuAAC. The authors note that these materials may find use in applications where the key challenges are adhesion, metal complexation, and thermal properties.

4.4. Metathesis polymerization

Acyclic diene metathesis (ADMET) polymerization has been explored to synthesize polyesters with long alkyl spacers (10-undecenoic acid) in between each isosorbide moiety (**36**; Fig. 13) [55–57]. These spacers are derived from castor oil and yield α,ω-dienes upon linkage to isosorbide that are amenable to ADMET polymerization. The initial report focused on the isomerization during polymerization of low molecular weight polyesters (**37**) [55].

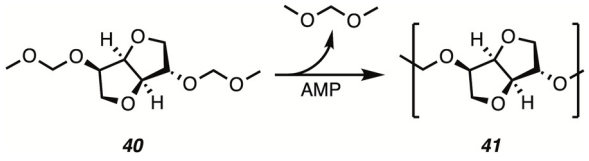

Fig. 14. Polyacetal synthesis via acetal metathesis polymerization (AMP) of bis-methoxymethyl isosorbide **40** [58]. *Reagents and conditions*: *p*-toluenesulfonic acid, 60 °C.

Later studies investigated the thermal properties of these brittle materials (M_n = 51 kg mol^{-1}), exhibiting T_g = −10 °C, T_m = 38 °C, and T_d = 369 °C [56,57]. Copolymers were also synthesized with glucarodilactone undecanoate (**38**) and 2,5-bis(hydroxymethyl)furan undecanoate (**39**). Copolymer **38** was degradable under basic conditions within several days and also showed rubbery tensile properties with shape memory, in contrast to the brittle parent homopolymers. The shape memory properties are postulated to stem from transient networking in the materials due to the glucarodilactone units. Introduction of 2,5-bis(hydroxymethyl)furan had a softening effect, resulting in materials that were unable to be tensile tested.

Acid-degradable polyacetals were produced from isosorbide by acetal metathesis polymerization (AMP) (Fig. 14) [58]. This method is similar to ADMET polymerization because both rely on the loss and removal of small molecules with low boiling points (ADMET = ethylene; AMP = dimethoxymethane). Bis-methoxymethyl acetal **40** was synthesized and subsequent

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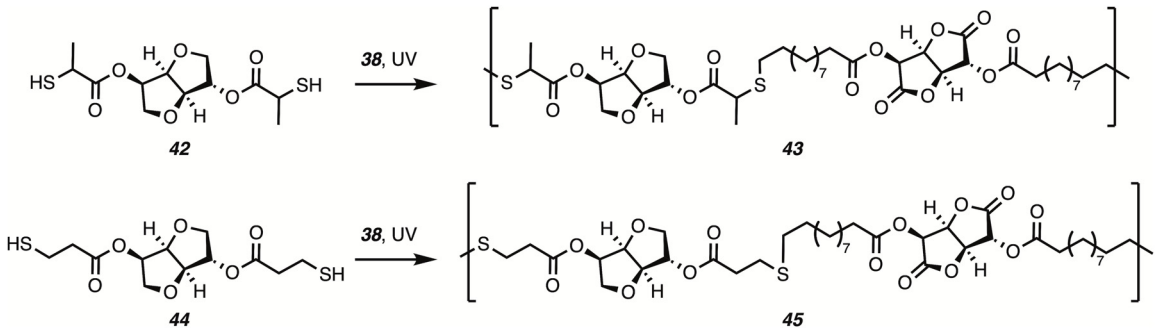

Fig. 15. Thiol–ene "click" photopolymerization of isosorbide dithiols (**42**, **43**) and **38** [59]. *Reagents and conditions*: DMPA, UV, rt.

treatment with *p*-toluenesulfonic acid afforded polyacetal **41** with M_n = 4.9–27.6 kg mol^{-1} and $T_g \approx 58\,^{\circ}C$; interestingly, these polymers also exhibited a T_m (103–117 °C) despite the short alkyl spacer length.

4.5. Thiol–ene click

Another polymerization that has been growing in popularity makes use of the efficient, 100% atom economic thiol–ene "click" reaction. For example, the production of linear poly(ester-thioether) analogs to the previously described ADMET polyesters was demonstrated by photopolymerization of **38** and isosorbide dithiols **42** and **44** (Fig. 15) [59]. Polymers **43** and **45** with M_n = 17–49 kg mol^{-1} and T_g = −1.3–19 °C were prepared. Additionally, complete loss of crystallinity in these materials was observed and attributed to the absence of a long, flexible aliphatic unit in the backbone. Nonetheless, excellent mechanical strength (26–42 MPa) and ductility (440–590%) were reported—comparable to or exceeding that of commercial elastomers.

