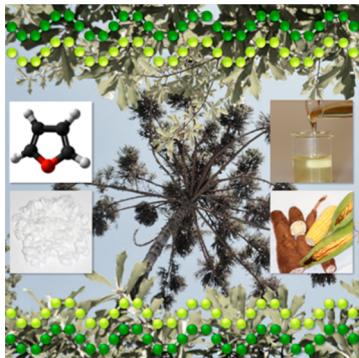


## Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides

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### 1. INTRODUCTION

The interest in polymers from renewable resources has been witnessing an incessant growth in both academia and industry, with these blooming activities covering a progressively wider domain of sources and approaches worldwide. The association of these innovative scientific and technological investigations with the need of introducing a growing dose of green chemistry connotations in their conception is opening the way to an all-inclusive sustainability for this new generation of polymers, which justifies their vision as macromolecular materials for the 21st century.

After the first comprehensive monograph dealing with these materials, published in 2008,<sup>1</sup> numerous reviews and books have appeared, mostly dealing with specific topics or brief analyses of the overall state of the art,<sup>2,3</sup> with a recent update,<sup>4</sup> which was devoted to highlighting trends, more than to detailing the numerous papers covering different aspects of the vast field. The purpose of the present review is different in the sense that it discusses trends related to the topics being investigated in our laboratory, by comparing our working

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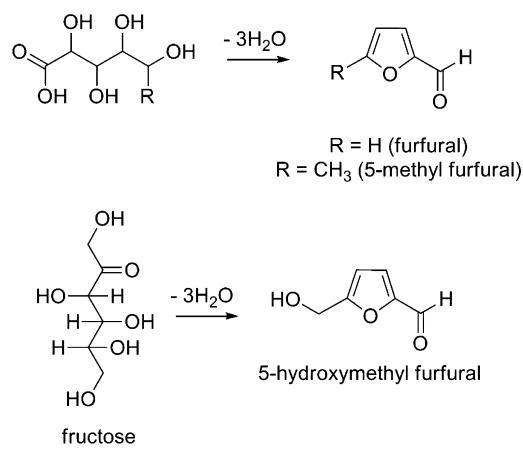
philosophy and ongoing strategies with those of colleagues working on the same research areas. These areas are (i) furan-based polymers, (ii) vegetable oils as a source of macromolecular materials, (iii) starch processing, and (iv) nanocellulose-based composite materials. The topics often overlap and include the use of natural rubber, another important natural polymer witnessing a revival of interest.

Some of the studies outlined here reflect work in progress, or recently finalized work, and are therefore reported for the first time. Others were published within the past several years. To set the stage, however, background notions on the specific topic are provided each time.

## 2. POLYMERS BASED ON FURAN MONOMERS AND FURAN CHEMISTRY

The rationale behind the growing interest in furan-based polymers stems from two complementary considerations, one based on sustainability, i.e., the fact that furan monomers are readily prepared from widely available renewable resources, and the other on the possibility of exploiting the peculiar chemical features associated with that heterocycle to prepare materials with original properties. The former aspect has been strengthened by introducing green chemistry connotations in the synthetic approaches to the polymerization processes. Reviews covering this realm span through the past two decades.<sup>5–10</sup> Since then, considerable progress has been made, which justifies the present update. Both the previously reviewed literature and the recent contributions discussed here are built on the same basic work premises, namely, the existence of two first-generation furan derivatives, furfural (F) and (hydroxymethyl)furfural (HMF), which are readily prepared from C5 and C6 sugars or polysaccharides, respectively. Scheme 1 shows the simplified pathways leading to F and HMF.

**Scheme 1.** Acid-Catalyzed Dehydration of Pentoses and Hexoses Leading to F and HMF

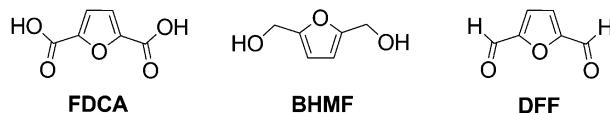


Whereas the former has been a chemical commodity for about a century, the latter has only recently reached that industrial status. The vast majority of furan monomers that were synthesized and polymerized or copolymerized<sup>5–10</sup> were prepared from either of those precursors, with F dominating in the past and HMF becoming a very important alternative counterpart, as detailed below.

The most relevant contributions in terms of novelty and potential applications are privileged here, rather than a list of

cursory mentions of the numerous publications dealing with a variety of systems, many of which bear, in our opinion, a modest impact. Two research strategies have emerged lately as the dominant trends in furan-based polymers, although of course other original approaches also receive some attention in the present review.

The first strategy has to do with polycondensation reactions involving mostly monomers related to 2,5-furandicarboxylic acid (FDCA) and, to a lesser extent, to 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-diformylfuran (DFF).



This situation is directly related to the extremely lively interest in the preparation of HMF as a promising platform chemical derived from renewable resources, more specifically from mono-, oligo-, or polysaccharides. The search for the most efficient catalytic systems and media has literally flooded the specialized literature in the past decade, as detailed in a very thorough review published in 2013, which also highlights the relevance of HMF as a precursor to monomers, fine chemicals, and fuel components.<sup>11</sup> This research and development ferment has continued unabated since that monograph, confirming the predictions put forward at the beginning of the third millennium concerning the importance of this chemical commodity within the future development of carbohydrate-based biorefineries.<sup>12</sup>

In the present context, the oxidation of HMF to its diacid FDCA and its reduction to the corresponding diol BHMF represent the most straightforward pathways to furan monomers suitable for polycondensation reactions, although many other such building blocks have also been prepared and polymerized, as amply discussed previously.<sup>5–10</sup>

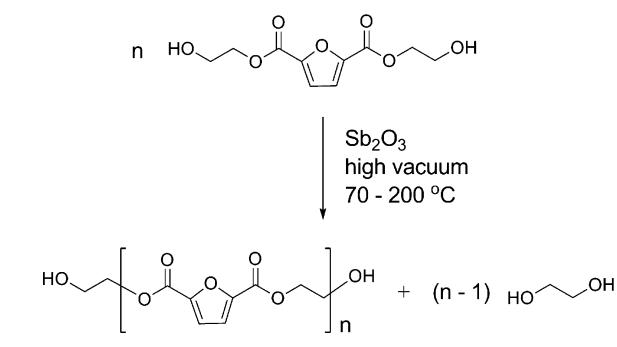
The second strategy concerns the application of the Diels–Alder (DA) reaction applied to the furan/maleimide diene/dienophile combination to the synthesis of novel thermally reversible polymers using a variety of approaches, as recently reviewed.<sup>13,14</sup> In the short lapse of time since the publication of that review, a considerable body of further investigations has appeared from both our and other laboratories, whose most relevant contributions are discussed here.

### 2.1. Polycondensation Systems

Research on furan polyesters was mostly focused on the use of difuran diacids prepared from 2-substituted furans,<sup>5–10</sup> before FDCA arrived on the scene as a consequence of the surge of interest in HMF.<sup>11</sup> The most extensively studied homologue of poly(2,5-furandicarboxylate)s is the heterocycle counterpart of poly(ethylene terephthalate) (PET), viz., poly(ethylene 2,5-furandicarboxylate) (PEF), because of its similarities to that commercially dominant polyester. Its synthesis by polytransesterification was first reported in 2009 using the approach shown in Scheme 2.<sup>15</sup> The idea of course was to prepare and characterize a polyester entirely based on renewable resources, which might display properties similar to those of PET and hence become its alternative sustainable material.

The initial characterization of PEF showed that the idea seemed promising<sup>8</sup> and therefore sparked intense and wide-ranging efforts in optimizing its synthesis and determining a wide range of properties and thus assessing its technical viability. A study of alternative synthetic processes was carried

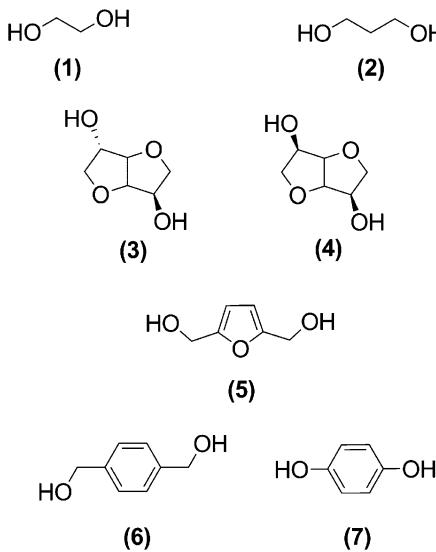
**Scheme 2. Synthesis of PEF via a Transesterification Mechanism**



out, coupled with an assessment of the mechanical properties.<sup>16,17</sup> The thermal properties were examined in terms of glass transition, melting and crystallization temperatures, and degradation threshold.<sup>15,17,18</sup> Its nonisothermal crystallization was the object of another thorough study.<sup>19</sup> Finally, the sorption behavior of PEF was investigated with water,<sup>20,21</sup> oxygen,<sup>22</sup> and carbon dioxide.<sup>23</sup> A process analysis was also conducted<sup>24</sup> to establish energy and greenhouse gas balances comparing PEF and PET production systems, which showed important advantages for the former polymer. On the basis of this comprehensive set of studies, it can be concluded that PEF has become the material to watch, since active industrial efforts are being devoted to its scale-up in view of its application for soft drink bottles, among other potential implementations, as a replacement for PET.

A number of diols other than ethylene glycol have been used to widen the range of furan polyesters based on FDCA. The first of these studies<sup>25</sup> covered a variety of structures, as shown in Scheme 3, and reported the structural characterization of the ensuing materials together with their thermal properties in terms of glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and the onset of degradation. Whereas the conventional aliphatic homologues **1** and **2** (Scheme 3), which gave the expected decrease in  $T_g$  associated with the progressively higher

**Scheme 3. Diols Used for the Synthesis of the Corresponding FDCA-Based Polyesters in the First of Such Studies<sup>25</sup>**



mobility arising from the corresponding increase in the number of methylene units in the diol structure, isosorbide **3** ( $T_g = 180$  °C) and isoidide **4** ( $T_g = 140$  °C) introduced a higher macromolecular stiffness induced by their molecular rigidity. The latter two polyesters were entirely based on renewable resources, since **3** and **4** are derived from sugars, and the same applies of course to the entire furan polyester prepared from FDCA and BHMF **5** ( $T_g = 87$  °C). Of the two aromatic diols **6** and **7**, the latter gave a material displaying a highly crystalline character, but was recalcitrant to dissolution, like the fully aromatic counterparts.

Further investigations have widened to a range of structures of these furan polyesters<sup>26–29</sup> and of their properties with a particular intent to compare them with those of the corresponding counterparts based on terephthalic acid. On the whole, the differences are minor, e.g., moderately lower values of  $T_g$  and  $T_m$  for the furan polyesters. Table 1 gives a selection of data related to furan aliphatic polyesters. Apart from the variations of certain values as a function of the specific structure, it is interesting to note that all these materials displayed very good thermal stability, mostly well above 300 °C.