Other thiol–ene reports often derivatize isosorbide to incorporate alkenes that can be reacted with commercially available thiols. In particular, diallyl isosorbide (**46**) has been studied by several groups in this capacity (Fig. 16) [60–63]. In one instance, hybrid networks were synthesized by appending a terminal trimethoxylsilyl group (**47**), which could be crosslinked under acidic or basic conditions, resulting in self-organized nanoscale materials [61]. Thiol–ene crosslinking of diallyl isosorbide **46** with tris(3-mercaptopropionate) **49** has also been explored for antibacterial materials. Antibacterial components were incorporated by use of linalool (**48**) as a comonomer [62] or by immobilizing silver nanoparticles in the films and coatings [63]. The linalool-based materials showed adherence resistance to *S. aureus* and the materials containing silver nanoparticles led to a 98% growth reduction of both *S. aureus* and E. *coli*. Cell adhesion and proliferation studies suggest that these materials may find utility as coatings for medical devices (e.g. catheters).

Functionalization of isosorbide with alloc groups—which are the carbonate analog of allyl groups—has also been demonstrated (**50**, Fig. 17) [64]. Photocrosslinking with **49** was performed and the effects of post-cure time on the thermal, mechanical, and surface properties were studied. The thermal and mechanical properties were relatively unchanged throughout, with T_g values of all samples slightly below room temperature, $T_d \sim 320\,^{\circ}C$, moduli ranging from 1.9 to 2.8 MPa, and elongation at break from 220 to 340%. These thermosets were hydrolytically degradable under basic conditions at elevated temperature and slightly degradable under physiological conditions. High cell viability was also observed, potentially allowing for use in bioelastomer applications, such as medical scaffolds or soft tissue engineering, as well as renewable plastics.

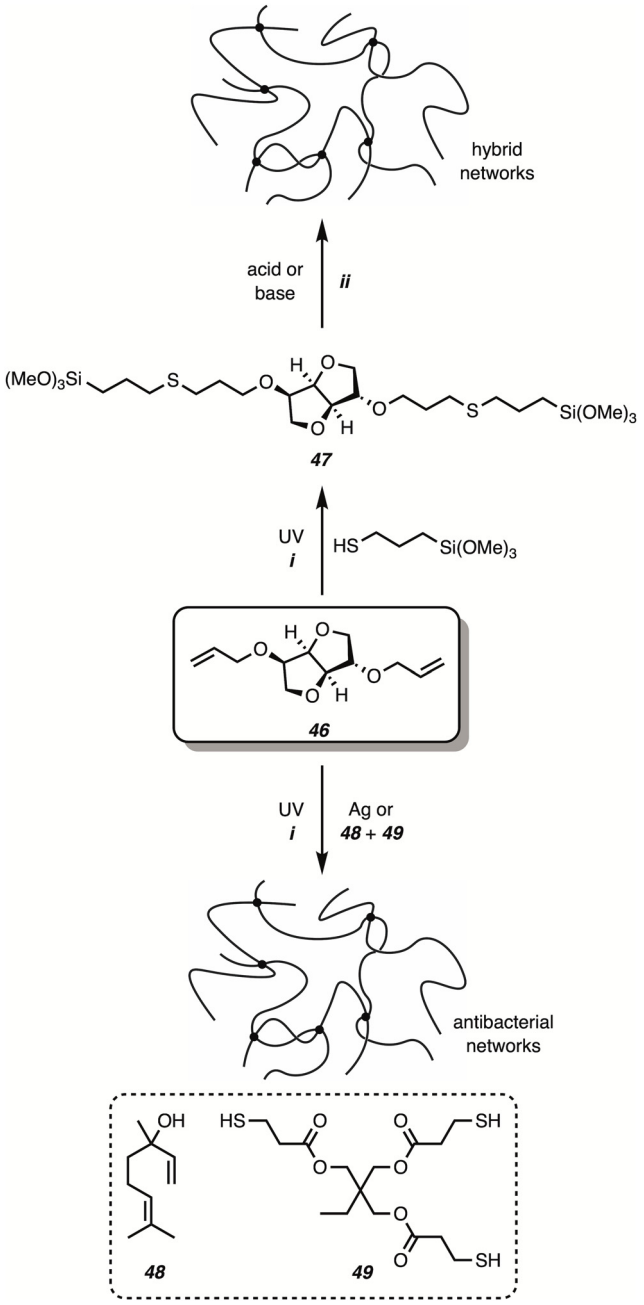

Fig. 16. Hybrid and antibacterial networks prepared via photo-mediated thiol–ene "click" chemistry of diallyl isosorbide (**46**) [60–63]. *Reagents and conditions*: (*i*) DMPA, UV, rt; (*ii*) HCl or NaOH, rt.

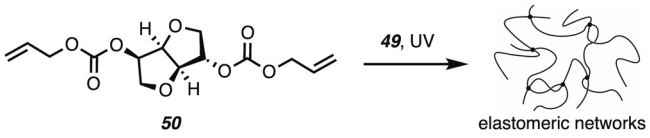

Fig. 17. Thiol–ene "click" photocrosslinking of dialloc isosorbide (**50**) and trithiol **49** [64]. *Reagents and conditions:* DMPA, UV, rt; post-cure 100 °C.

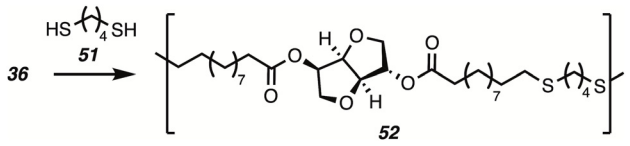

Fig. 18. Thiol–ene "click" polymerization of **36** and 1,4-butanethiol (**51**) [65]. *Reagents and conditions*: AIBN, 60–90 °C.

More recently, thiol–ene miniemulsion polymerization of **36** and 1,4-butanethiol (**51**) to synthesize poly(thioether-ester) nanoparticles was reported (Fig. 18) [65]. Miniemulsions—which are heterophasic systems consisting of sub-micrometric droplets of one phase dispersed in a second phase—are formed prior to polymerization by a high shear energy process (e.g. ultrasonication). The formed semi-crystalline polymer **52** (T_m = 68 °C) had average molecular weights up to 11 kg mol^{-1}, which could be improved with increasing polymerization temperatures. As a proof of concept, Coumarin 6 was encapsulated in the waterborne poly(thioether-ester) particles in near quantitative efficiency; additionally, these nanoparticles were biocompatible in murine fibroblast and uterine colon cancer cells, suggesting their potential efficacy as drug delivery vehicles.

In 2018, homo- and co-polymers partially derived from isosorbide diacrylate (**53**) were examined as biomedical scaffolds (Fig. 19) [66]. Linear polymers from **53** were synthesized using the base-mediated thiol–Michael reaction with various commercially available dithiols (**54**–**57**). Molecular weights up to 52.3 kg mol^{-1} were achieved, exhibiting T_g values from −14 to 15 °C. Addition of bisacrylamide **58** (5–20 wt%) resulted in the enhancement of the mechanical properties through hydrogen bonding, thus increasing their efficacy as a biomedical scaffold. Preliminary biological studies indicated enhanced cell attachment to the polymer film surfaces and a lack of toxic byproducts, serving as additional evidence of the potential for poly(β-thioester) biomedical scaffolds.

5. Novel chain-growth approaches towards isosorbide-based polymers

Although substantial advances have been made regarding new step-growth techniques to incorporate isosorbide into polymers, controlled polymerization offers the advantage of enabling the development of tailored polymer compositions and architectures—including statistical and block copolymers. These goals can be achieved using chain-growth strategies under mild conditions. Here, we discuss isosorbide-based materials synthesized by chain-growth polymerization and speculate on their potential applications.

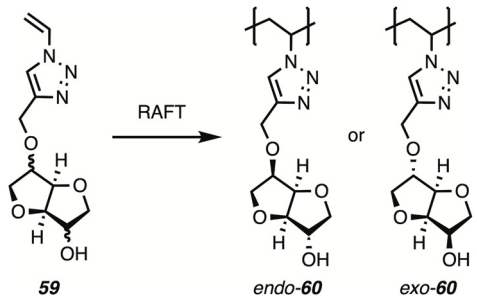

Fig. 20. Poly(vinyl triazoles) with pendant isosorbide groups [67]. *Reagents and conditions*: AIBN, OEPED, DMSO, 80 °C.

5.1. Free- and controlled-radical polymerization of mono-functional isosorbides

Radical polymerization of vinyl and (meth)acrylic derivatives of isosorbide has been a particularly well-used chain-growth polymerization technique. Thermal- and photo-initiated free-radical polymerization (FRP) of such monomers has been used in order to synthesize both homopolymers and thermosets. Moreover, controlled radical polymerization methods such as Reversible Addition–Fragmentation Chain Transfer (RAFT) polymerization have been used to create well-defined polymer architectures such as di- and tri-block copolymers. In an early report, a vinyl triazole isosorbide bearing a free hydroxyl group (**59**) was prepared and polymerized via RAFT polymerization (M_n = 15–20 kg mol^{-1}) (**60**, Fig. 20) [67]. The authors noted stark differences in the polymer properties depending on whether the free alcohol is *exo* (T_g = 71 °C) or *endo* (T_g = 118 °C); although no explanation is provided, we hypothesize this may be due to differences in hydrogen bonding. Polymethacrylate analogs were also prepared with acetate protecting groups via FRP (M_n = 90–105 kg mol^{-1}) (**63**, Fig. 21) [68]. The position of the acetate (*exo* vs. *endo*) was discovered to have little impact on the polymer properties as both had a $T_g \approx 130$ °C. Controlled radical polymerization via RAFT was also performed and subsequent chain extension with *n*-butyl acrylate was used to make diblock copolymer **64**.