One of the strongest potentials of these polyesters seems to lie in their improved barrier properties, with PEF exhibiting a water diffusion coefficient 5 times lower than that of PET, a 10 times lower oxygen permeability, and a 30-fold reduction in the carbon dioxide sorption rate, despite its higher free volume.<sup>20–23</sup> These reductions are attributed to fundamental differences in segmental mobility due to the higher rigidity of the furan ring. Indeed, the nonlinear axis of ring rotation coupled with the dipolarity of the heterocycle in PEF significantly hinders the furan ring-flipping mechanism. This peculiarity could make the furan-based polyesters powerful and innovative materials for food packaging applications.

The homopolymerization studies have been extended to copolymerizations, in which two diols or a second diacid, other than FDCA, are employed. The first and simplest system concerned the random copolymerization of FDCA with a mixture of ethylene glycol and 1,3-propanediol.<sup>25</sup> A more systematic study<sup>30</sup> indicated that the lower reactivity of ethylene glycol toward FDCA, as compared with 1,4-butanediol, directly influenced the relative diol incorporation and hence the final properties of the copolymers.

The use of an aliphatic diacid as the second comonomer has been the subject of investigations by Dubois's group. The first such study described the synthesis and characterization of fully biobased poly(butylene succinate-*co*-butylene furandicarboxylate)s,<sup>31</sup> followed by a similar approach for preparing poly(butylene adipate-*co*-butylene 2,5-furandicarboxylate)s,<sup>32</sup> in which the important issue of the purity of FDCA (often questioned and assumed to be the source of coloring in the ensuing polymers) was tackled with an original alternative purification process. These two copolymer families were shown to afford tunable properties as a function of the comonomer composition, ranging from crystalline polymers, possessing a good tensile modulus (360–1800 MPa) and strength (20–35 MPa), to essentially amorphous polymers with a low  $T_g$  and very high elongation at break (about 600%), useful as thermoplastics, elastomers, or impact modifiers. The copolyesterification system ethylene glycol/FDCA/succinic acid was also studied,<sup>33</sup> and it showed that this material was a suitable alternative to poly(ethylene tereph-

**Table 1. Properties of Furan Aliphatic Polyesters**

ref	$M_n$ ( $\times 10^3$ )	$M_w$ ( $\times 10^3$ )	$\eta_{sp}$ (dL g $^{-1}$ )	$T_c$ (°C)	$T_g$ (°C)	$T_m$ (°C)	$T_d$ (°C)	Young's modulus (MPa)	$\sigma_{max}$ (MPa)	$\epsilon_{break}$ (%)
PEF										
9	8.0	15.2			77	214				
8	22.4	44.5		165	80	215	300			
18	23			156	85	170	332			
19	105	252	1.20		90	210	389	2070	66.7	4.2
				Poly-1,3-propyl						
9	10.1	16.3			40	171				
18	15			102	39	150	335			
8	21.6	27.6		127	50	174	295			
19	60.2	89.8	1.21		58		375	1550	68.2	46
				Poly-1,4-butyl						
9	11.8	21.2			36	177				
19	17.8	42.3	1.41		31	172	373	1110	19.8	2.8
21	23.2	65			39	172		959	31.8	1055
18	60			90	31	170	338			
				Poly-1,6-hexyl						
19	32.1	66.7	1.04		28	148	375	493	35.5	210
				Poly-1,8-octyl						
19	20.7	47.5	0.69		22	149	375	340	20.3	15

thalate-*co*-ethylene succinate) (PETs), a well-known PET copolymer.

An interesting recent study looked into a family of copolymers synthesized from terephthalic acid and FDCA on one hand and ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and 1,8-octanediol on the other hand, via direct esterification using tetrabutyl titanate (TBT) as the catalyst.<sup>34</sup> This variety of combinations and compositions provided a useful set of data related to properties such as  $T_g$ , onset of thermal degradation, and mechanical features. In a similar vein, comparisons were established between succinic acid/1,4-butanediol/FDCA/isosorbide copolymers and counterparts prepared with the same two first monomers and terephthalic acid.<sup>35</sup> Again, the incorporation of isosorbide units in the copolymers produced an increase in the glass transition temperature, and their mechanical properties were affected by the degree of crystallinity, with an important increase in the elongation at break related to the increase of the amorphous character.

The introduction of hydroxyl moieties in furan polyesters, e.g., by using glycerol as a comonomer, and their subsequent crosslinking with a diisocyanate produced interesting biobased coating resins.<sup>36</sup>

The use of the furandiol BHMF has been the object of the preparation of aliphatic polyesters through enzymatic catalysis.<sup>37</sup>

Some research has recently been published dealing with furan polyesteramides. Triki et al.<sup>38</sup> prepared amorphous polyesteramides by the melt copolycondensation of FDCA with hexamethylenediamine and ethylene glycol, giving materials with  $T_g$  values increasing with increasing amide content. Wilsens et al.<sup>39</sup> compared the properties of some polyesteramides containing isophthalic, terephthalic, or furandicarboxylic units and found that the presence of the furan ring perturbed the formation of intermolecular hydrogen bonds, resulting in a lowering of  $T_g$  and  $T_m$  as compared with those of the analogous materials bearing the aromatic rings.

Apart from the comprehensive investigation on furan polyamides based on difuran diacid monomers,<sup>5–10</sup> work on homologues based on FDCA has not progressed significantly

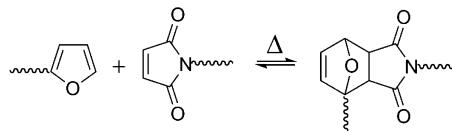
since a pioneering study dating back to 25 years ago.<sup>40</sup> In 2009, FDCA/aliphatic polyesters and polyamides were synthesized and briefly characterized,<sup>41</sup> but regrettably this interesting approach was not pursued. This family of furan polymers clearly deserves more attention, given the present status of FDCA as a commodity chemical, as pointed out by van Es<sup>42</sup> in a stimulating review on the use of rigid biobased building blocks as promising monomers.

## 2.2. Furan Diels–Alder Reaction Applied to the Synthesis of Thermally Reversible Macromolecular Architectures

Considerable interest has been placed in the past decade on the application of the thermoreversible furan/maleimide DA reaction for the synthesis of macromolecular materials with useful properties, including self-mendability, thermal de-cross-linking, and recyclability, as recently reviewed.<sup>13,14</sup> This trend is accelerating, as discussed here for the latest contributions. In all these systems, both the polycondensation steps and their reverse counterparts are based on the actual DA coupling–uncoupling equilibrium, which can be shifted within a mild range of temperatures, viz., around 60 °C for the forward reaction (polymerization through adduct formation) and 110 °C for the depolymerization by adduct opening, as shown in Scheme 4. The click chemistry connotation of these interactions provides an additional positive aspect in terms of their clean behavior, even after repeated cycles.

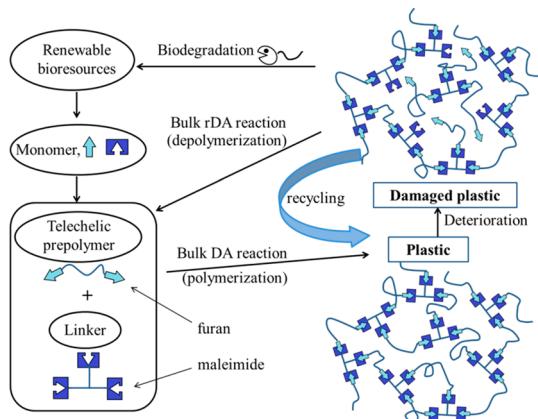
This reaction is not marred by side reactions, and no other degradation is envisaged within that temperature range. Moreover, even if these reactions produce two different stereoisomers (*exo* and *endo*), their relative abundance is not

### Scheme 4. DA Equilibrium Governing the Polycondensations of Monomers Bearing Furan and Maleimide Moieties



relevant in the polymer context, since both play the same role as chain links between monomer units.

The most salient feature here is of course the thermoreversible character of this DA reaction, which provides the ensuing materials with limitless possibilities, such as removable thermosets, thermoresponsive optical polymers, nanoscale probe lithography and data storage, modular polymeric color switches, and smart coatings.<sup>13,14</sup> The unique self-healing and recyclability properties of these systems are illustrated in Figure 1.



**Figure 1.** Schematic representation of recyclable and self-mendable bio-based polymer systems.

Polyesters were prepared by coupling bis(hydroxymethyl)furan with succinic acid, and their reversible DA crosslinking with different bismaleimides (BMIs) was studied,<sup>43,44</sup> as shown in Scheme 5. Variable amounts and different types of BMIs led to materials displaying tunable mechanical properties with excellent self-healing ability. Interestingly, mendability is

achievable even if furan moieties are present in modest proportions, as in the case of chain ends, as shown by a study in which recyclable plastics were prepared by the synthesis of furyl telechelic poly(lactic acid) and poly(butylene sebacate) crosslinked with bis- and trismaleimides.<sup>45</sup>

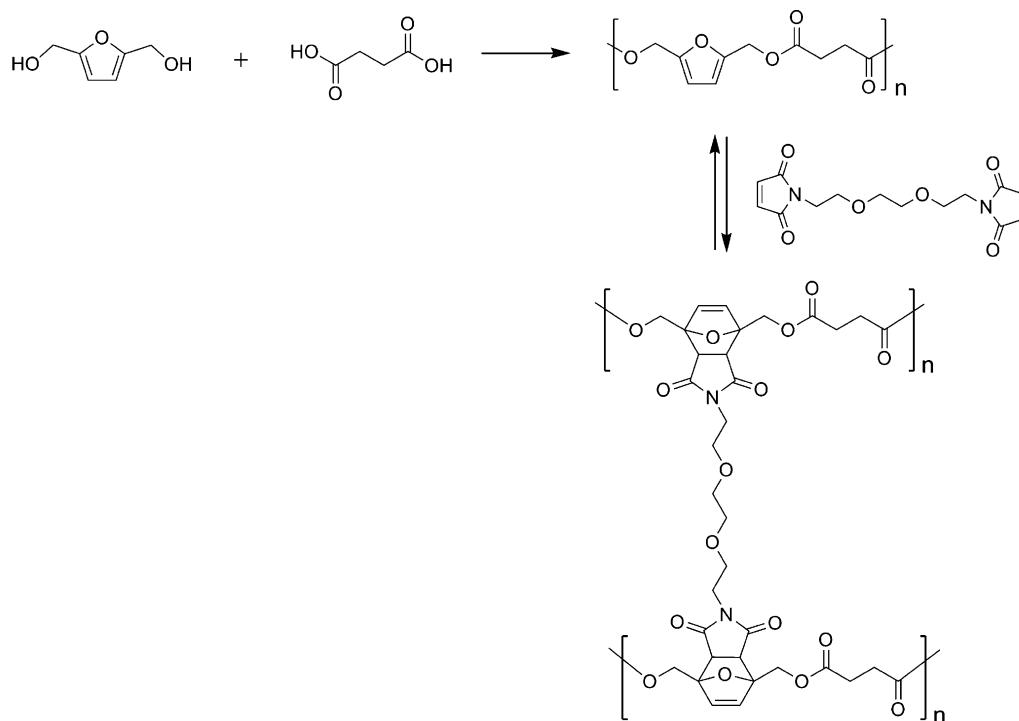
Gandini et al.<sup>46,47</sup> prepared biobased polyesters by the DA reaction between BMIs and novel monomers based on vegetable oils bearing a furan ring appended through thiol–ene click chemistry.

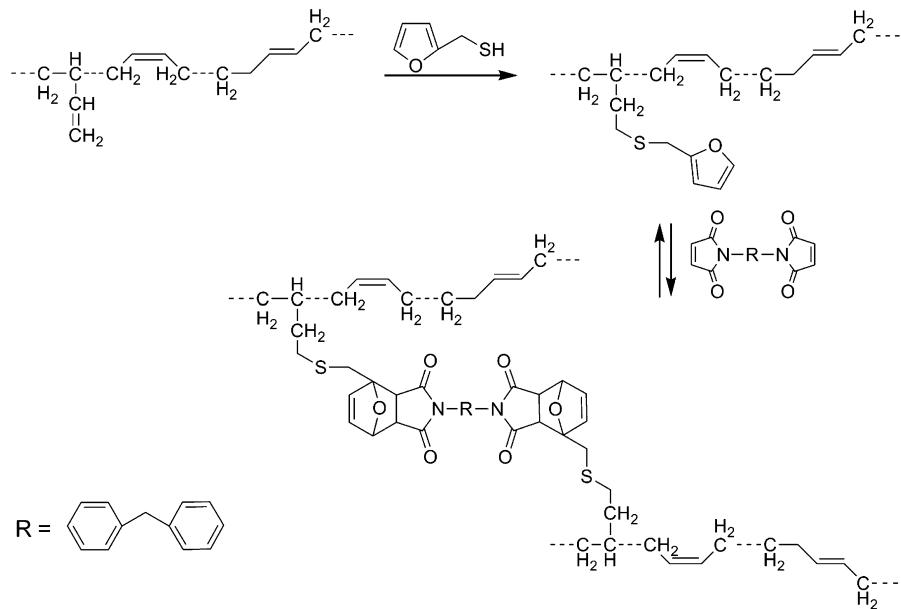
The application of these principles has proved very useful in processing, reshaping, and thermally self-repairing polyurethanes, thus extending their service life.<sup>48,49</sup> Rivero et al.<sup>50</sup> prepared tough, flexible, and transparent polyurethane networks with healing capability at mild temperature conditions. Remendability was achieved by combining the occurrence of two processes at 50 °C, namely, a fast shape memory effect that brought the free furan and maleimide moieties together, after which a progressive DA reaction could re-form the covalent bonds on a longer time scale.

A further important advance is the recent research into hydrogels prepared by the DA reaction, in which water-soluble polyacrylates bearing pendant furan and maleimide moieties,<sup>51</sup> furfural-modified gelatin,<sup>52</sup> and chitosan<sup>53,54</sup> were crosslinked in an aqueous medium. These materials were fully characterized and showed promising properties in terms of applications, among others, in the biomedical realm.

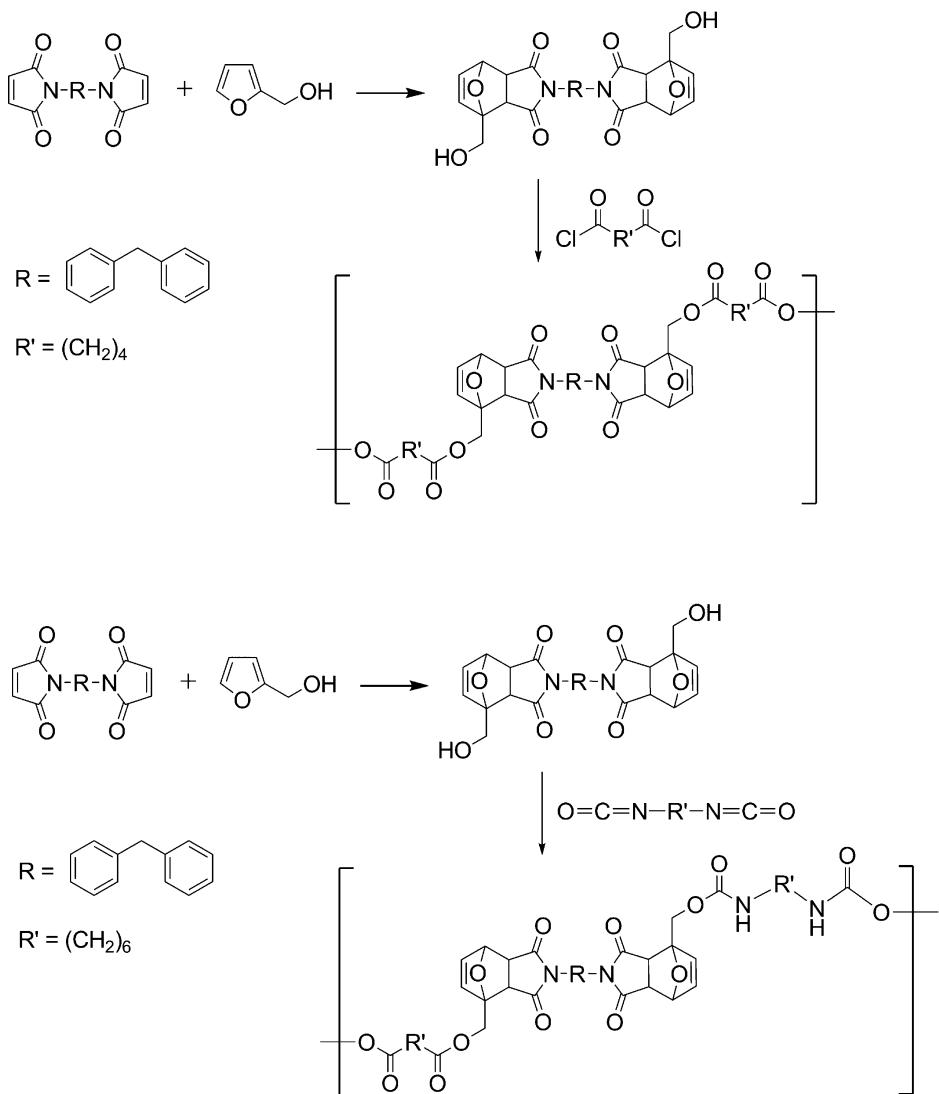
Elastomers based on natural rubber, polybutadiene, and other synthetic rubbers used in the preparation of tires and other elastomeric artifacts are normally crosslinked with sulfur to attain their required properties. At the end of their lifetime, such materials represent one of the largest sources of waste and disposal problems because the crosslinking reaction between the elastomer molecules is not reversible through viable processes. A new strategy to synthesize thermally reversible crosslinked elastomers was recently proposed and successfully

**Scheme 5. Synthesis of Poly(2,5-furandimethylene succinate) and Its Thermally Reversible DA Crosslinking with a BMI<sup>43,44</sup>**

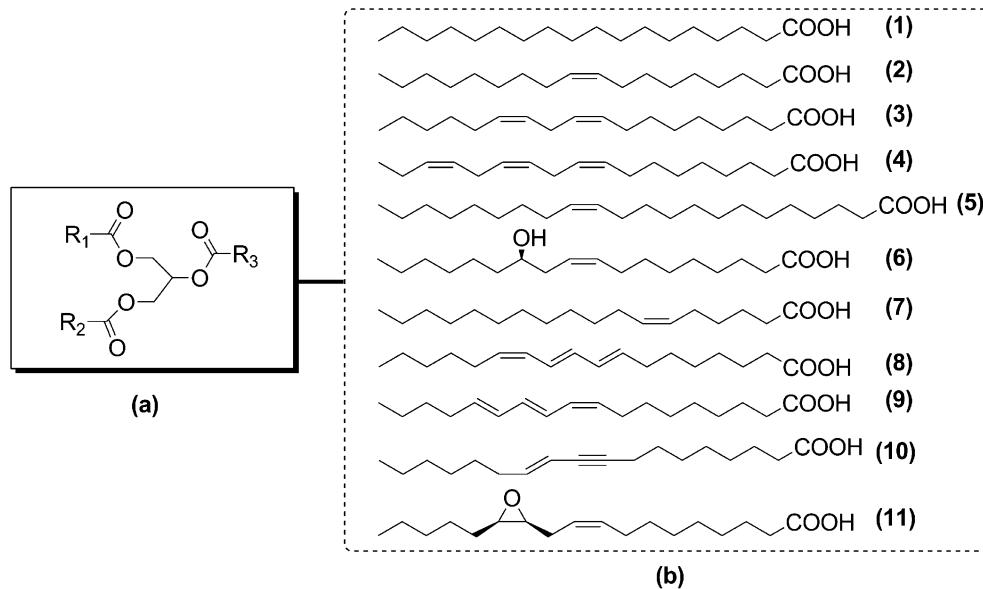


Scheme 6. Synthesis of Recyclable PBD via the DA/Retro-DA Reaction<sup>55</sup>

Scheme 7. Synthesis of a Polyester and a Polyurethane Using a Diol Incorporating a DA Adduct



**Scheme 8.** (a) Schematic Representation of a General Triglyceride and (b) the Most Common Fatty Acids That Constitute Them: (1) Stearic Acid, (2) Oleic Acid, (3) Linoleic Acid, (4) Linolenic Acid, (5) Erucic Acid, (6) Ricinoleic Acid, (7) Petroselinic Acid, (8) Calendic Acid, (9)  $\alpha$ -Eleostearic Acid, (10) Santalbic Acid, and (11) Vernolic Acid



tested.<sup>55</sup> The method involved the incorporation of furan heterocycles (Fu) as side groups to poly(1,2-butadiene) (PBD) using the thiol–ene reaction of furfuryl thiol (FT) with some of the PBD unsaturations and the subsequent DA crosslinking of the ensuing PBD–Fu with an aromatic BMI, as shown in Scheme 6. The ensuing elastomeric network was de-crosslinked through the retro-DA reaction at 110 °C. The thermoreversibility was successfully tested in four heating–cooling cycles, with no degradation of the material. This study opens the way to a more systematic investigation involving different elastomeric structures, including natural rubber.

Other examples of original exploitations of the DA/retro-DA principle applied to polymer synthesis are given in other sections of this review, namely, with vegetable oils and starch.

A novel approach within the exploitation of these features is put forward here, based on a different working hypothesis, which calls upon standard polymerizations of monomers incorporating a DA adduct within their structure and the subsequent exploitation of these adducts inside the ensuing macromolecules for the synthesis of a wide variety of copolymer structures.<sup>56</sup> The principle of this strategy rests on the basic properties illustrated in Scheme 4, but applied here with a very different scope, namely, the heating of a solution containing *two or more* different DA polymers to induce their partial or total depolymerization through the retro-DA reaction, and its subsequent cooling to promote the DA couplings of these fragments, thus generating copolymers whose composition and extent of random or blocky nature can be readily manipulated. An example of this process is the use of a diol with a central DA adduct as a comonomer for the synthesis of a polyester and a polyurethane (Scheme 7).