Acrylic ABA triblock copolymers were also studied with acetylated acrylic isosorbide (**61**) as the hard 'A' blocks and *n*-butyl acrylate as the soft 'B' block (**65**, Fig. 21) [69]. The pressure-sensitive adhesive performance of these materials was tested, showing good peel forces (2.9 N cm^{-1}), tack forces (3.2 N cm^{-1}), and no shear failure (up to 10,000 min). It was later shown that the peel adhesion of triblock **65** could be increased to 8.74 N cm^{-1} by having a more entangled midblock (i.e. increasing the M_n of *n*-butyl acry-

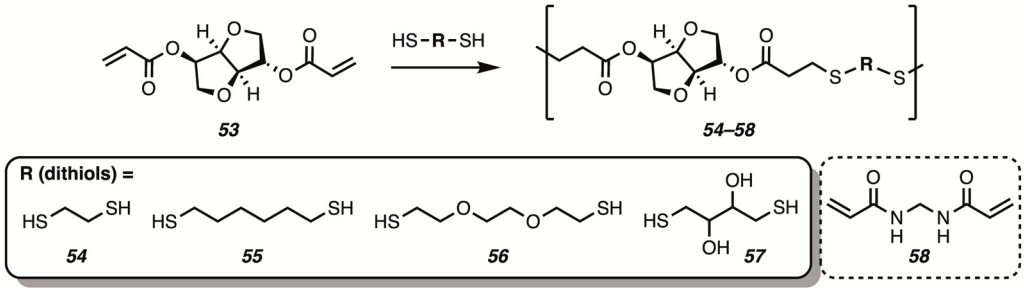

Fig. 19. Thiol–Michael polymerization of isosorbide diacrylate (**53**) and various dithiols [66]. *Reagents and conditions*: DBU, rt.

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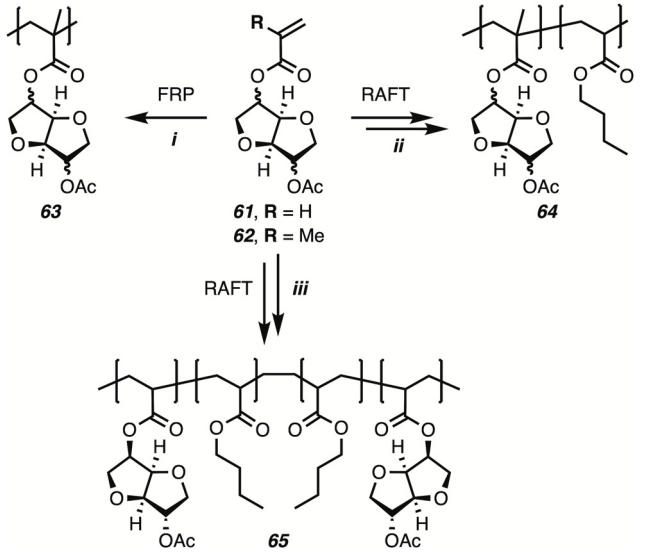

Fig. 21. Homo- and block co-polymers from isosorbide (meth)acrylate (**61**, **62**) [68–70]. *Reagents and conditions*: (*i*) AIBN, DMF, 70 °C; (*ii*) AIBN, HO-CPAD, DMF, 70 °C; (*iii*) a) *n*-butyl acrylate, AIBN, BTCBA, DMF, 70 °C; b) **61**, AIBN, DMF, 70 °C.

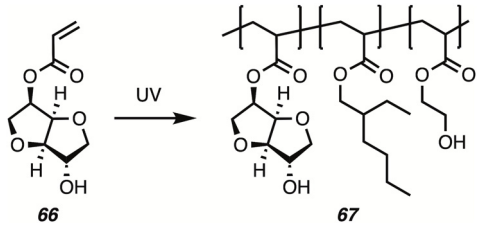

Fig. 22. Statistical copolymerization of acrylates for pressure-sensitive adhesives [71]. *Reagents and conditions*: Irgacure 184, UV, bulk.

late and increasing tackifier content) [70]. Moreover, increasing the wt% of isosorbide endblocks enhanced the stress and elongation at break of the thermoplastic elastomers (6.5 MPa and 620%, respectively), widening the scope of their applicability. Other studies have demonstrated that acrylic isosorbide **66** may also be useful for pressure sensitive adhesive applications when statistically copolymerized with 2-ethylhexyl acrylate and 2-hydroxyethyl acrylate to high molecular weight (M_n > 450 kg mol^{-1}) via photoinitiation (**67**, Fig. 22) [71]. The T_g and adhesive properties could be modified by the amount of isosorbide incorporated, with higher isosorbide content resulting in higher peel strength, probe tack, and shear strength.