When these two polymers are heated together, they will be spliced through the retro-DA reaction of the adducts incorporated into the original diol, and the ensuing fragments will then couple statistically with each other upon cooling to form ester–urethane copolymer architectures. Apart from the variable based on the actual composition of the initial polymer mixture, which will determine the corresponding composition

of the copolymer, the temperature and duration of the retro-DA process will determine the extent of the depolymerizations and hence the extent of the splicing, so that the subsequent recombination through DA coupling upon cooling can be made to generate copolymers with a predetermined choice of random-to-block features. Of course, the other comonomers in these step-growth reactions can also incorporate a DA adduct, making the reshuffling more thorough.

The wide-ranging implications of this approach are obvious, since the combinations are unlimited in terms of both the chemical nature of the specific moiety involved (ester, amide, urethane, ether, epoxide, etc.) and the number of polymers to be mixed to prepare copolymers, terpolymers, etc. In addition to all these manipulations of polycondensates, polymers prepared from chain-growth reactions, e.g., of divinyl or diacrylic monomers incorporating DA adducts, can also be used to generate the corresponding copolymers, whose architecture can be modified through the use of monofunctional comonomers, to give branched structures rather than networks.

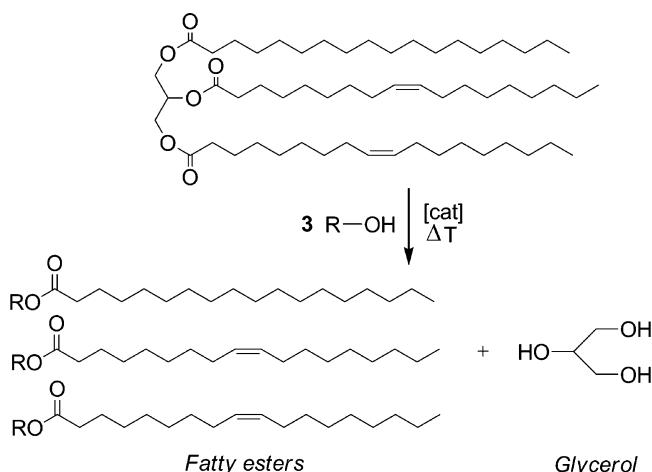
### 3. GLYCEROL AND PLANT OILS AND THEIR FATTY ACIDS IN POLYMER SYNTHESIS

The high number of different vegetable oils (VOs) that are naturally available and the vast range of possibilities that they open to the chemical, fuel, and materials industries, associated with their democratic geographic distribution, put them today in a prominent position among other renewable resources. Formed photosynthetically to serve as energy storage in the seeds of plants, VOs consist of triglycerides, i.e., saturated and unsaturated fatty acid esters of glycerol (Scheme 8).

The main composition of each vegetable oil is highly related to the species from where it is extracted, which determines its physical and chemical properties and, hence, its possible applications as renewable feedstock. The number of double bonds, as well as their positions within the aliphatic chain, also strongly affects the oil properties.<sup>57</sup>

Apart from the food industry, considering the current applications of VOs, the most relevant is undoubtedly the production of *biodiesel*, i.e., monoalkyl ester molecules that act exactly like the common petroleum-based fuel *petrodiesel*. Starting from a crude VO, the synthesis of biodiesel basically consists in cleaving the triglyceride structure by transesterification with an alcohol, normally methanol or ethanol, to generate the corresponding esters, with glycerol being formed as the byproduct (**Scheme 9**).

**Scheme 9.** Chemical Conversion of a Triglyceride into the Corresponding Fatty Acids by Transesterification

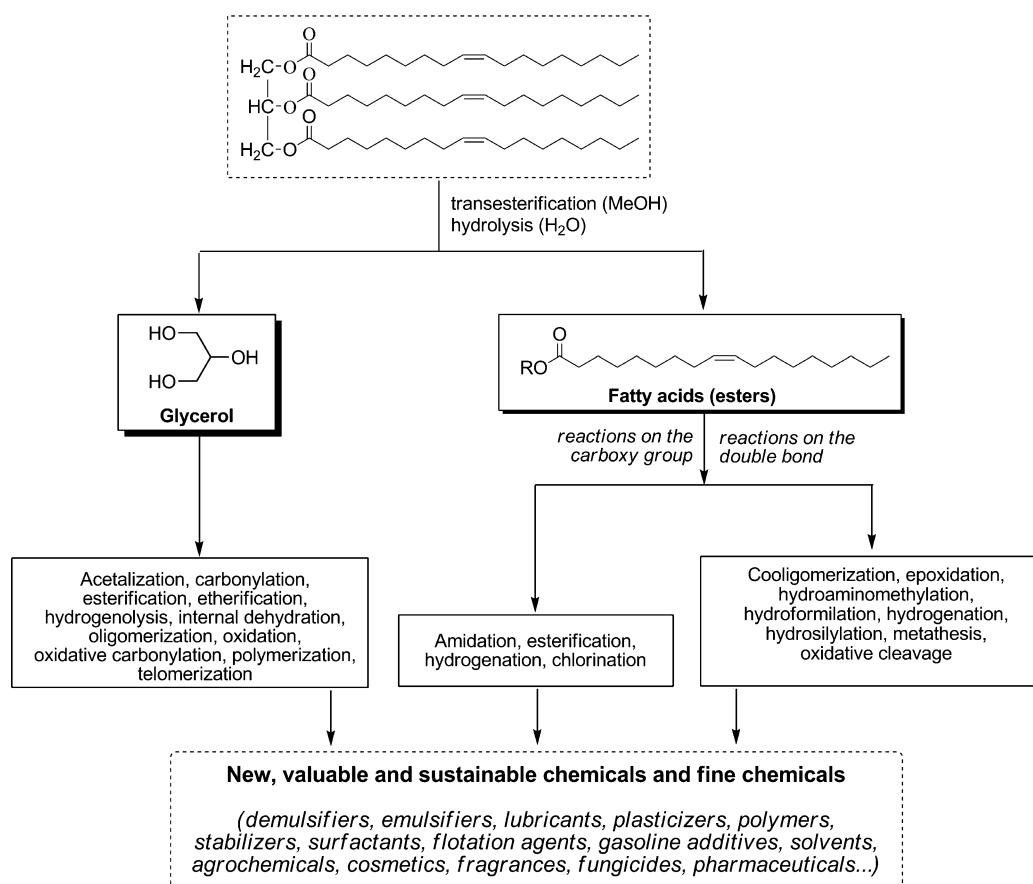


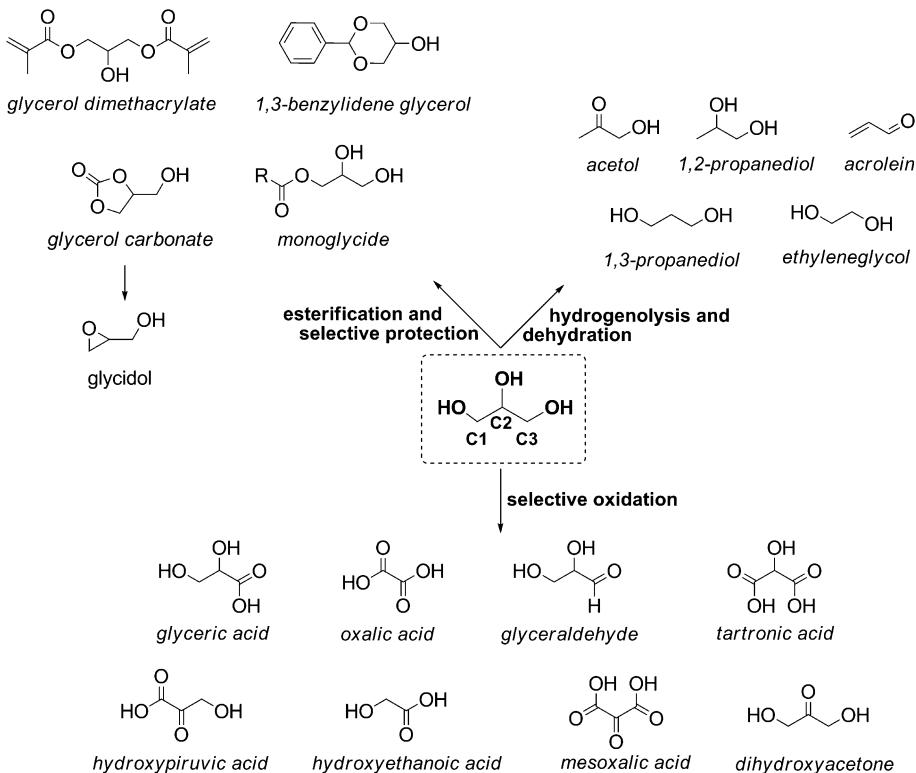
Because of the recent growing demand for biodiesel as partial replacement for fossil fuels, together with the need to feed an increasing global population, the world production of major oilseeds in the past decade went from 332 to 529 Mt and the harvested area from 186 to 234 Ma.<sup>57–59</sup>

The beauty in VO chemistry goes far beyond biodiesel production. Both fatty acids and glycerol have great potential to be exploited as raw materials for many other applications, such as the utilization of fatty acid methyl esters (FAMEs) as lubricants, stabilizers, surfactants, pharmaceuticals, and polymers. Glycerol is traditionally applied in foods, pharmaceuticals, and cosmetics, but new alternative routes are being intensively investigated, aiming to add value to the increasing excess of glycerol generated in biodiesel production.

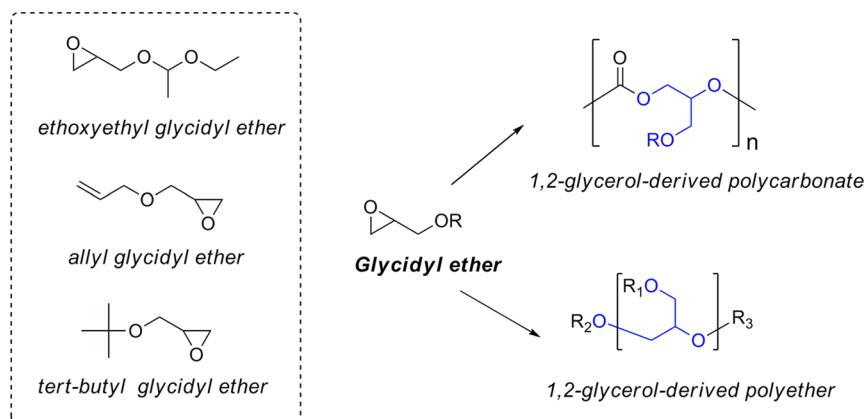
Behr and Gomes<sup>58</sup> described in detail some specific practical examples of the most important possible applications highlighted in **Scheme 10**. The majority of reactions performed with fatty acids have as the main goal their functionalization, mostly through the unsaturations along their aliphatic chains, and include oxidation, hydroformylation, hydroaminomethylation, and hydrovinylation. The metathesis reaction has also been extensively used for the preparation of VO derivatives, mainly to be applied in polymer synthesis. The major reactions of glycerol involve (i) addition of a reactive alkene to form glycerol alkyl ethers, (ii) oligomerization into di-, tri-, or even oligoglycerols, (iii) oxidation to generate aldehydes, ketones, and carboxylic acids, and (iv) action as a nucleophile in atom-efficient and transition-metal-catalyzed telomerization reaction, i.e., the oligomerization of dienes.