A regioselective, biocatalytic approach was recently demonstrated to synthesize isosorbide *endo*-/*exo*-methacrylates in high yield and purity using Lipozyme RM IM (*Rhizomucor miehei* lipase) (Fig. 23) [72]. The polymer T_g could be tuned depending on the structure and location (*endo* or *exo*) of the other substituent [dodecyl (**68**) = 54–66 °C; acetyl (**63**)/cyclohexyl (**69**) ≈ 130 °C; hydroxyl (**70**) = 167 °C]. The *endo*-**68** polymethacrylates exhibited a T_m at 83 °C while the corresponding *exo*-**68** polymers showed no melting transition, the difference likely being caused by the increased steric hinderance endured by substituents in the *endo* position as compared to the *exo* position. The overall synthetic approach enables straightforward, scalable synthesis of a range of monomers for tunable polymethacrylates suitable for the packaging and coating industries.

Isosorbide methacrylate *endo*-**70** can be grafted from or copolymerized with vinylsilylated clay (**71**) to form polymer–clay nanocomposites via FRP (**72**, Fig. 24) [73]. These polymer-grafted nanoparticles served as a compatibilizer to create robust composites for dental fillers, exhibiting increased thermal stability scaling with higher clay loadings (up to 5 wt%).

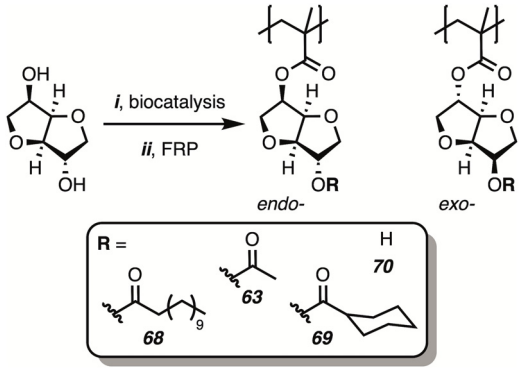

Fig. 23. Poly(methacrylates) from isosorbide with various ester protecting groups [72]. *Reagents and conditions*: (*i*) a) vinyl methacrylate or methacrylic anhydride, Lipozyme RM IM, MTBE, rt; b) **63**-anhydride/vinyl-**68**/chloro-**69**, NEt_3, MeCN, rt; (*ii*) AIBN, EtOAc/DMSO, 60 °C.

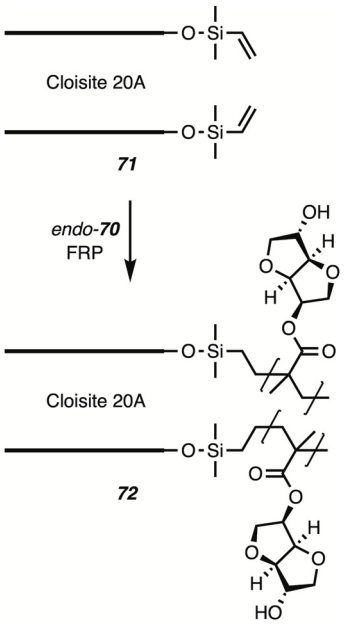

Fig. 24. Nanoclay composites (**72**) derived from vinylsilylated clay (Cloisite 20A) via poly(methacrylic isosorbide) grafting [73]. *Reagents and conditions*: AIBN, THF, 75 °C.

5.2. Thermosets from multi-functional isosorbides

Isosorbide bis-(meth)acrylates have also shown promise in thermosetting applications (Fig. 25). The bis-methacrylate **73** was shown to have low viscosity—eliminating the need for reactive diluents—and reach an extent of cure of 85% [74]. The resulting network has excellent thermal (T_g > 240 °C and T_d ~ 400 °C) and mechanical properties (modulus ~ 4 MPa; strength = 85 MPa), indicating that they have a higher temperature operating window than vinyl ester resins and similar performance to expensive, high-temperature epoxy resins often used in the aerospace industry. Furthermore, it was shown that UV-mediated photopolymerization of **53** or **73** could be crosslinked to high conversion [75]. Various formulations were prepared with the diacrylates of 1,4-butanediol (**74**) as well as telechelic poly(ethylene glycol) (**75**), poly(tetramethylene glycol) (**76**), and poly(caprolactone) (**77**). Consequently, the thermal and mechanical properties (T_g =