**Scheme 10.** Overview of Possible Reactions of VOs and Their Derivatives<sup>58</sup>



Scheme 11. Conversion of Glycerol into Value-Added Compounds via Different Catalytic Pathways<sup>61</sup>

Scheme 12. Glycerol-Based Polycarbonates and Polyethers Prepared from Glycerol-Ether Derivatives



The chemical composition and the oligomeric character of plant oils strongly favor the development of novel biobased macromolecular materials with different properties. Given the uneven composition of crude VOs, it is not possible to set a fine correlation between the material properties and these mixed structures when they are used as pristine precursors, as opposed to conventional petrochemical-based polymers.<sup>60</sup> The present section critically discusses the most recent contributions to the search of new routes to prepare polymeric materials starting from glycerol and VOs.

### 3.1. Polymers from Glycerol

The enormous increase in glycerol production, associated with the development of the biodiesel industry in the past few decades, has produced a drastic decrease in its market value and stimulated a vast array of academic and industrial investigations related to novel pathways of valorization.

As depicted in Scheme 11, the multifunctional character of glycerol makes it susceptible to a large number of chemical transformations such as selective oxidation, hydrogenolysis and dehydration, selective protection, and esterification, i.e. processes that offer many possibilities for the synthesis of interesting building blocks for the preparation of both chemicals and polymers.<sup>61</sup>

Despite their relevance, the glycerol-derived chemicals will not be treated here, and the interested reader will find ample information in recent monographs.<sup>61–67</sup>

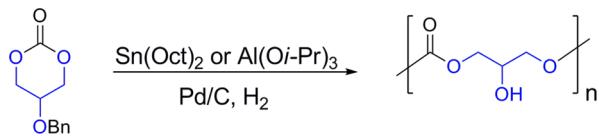
The most common glycerol-derived polymers can be roughly split into three categories according to their structural characteristics.

The first and most important group relates to the linear 1,2-linked glycerol polymers,<sup>61</sup> in which the glycerol units are positioned within the polymer main chain in such a way that they are linked by the oxygen atoms directly attached to the C1

and C2 carbon atoms (**Scheme 12**), leaving pendant free hydroxyl ( $-\text{CH}_2\text{OH}$ ) or aryl-protected ( $-\text{CH}_2\text{OR}$ ) groups. The final products, often polyethers and polycarbonates, are mostly obtained from glycidyl ether derivatives obtained from glycidol, which in turn is derived from glycerol carbonate (**Scheme 11**). Both polyethers and polycarbonates exhibit excellent biocompatibility, the latter being readily biodegradable due to the facile breakage of the carbonate bonds under mild conditions.

The second category consists of linear 1,3-linked glycerol polymers<sup>61</sup> whose structure is homologous to that of the former family, except for the 1,3-conformation of the repeat units. These materials are polyesters generated by the classical polycondensation of glycerol with diacids, or polycarbonates formed by ring-opening mechanisms, as illustrated in **Scheme 13**.

**Scheme 13. Illustrative Example of the Synthesis of Polycarbonates via the Ring-Opening Reaction of a Glycerol Derivative<sup>61,68</sup>**



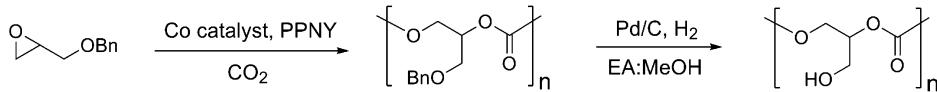
The third category includes dendritic and hyperbranched glycerol polymers, a very interesting and versatile class of materials that exhibit useful characteristics such as high surface area-to-volume ratio, numerous end groups for further functionalization, and the aptitude of encapsulating small molecules.<sup>61</sup>

Geschwind and Frey<sup>69</sup> described a two-step synthesis of poly(1,2-glycerol carbonate)s starting from the preparation of protected copolymers with  $M_n$  values ranging from 16 to 25 kDa by the combination of ethoxyethyl glycidyl ether or benzyl glycidyl ether with carbon dioxide at room temperature in the presence of a catalytic system based on  $\text{ZnEt}_2$  and pyrogallol (1,2,3-trihydroxybenzene). The second step involved the removal of the pendant protecting groups via acidic cleavage or hydrogenation, with very little chain degradation.

Equally innovative is the work described in the same year by Zhang and Grinstaff,<sup>70</sup> also for the preparation of poly(1,2-glycerol carbonate)s via the ring-opening copolymerization of *rac*/(*R*)-benzyl glycidyl ether with  $\text{CO}_2$  using cobalt complexes (**Scheme 14**).

A preliminary study described the direct microwave irradiation of glycerol carbonate for the preparation of poly(1,3-glycerol ether)s.<sup>71</sup> This one-pot process led to the formation and ready polymerization of glycidol under mild conditions compared to the polyetherification reaction, which often involves high temperatures, i.e., high energetic costs, and basic conditions. Although only low-DP (degree of polymerization) materials were obtained, this original approach deserves further studies.

**Scheme 14. Synthesis of Poly(benzyl 1,2-glycerol carbonate)s with Cobalt Catalysts<sup>70</sup>**



The synthesis of branched and crosslinked poly(1,3-glycerol ether)s was elegantly conducted from glycerol diglycidyl ether and propylene glycol diglycidyl ether with three different dithiols, based on the high susceptibility to polyaddition reactions between thiols and epoxide groups, even at ambient or subambient temperatures.<sup>72</sup> The ensuing materials were biodegradable, with glass transition temperatures ranging from 33 to 59 °C and thermal degradation in the range from 230 to 290 °C.

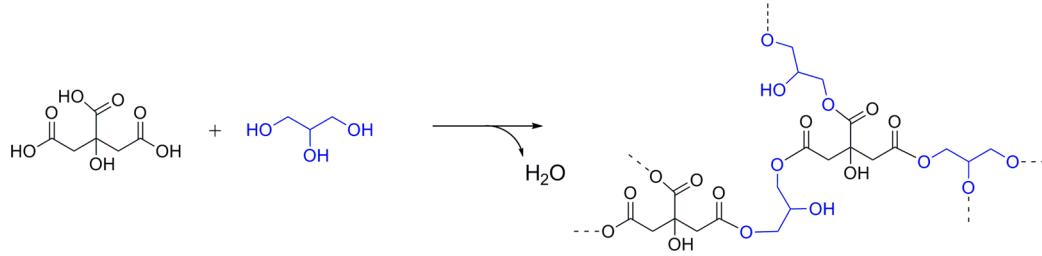
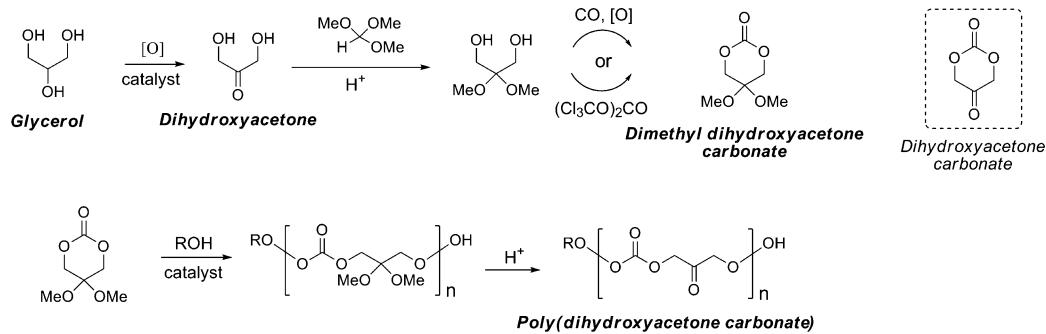
The synthesis of glycerol-based epoxy resins was first described by Karak et al.,<sup>73</sup> starting from glycerol, bisphenol A, and epichlorohydrin under basic conditions, with excellent yields (95–97%). The materials exhibited good toughness and thermostability up to 268 °C. Glycerol-based thermosetting resins were also reported using two renewable monomers, i.e., glycerol and lactic acid.<sup>74</sup> In this study, lactic acid was first reacted with glycerol by direct condensation, and the resulting branched molecule was treated with methacrylic anhydride to form methacrylate-functionalized glycerol–lactic acid resins. The resins were cured using 2 wt % dibenzoyl peroxide as the initiator, and the final materials exhibited good thermal and mechanical properties. Poly(glycerol methacrylate)s were also synthesized as linear and star-shaped materials to be further modified with aliphatic amines, for potential applications as drug-delivering substrates.<sup>75</sup>

The preparation of hyperbranched materials has also been investigated. Glycerol/citric acid-based polymers were recently reported<sup>76</sup> as a simple and effective  $\text{A}_3 + \text{B}_3$  melt polycondensation system in the absence of catalysts (**Scheme 15**). The authors stated that the main characteristics of the materials, such as physical properties, degree of branching, and biodegradability, could be easily tuned by varying the amounts of inserted glycerol, and their potential for drug delivery was proven by the successful incorporation of an antibiotic (gentamicin) into the polymer.

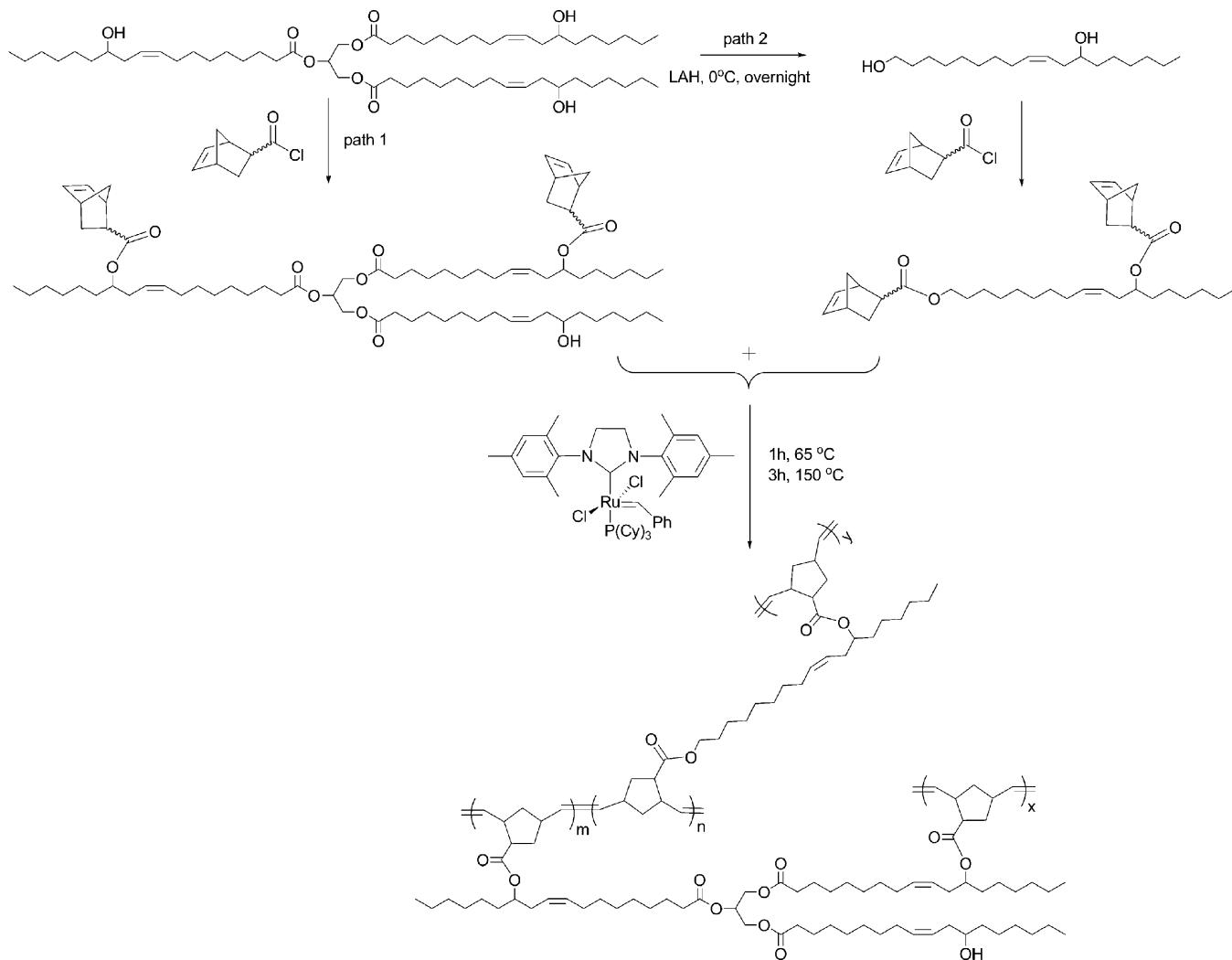
Wyatt and Strahan<sup>77</sup> synthesized and evaluated the degree of branching of glycerol-based polyesters accessed by the polycondensation of glycerol with diacids with varying carbon chain lengths (succinic, glutaric, or azelaic acids) in the presence of a Lewis acid (dibutyltin oxide) catalyst. A few years later, a similar but more detailed study corroborated this interesting approach by describing the preparation of hyperbranched glycerol adipic acid polyesters.<sup>78</sup>

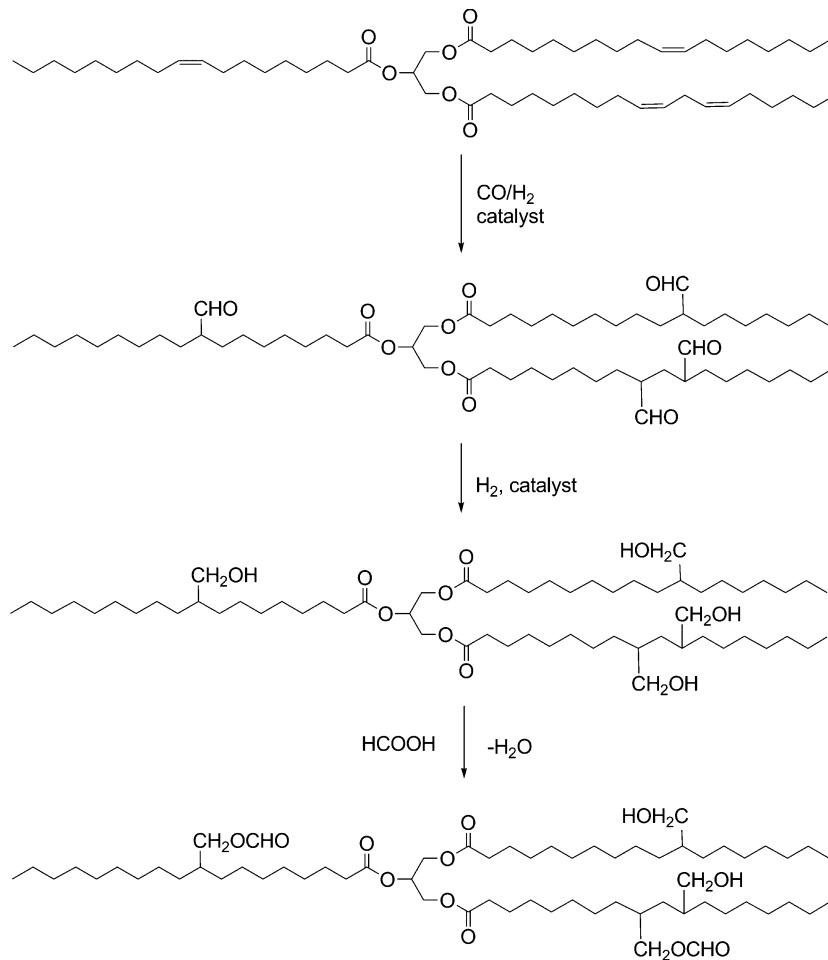
Another important class of glycerol-derived polymers is based on dihydroxyacetone (**Scheme 11**). Waymouth and co-workers<sup>79</sup> worked on the ring-opening polymerization of dimethylacetal dihydroxyacetone carbonate (**Scheme 16**) with different catalytic systems and on its copolymerization with  $\epsilon$ -caprolactone to afford, respectively, poly(dihydroxyacetone carbonate) and poly(carbonate ester) copolymers.

The authors investigated useful catalytic tools, previously developed by them, to achieve mild and highly selective catalytic oxidation of glycerol into dihydroxyacetone, and also focused on the search for more environmentally benign oxidative carbonylation strategies for the synthesis of dimethylacetal dihydroxyacetone carbonate.

Scheme 15. Polycondensation Reaction of Glycerol and Citric Acid To Produce a Thermoset Polyester<sup>76</sup>Scheme 16. Reaction Pathway to the Synthesis of Poly(dihydroxyacetone carbonate) from Glycerol<sup>79</sup>

Scheme 17. Preparation and ROMP of a Norbornenyl-Functionalized Castor Oil and Castor Oil Alcohol



Scheme 18. Synthesis of Polyols with Different Hydroxyl Numbers by Hydroformylation and Esterification with Formic Acid<sup>109</sup>

In conclusion, glycerol and its derivatives are performing a growing number of potential roles as monomers, and the ensuing materials display properties particularly suitable for biomedical applications.

### 3.2. Polymers from Vegetable Oils and Their Corresponding Fatty Acids

The realm of macromolecular materials synthesized from VOs has changed drastically in the past 50 years, evolving from a very modest presence as basic constituents of macromolecular materials, which can be exemplified by Rilsan, a nylon-11 based on castor oil commercialized from the 1950s onward, to the main component of sophisticated materials based on synthetic processes for the design of polymers with very specific applications.

In 2010, Xia and Larock published a review<sup>80</sup> discussing the most relevant contributions to the field of vegetable-oil-based polymers up to that date.

Driven by the impressive increase of interest in the past decade, from both academia and industry, in developing renewable materials that could mimic petroleum-derived counterparts, several other reviews with different coverages have appeared on plant-oil-based polymers.<sup>57,61,80–86</sup> Here, we aim to complement these monographs with the present state of the art, covering only the most original and promising studies. This section is divided into three main subsections that will describe (i) hyperbranched and crosslinked materials arising from polymerization reactions of (often multifunctional)

triglycerides, (ii) linear materials, obtained by the isolation (and sometimes subsequent chemical modification) of fatty acids, frequently bifunctional molecules, and (iii) the special case of the successful association between VOs and furans, a strategy adopted by our group that opens the way to the preparation of both crosslinked and linear structures, with the additional feature of thermoreversibility, based on the DA diene–dienophile click reaction.

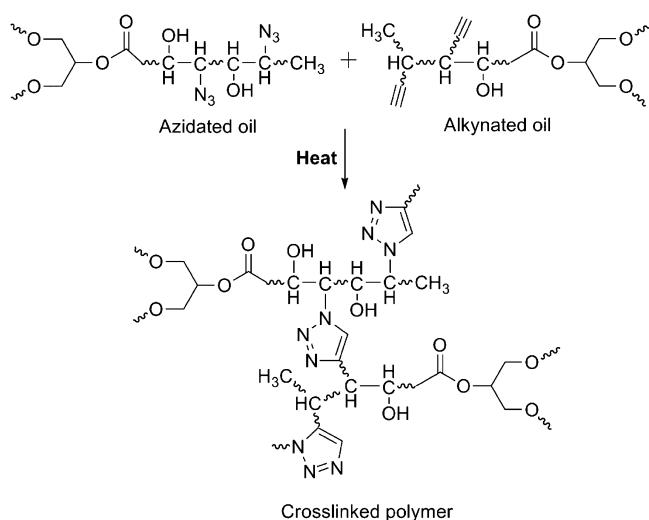
**3.2.1. Plant Oils for the Synthesis of Hyperbranched and Crosslinked Materials.** Pioneering investigations by Larock's group on the acyclic diene metathesis (ADMET) polymerization of various VOs were reported at the end of the 1990s,<sup>87</sup> based on the synthesis of high molecular weight oligomers (up to 4 kDa) catalyzed by the first generation of Grubbs catalysts, and the specific case of the polymerization of metathesized soybean oil was further treated in more detail.<sup>88,89</sup> VOs from different sources were used to prepare thermosets by cationic polymerization with divinylbenzene or a combination of styrene and divinylbenzene as comonomers.<sup>90</sup> Cationic polymerization was also used to prepare copolymer networks of regular and conjugated soybean oil with dicyclopentadiene.<sup>91,92</sup> In addition, the free radical polymerization of conjugated soybean or linseed oil, divinylbenzene, and *n*-butyl methacrylate produced thermosets used as matrixes for biocomposites reinforced with soy hull,<sup>93</sup> corn stover,<sup>94</sup> and rice hulls.<sup>95,96</sup> Maleic anhydride was added to serve as an additional comonomer to prepare biocomposites reinforced with wood

flour and wood fibers,<sup>97</sup> sugar cane bagasse,<sup>98</sup> and switchgrass.<sup>99</sup> Further studies involved the synthesis of thermosets by ring-opening metathesis polymerization (ROMP) of norbornene-modified oils,<sup>100–103</sup> and Scheme 17 illustrates one such approach. Larock's group also contributed to the development of novel oil-derived waterborne polyurethane systems.<sup>104–106</sup>

The synthesis of novel plant-oil-based polyurethane networks has also been one of the main topics of Petrović's research interests. One of the first studies reported by his group<sup>107</sup> dealt with the preparation of a series of polyols from different VOs, further converted into polyurethanes by the reaction with a commercial polycarbodiimide-modified diphenyl diisocyanate (Isonate 143L). Hydroformylation was used to convert the double bonds of soybean oil into aldehyde functions which were then hydrogenated to alcohols, and these triglyceride-derived polyols were finally reacted with polymeric 4,4'-methyleneidiphenyl diisocyanate (pMDI) to yield polyurethanes.<sup>108</sup> In a subsequent approach,<sup>109</sup> the partial esterification of the hydroxyl groups allowed the synthesis of polyurethanes with different crosslinking densities to be carried out (Scheme 18).