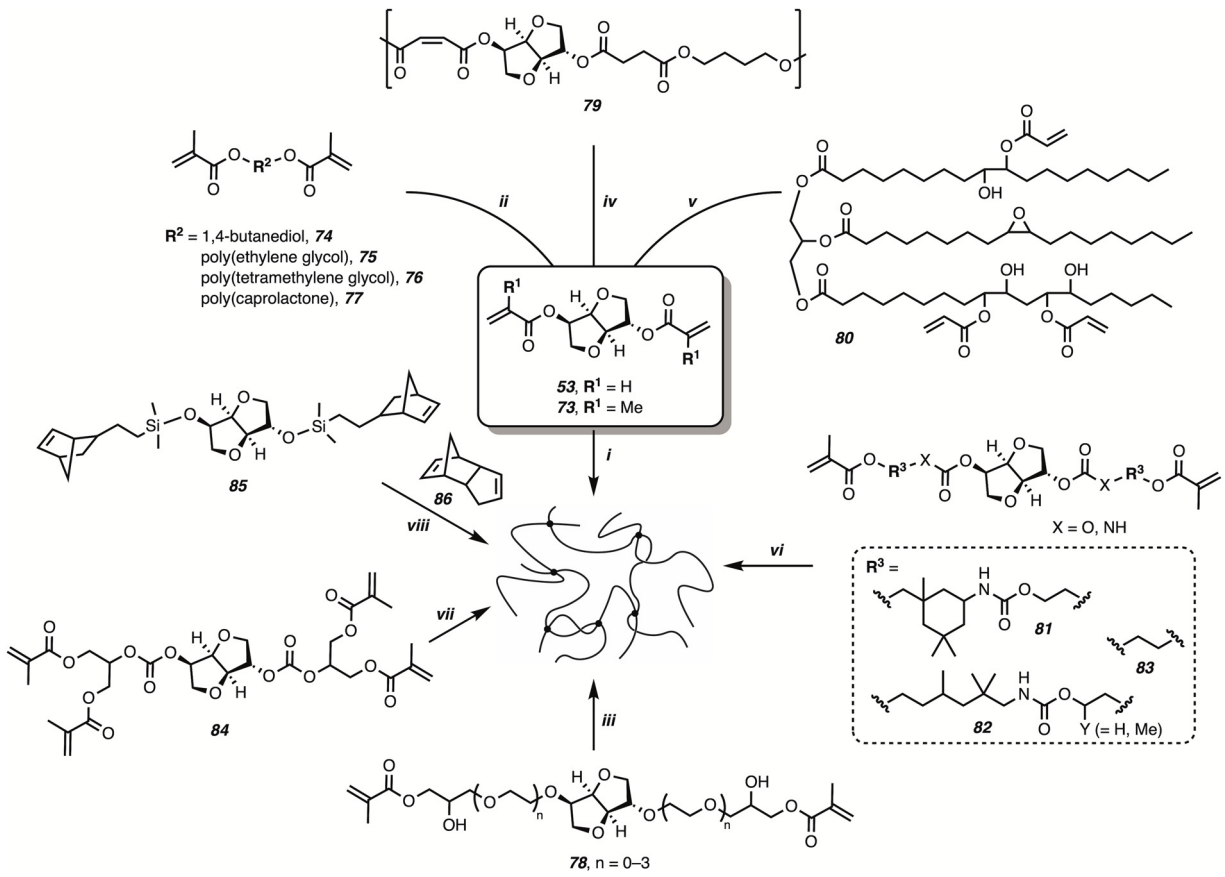

Fig. 25. Thermosetting polymers prepared from multifunctional isosorbides [74–82]. *Reagents and conditions*: (*i*) Trigonox 239A, CoNap, rt; post-cure 180 °C; (*ii*) Darocur 1173, UV, rt; (*iii*) TPO, UV, rt; (*iv*) BPO, 90 °C; post-cure 140 °C; (*v*) TBPB, 120 °C; post-cure 160 °C; (*vi*) CQ/DAB, blue LED, rt; (*vii*) DBTDL, 30–35 °C; (*viii*) Grubbs G2, 50–130 °C.

–62–36 °C; T_d = 270–350 °C; E' = 31–98 MPa) were tunable to fit a range of coatings applications. Additionally, isosorbide glycidyl methacrylate **78** (n = 0) was shown to be a good candidate for the replacement of bisphenol A glycidyl methacrylate, exhibiting a similar photopolymerization rate as well as comparable adhesion properties, compressive strength, and flexural strength [76].

Isosorbide bis-methacrylate **73** has been employed as a reactive diluent for crosslinking [77,78]. A bio-based, unsaturated polyester derived from isosorbide, ethylene glycol, succinic anhydride, and maleic anhydride (**79**, Fig. 25) was first synthesized in a two-step bulk polycondensation followed by thermal curing [77]. A range of chemical structures and T_g values could be obtained by small variations in the feed ratio (T_g = 57–84 °C; T_d ~ 250 °C; G' = 0.5–3.0 GPa). These thermosets have a high bio-content and exhibit comparable properties to their petroleum-derived counterparts. Likewise, copolymerization of **73** with acrylated-epoxidized soybean oil (**80**) afforded thermosets with improved mechanical properties compared to neat acrylated epoxidized soybean oil [78]. The isosorbide-based materials also showed superior processability to other soybean oil-based thermosets due to the lower viscosity of the reactive diluent, making them suitable for high-performance applications.

Other methacrylic isosorbide thermosets have been developed—including resins to replace bisphenol A in dental composites—by incorporating a spacer between isosorbide and the methacrylate to further influence the material properties. For example, a cyclohexyl-based diisocyanate was coupled to the isosorbide hydroxyl groups, followed by installation of hydroxyethylmethacrylate, which could then be photopolymerized (**81**, X = NH; Fig. 25) [79]. A reduction in the volume shrinkage of the dental composite, a decrease in water sorption, and reduced microleakage was observed in formulations containing isosorbide. Alkyl diisocyanates (**82**, X = NH) were also reported for this purpose, as well as direct urethane formation with isocyanoethylmethyacrylate (**83**, X = NH) [80]. Moreover, carbonate spacers were incorporated via carbonyldiimidazole functionalization of isosorbide and subsequent substitution with hydroxylethylmethacrylate (**83**, X = O) or 1,3-dimethacrylated glycerol (**84**). The resulting resins were targeted for use in dental applications, such that they would have specific flow properties that allowed the pre-polymerized resin to be able to be placed in a cavity and the post-polymerized resin to have the fracture resistance and mechanical stability required for filling. These isosorbide materials behaved similarly to bisphenol A-based dental materials, making them a promising, and potentially less harmful substitute for traditional dental composites. Longer alkyl spacers were synthesized by first functionalizing with oligomeric ethylene glycol (mono-, di-, or tri-ethylene glycol) and subsequently reacting with glycidyl methacrylate, which provides more flexibility (**78**, n = 1–3, respectively; Fig. 25) [81]. Maintaining low viscosity, high polymerizability, low shrinkage upon polymerization, an ability to adhere to tooth material, biocompatibility, and robust mechanical strength are requirements of dental monomers that are met with various methacrylic isosorbides [81].

Ring-opening polymerization (ROP) has been a scarcely used method for the incorporation of isosorbide into polymers. In one example, isosorbide bis-norbornenyldimethylsilane (**85**) and derived thermosets were prepared via ring-opening metathesis polymerization (ROMP) with dicyclopentadiene (**86**, Fig. 25) [82]. The flexibility of the C–Si segments allowed for more backbone flexibility while maintaining a high T_g (115 °C). Monomer **85** also increased the low temperature reactivity compared to conven-

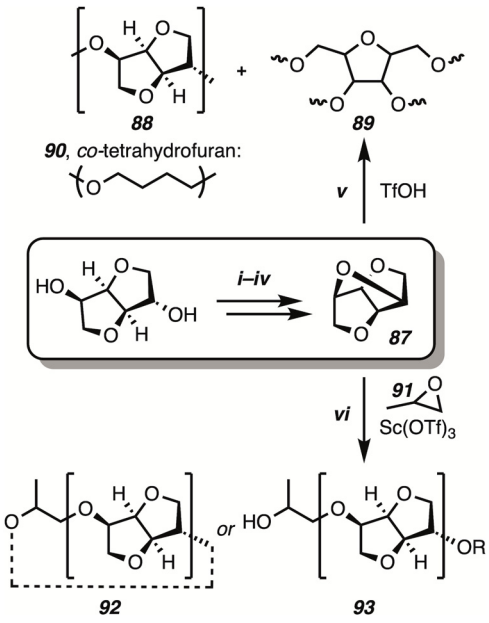

Fig. 26. Cationic ring-opening (co)polymerization of annulated isosorbide **87** [83–85]. *Reagents and conditions*: (*i*) vinyl acetate, Amano lipase (*Pseudomonas fluorescens*), acetone, rt; (*ii*) *p*-TsCl, pyridine, rt; (*iii*) K_2CO_3, MeOH, rt; (*iv*) KO^{t}Bu, THF, rt; (*v*) CH_2Cl_2, –30–4 °C; (*vi*) CH_2Cl_2 or MeCN, rt.

tional ROMP of dicyclopentadiene, allowing for a lower catalyst loading and curing temperature. Such characteristics are important for these materials to undergo self-healing without the need for high temperature processing.