An alternative technique for obtaining polyols from plant triglycerides is the utilization of epoxidized vegetable oils, which was the case for polyurethanes prepared from midoleic sunflower, canola, soybean, sunflower, corn, and linseed oils by epoxidation of their double bonds, followed by oxirane ring opening with boiling methanol in the presence of a tetrafluoroboric acid catalyst.<sup>110</sup> Alternatively, full hydrogenation of epoxidized soybean oil (ESO) was achieved from a mixture of ESO, isopropyl alcohol, Raney nickel catalyst, and 4 MPa of hydrogen.<sup>111</sup> The same group reported, in sequence, the synthesis of a noncrystallizing triol from the transesterification reaction of methyl esters of ricinoleic acid with trimethylol propane.<sup>112</sup> Another important contribution of Petrović's research involved the introduction of azide groups into triglycerides from different sources.<sup>113–115</sup> This modification opens the way to an environmentally benign “click” polymerization with dialkynes<sup>114</sup> or polyalkynes<sup>113</sup> to achieve fully crosslinked polymers (Scheme 19).

**Scheme 19.** “Click” Polymerization of Azide- and Alkyne-Modified Oils for the Preparation of Fully Crosslinked Materials<sup>113</sup>



Cádiz's group contributed to the preparation of polyurethanes with specific properties, such as flame retardancy, including the incorporation of high contents of silicon-containing polyols.<sup>116</sup> The synthesis of partially biobased aromatic polyols from castor oil and sunflower oil (parts a and b, respectively, of Scheme 20) was also described for the preparation of polyurethanes with butanediol as the chain extender and 4,4'-methylenediphenyl diisocyanate (MDI) as the coupling agent.<sup>117</sup>

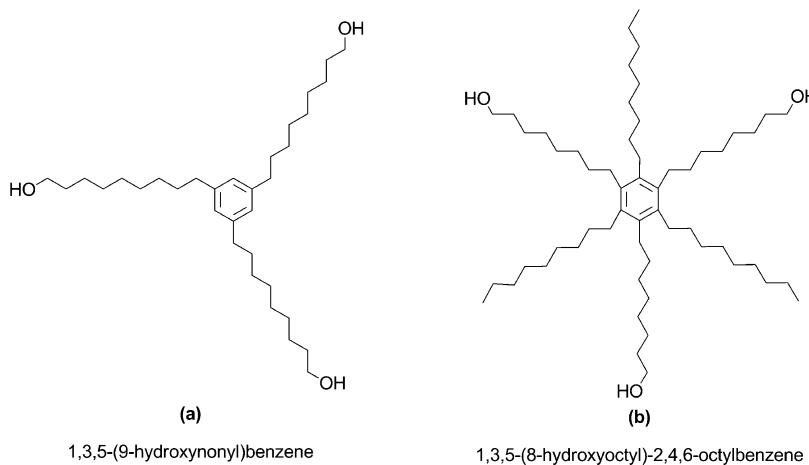
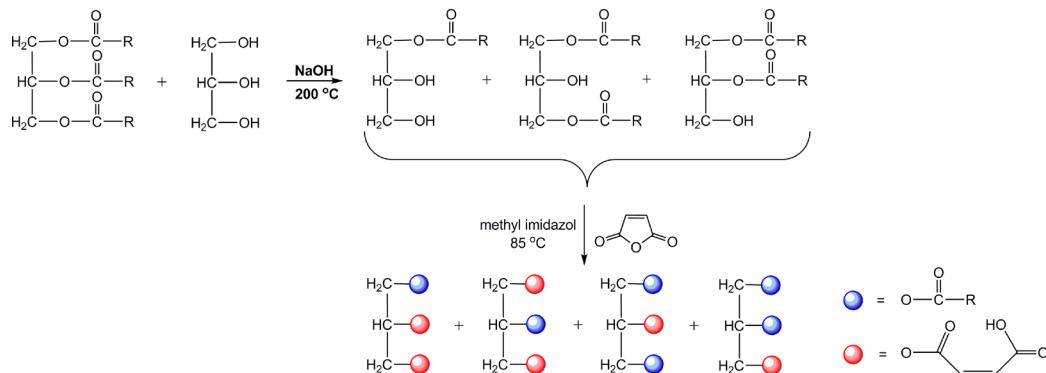
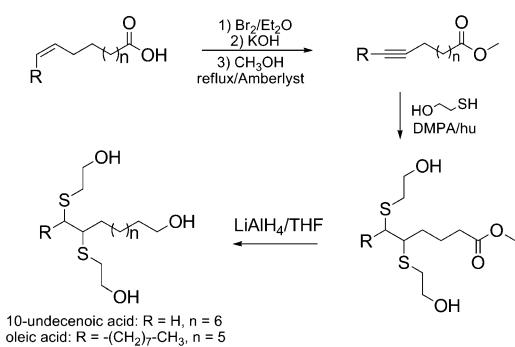
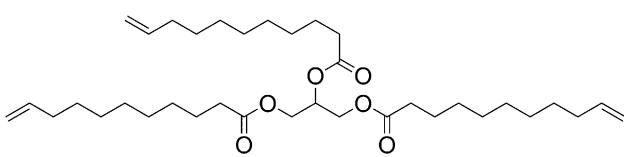
Castor oil derivatives were also used for the preparation of polyether polyols,<sup>118</sup> which were then reacted with 1,3-propanediol and MDI or 2,6-diisocyanate methyl caproate (LDI) to obtain poly(ether urethane) networks with varying hard segment contents.<sup>119,120</sup> Epoxy resins with flame retardancy properties were prepared from epoxidized 10-undecenoyl triglyceride and epoxidized methyl 3,4,5-tris(10-undecenoxy)benzoate with MDI as the coupling agent.<sup>121</sup> Other flame-retardant materials from plant oils also cover silicon-containing,<sup>122,123</sup> boron-containing,<sup>124</sup> and phosphorus-containing<sup>125</sup> polymers, obtained by cationic polymerization of soybean oil with styrene, divinylbenzene, and, respectively for the insertion of silicon and boron, *p*-(trimethylsilyl)styrene and 4-vinylphenylboronic acid. More recently, an interesting one-step reaction which promotes the insertion of phosphorus and the crosslinking of the material was based on the phospho-Michael addition of a difunctional secondary phosphine oxide (1,3-bis(phenylphosphino)propane) on an  $\alpha,\beta$ -unsaturated ketone derived from high-oleic sunflower oil,<sup>126</sup> leading to a thermoset coating material with good flame retardancy properties.

Thiol–ene<sup>127</sup> and thiol–yne<sup>128</sup> click reactions also served as tools for the formation of polymeric networks. Maleated soybean oil glycerides were synthesized (Scheme 21) and crosslinked with multifunctional thiols via thiol–ene photopolymerization.<sup>127</sup>

Less common alkynic fatty acid derivatives were obtained by dehydrobromination, and a subsequent photoinitiated thiol–yne addition was selected to functionalize them with hydroxyl moieties (Scheme 22) to be further applied in polyurethane synthesis with MDI.<sup>128</sup>

Meier's group used methyl 10-undecenoate in the context of the thiol–ene click reaction<sup>129</sup> to prepare novel macromolecular architectures. Polyesters from bi- and trifunctional ester/alcohol monomers were prepared using thiol derivatives, viz., thioglycerol, mercaptoethanol, methyl mercaptoacetate, or 1,4-butanedithiol. The reaction with thioglycerol, in particular, led to the formation of an AB<sub>2</sub>-type monomer, useful for the preparation of hyperbranched polyesters. However, methyl 10-undecenoate was previously applied as a raw material for the preparation of a triglyceride-like structure (glyceryl triundec-10-enoate, Scheme 23) with three terminal C=C unsaturations.

This macromonomer was then applied in acyclic triene metathesis (ATMET) polymerizations in the presence of the second-generation Hoveyda–Grubbs catalyst, with the aid of methyl acrylate as the chain stopper, for the synthesis of branched polymers with controlled molecular weight,<sup>130</sup> a strategy that was proven to be effective and thus was followed by a more detailed and systematic evaluation of the reaction, considering also the formation of highly functionalized dimeric triglycerides.<sup>131</sup> The same approach was described for high-oleic sunflower oil, with internal C=C double bonds, leading to highly branched polyesters.<sup>132</sup> Polyols were also synthesized

Scheme 20. (a) Castor-Oil-Based and (b) Sunflower-Oil-Based Polyols<sup>117</sup>Scheme 21. Glycerolysis and Maleinization Reactions of Soybean Oil<sup>127</sup>Scheme 22. Synthesis of Fatty Acid-Derived Polyols Starting from 10-Undecenoic and Oleic Acids<sup>128</sup>Scheme 23. Molecular Structure of Glyceryl Triundec-10-enoate<sup>130–133</sup>

by this method<sup>133</sup> via ATMET polymerization and then reacted with MDI to yield a series of polyurethane networks.

Another polymerizable vegetable-oil-derived macromonomer was synthesized by the reaction of epoxidized soybean oil with 4-vinylbenzenesulfonic acid (Scheme 24)<sup>134</sup> and subsequently

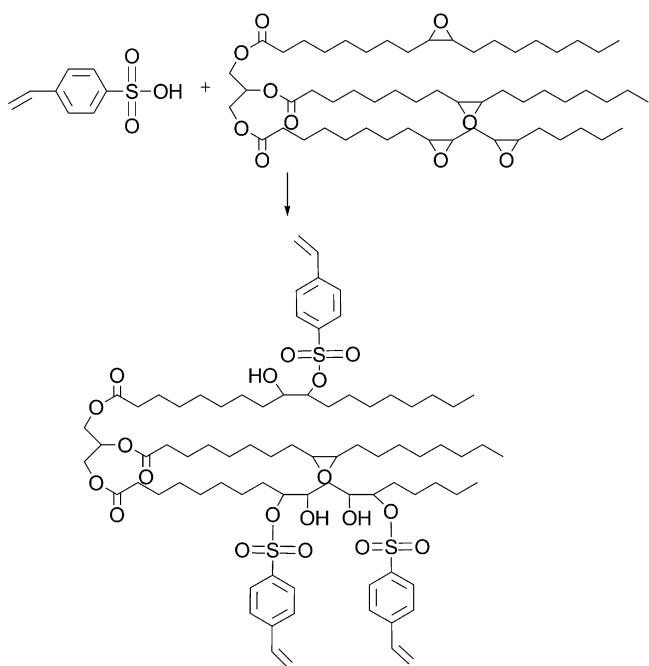
employed to prepare crosslinked materials via different mechanisms.