5.3. Cationic polymerization of modified isosorbide monomers

Reactive derivatives of isosorbide have been prepared without installation of a polymerizable group such as a (meth)acrylate. One example involves an annulated derivative of isosorbide (**87**, Fig. 26) that upon treatment with triflic acid undergoes cationic homopolymerization, resulting in oligomers (**88**, DP∼5) and crosslinked material (**89**, Fig. 26) [83]. In a follow-up study, copolymerization with tetrahydrofuran was performed (**90**), reaching $M_n \approx 10$ kg mol^{-1} and containing 6–10 mol% of isosorbide [84]. More recently, the ring-opening mechanism of **87** was studied in depth, employing high-throughput screening and computation to understand the system [85]. In this work, molecular weights up to ∼10 kg mol^{-1} were achieved with methyl triflate initiation, although a lack of microstructural control was observed. A Lewis acid catalyst [$Sc(OTf)_3$], in conjunction with an epoxide initiator (**91**), enabled selectivity in ring opening of **87** to control the repeat unit structure. MALDI-TOF MS experiments of low molecular weight polyethers (M_n = 1 kg mol^{-1}) uncovered a significant amount of macrocyclization in nonpolar solvents (**92**) [versus no cyclization in polar solvents (**93**)]. It was hypothesized that nonpolar solvents are unable to stabilize the zwitterionic propagating chain, resulting in cyclic polymers. Thus, changing the solvent dielectric constant allowed for specific polymer architectures to be targeted.

Another cationic polymerization approach was recently reported involving use of a monomer prepared by modification of isosorbide to form a cyclic vinyl ether (**94**, Fig. 27) [86]. While homopolymerization of this derivative was unsuccessful due to the sterics around the propagating cationic site, copolymerization with isobutyl vinyl ether (**95**) was achieved (**96**). Interestingly, in the presence of various Lewis acids, the incorporation of **94** was hindered due to degenerative ring opening to a chiral furan analog, which is likely driven by aromatization. This side reaction

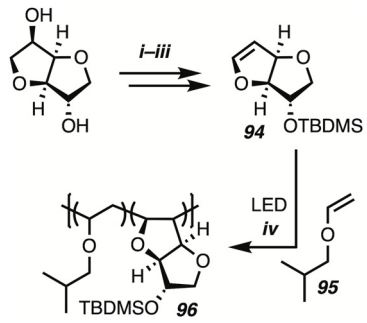

Fig. 27. Cationic copolymerization of cyclic vinyl ether **94** with isobutyl vinyl ether (**95**) [86]. *Reagents and conditions*: (*i*) $SOCl_2$, pyridine, 0–70 °C; (*ii*) KO^{t}Bu, THF, 0–80 °C; (*iii*) TBDMS-Cl, imidazole, CH_2Cl_2, 0 °C–rt; (*iv*) [TPP][BF_4], IBET, blue LED, CH_2Cl_2, rt.

was suppressed when a metal-free photoinitiated cationic copolymerization method was employed, affording copolymers with up to 42 mol% isosorbide. Incorporation of isosorbide increased the T_g of the polymers from –17.8 °C for the isobutyl vinyl ether homopolymer up to 6.6 °C. Molecular weights up to ∼25 kg mol^{-1} were achieved with dispersity values of 1.57–2.11. This work demonstrates the utility of **94** as a sustainable and value-added comonomer to tailor the properties of common poly(vinyl ethers), which are typically low T_g materials that have been used in industrial applications such as adhesives, coatings, and plasticizers.

6. Outlook and conclusion

Isosorbide has already proven to be a valuable renewable feedstock for a variety of polymers and applications, with further growth anticipated. Yet, there are critical areas where improvements can be realized. For example, the current yields of isosorbide production are quite low by industry standards. Furthermore, direct synthesis of isosorbide from lignocellulosic biomass, while an exciting revelation, needs refining. Increasing the yield and production capacity of isosorbide may considerably expand its usage as a versatile feedstock that can fulfill the need to develop sustainable materials, especially as the availability of petro-chemicals diminish over time [1]. Developing tailored polymer compositions and architectures necessary to modulate thermomechanical properties for an array of application spaces demand controlled polymerization methods under mild operating conditions. Additionally, a closed-loop life cycle (e.g. via degradation and/or recycling) is an essential component of next-generation polymers. Thus, creative synthetic polymer chemistry will be the driving force for future innovations and applications of sustainable polymers from isosorbide.

This trend article serves as an overview of the recent advances made in isosorbide production, polymerization, and applications. We have highlighted challenges and opportunities for the production of isosorbide as well as emerging polymerization strategies for isosorbide-based polymers. We are optimistic that these substantial efforts will lead to widespread usage of isosorbide-based polymers ranging from commodity to biomedical applications.

Declaration of Competing Interest

There are no conflicts of interest.

Acknowledgements

This work was supported by the National Science Foundation under the Center for Sustainable Polymers (CHE-1413862).

Please cite this article as: D.J. Saxon, A.M. Luke, H. Sajjad et al., Next-generation polymers: Isosorbide as a renewable alternative, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2019.101196

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Please cite this article as: D.J. Saxon, A.M. Luke, H. Sajjad et al., Next-generation polymers: Isosorbide as a renewable alternative, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2019.101196

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