**3.2.2. Plant Oils for the Synthesis of Linear Materials from Fatty Acids and Their Derivatives.** Initial examples of linear plant-oil-derived polyesters were based on 9-hydroxynonanoic acid methyl ester, an AB-type monomer obtained from ozonolysis and further reduction reactions of soybean or castor oils, as described by Petrović et al. between 2008 and 2010.<sup>135,136</sup> Much of the subsequent work on this topic is based on castor oil and its derivatives, because of (i) its availability, considering a world production of nearly two million tons of castor oil plant in 2013,<sup>137</sup> and (ii) the molecular structure of its corresponding fatty acid, containing a native hydroxyl group, susceptible to a set of different reactions that allow further derivatizations.

An interesting study concerns the synthesis of linear polyurethanes from oleic and 10-undecenoic acids,<sup>138</sup> the latter being a pyrolysis product of ricinoleic acid from castor oil. A set of four diols (Scheme 25) were polymerized with MDI, leading to high- $M_n$  materials. The same group used an oligomeric diol derived from 10-undecenoic acid as a source of soft segments, together with 1,4-butanediol and MDI for the hard segments in the synthesis of thermoplastic elastomers.<sup>139</sup>

Cramail's group has concentrated its research on novel linear polymers based on VOs, such as polyurethanes,<sup>140–144</sup> poly(ester/amide urethane)s,<sup>145</sup> and polyesters and poly(ester amides).<sup>146</sup> AB-type monomers, namely, a mixture of 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz), 12-hydroxy-9-cis-octadece-

**Scheme 24.** Ring-Opening Reaction of the Oxirane Rings from Epoxidized Soybean Oil with 4-Vinylbenzenesulfonic Acid<sup>134</sup>



noyl azide (HODEAz), and methyl N-(11-hydroxy-9-*cis*-heptadecenyl)carbamate (MHHDC), were prepared from methyl oleate and ricinoleic acid for the synthesis of polyurethanes.<sup>140</sup> Scheme 26 illustrates some of their subsequent polycondensations. A similar approach was further adopted for the same purpose, with the additional utilization of the thiol–ene click reaction, which offers a more direct insertion of hydroxyl groups.<sup>141,142</sup>

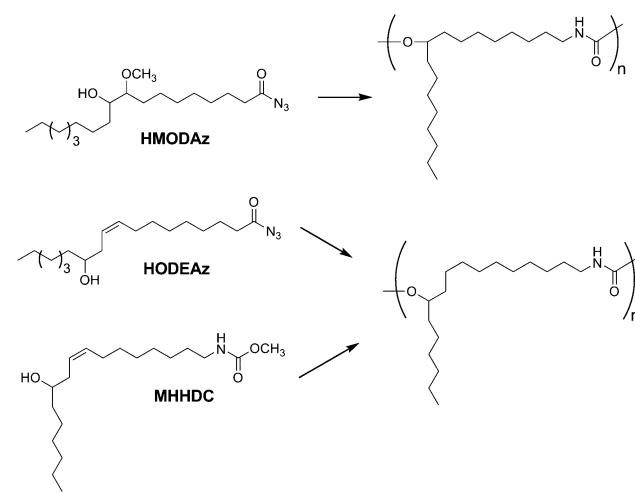
A less common approach was used to prepare oil-based diisocyanates via a non-phosgene and green method.<sup>144</sup>

Methyl oleate and methyl 10-undecenoate were converted into  $\alpha,\omega$ -diesters, potential nylon-11 and nylon-12 precursors, via their cross-metathesis reactions with allyl chloride.<sup>147</sup> Castor oil was also used to illustrate the cross-metathesis reaction serving as a useful tool for polymer side chain modification.<sup>148,149</sup> Recently, multicomponent reactions as tools for the synthesis of polymers with designed properties and architectures have also been investigated.<sup>150–152</sup>

A castor-oil-derived diene (10-undecenyl 10-undecenoate) was prepared by transesterification of methyl 10-undecenoate and 10-undecenol.<sup>153</sup> Its dithiol counterpart and a dithiol prepared from limonene were used as comonomers for thiol–ene polymerizations as shown in Scheme 27.

Another interesting source of plant oil monomers is erucic acid, a monounsaturated C22 fatty acid produced especially from members of the *Brassica* genus of green plants, such as

**Scheme 26.** Monomers and Polymers from Methyl Oleate and Ricinoleic Acid<sup>140</sup>



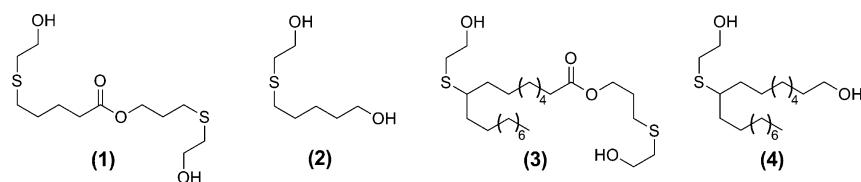
rapeseed (*Brassica napus*). Its toxicity to humans makes it nonedible, and while rapeseed oil contains significant amounts of erucic acid, the commercial, food-grade canola oil must contain less than 2%, which is achieved by plant breeding. Erucic acid was self-metathesized and hydrogenated to yield 1,26-hexacosanedioic acid, a long aliphatic chain AA monomer, and a further reduction reaction produced the corresponding diol, serving as a BB comonomer for the synthesis of 100% renewable polyesters.<sup>154</sup> Erucic acid was also used to prepare aliphatic–aromatic copolymers together with oleic acid and ferulic acid derivatives, also obtained from rapeseed (Scheme 28).<sup>155</sup>

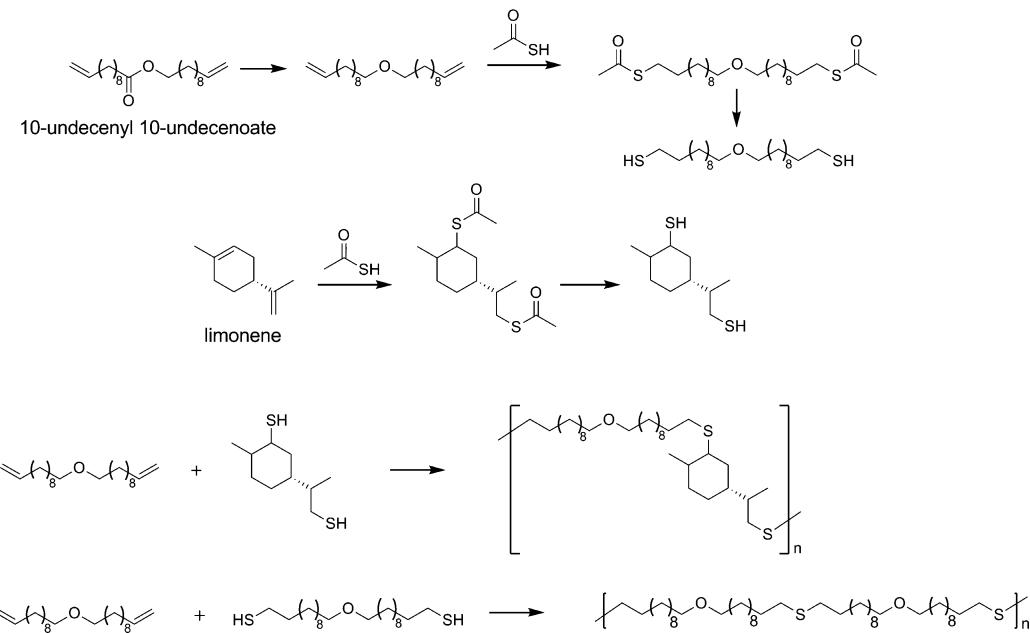
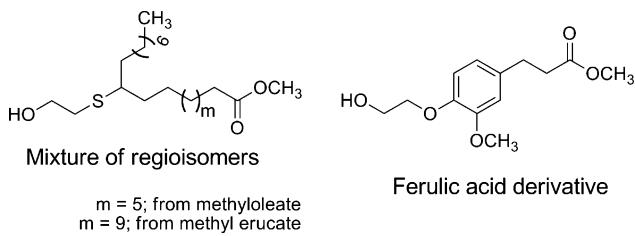
Methyl oleate and methyl erucate were employed to prepare AB-type monomers as precursors to renewable polyamides via different synthetic pathways.<sup>156–158</sup> Apart from olefin cross-metathesis,<sup>156</sup> two less frequent but interesting strategies bearing green connotations corresponded to the functionalization of the unsaturation present in methyl oleate and methyl erucate via bromination (Scheme 29)<sup>157</sup> and oxyfunctionalization (Scheme 30),<sup>158</sup> followed by the corresponding amino-functionalization.

The utilization of 1,4-cyclohexadiene, a byproduct of olefin metathesis reactions of polyunsaturated fatty acids, as an indirect plant-oil-based monomer in ring-opening copolymerizations led to renewable thermoplastic polyesters and polycarbonates.<sup>159</sup>

**3.2.3. Diels–Alder Reaction as a Tool for the Preparation of Thermoreversible Linear and Crosslinked Vegetable-Oil-Based Polymers.** The relevance and the wide practical applications of the chemistry of furan and its derivatives were discussed in the preceding section. Special attention was given to the fairly straightforward and efficient thermoreversible DA click reaction that occurs between the

**Scheme 25.** Diols Prepared from 10-Undecenoic Acid (1 and 2) and Oleic Acid (3 and 4) for Polyurethane Synthesis<sup>138</sup>

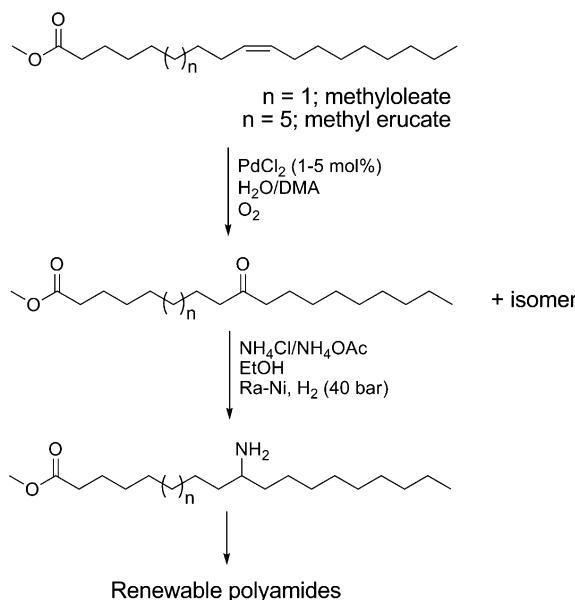
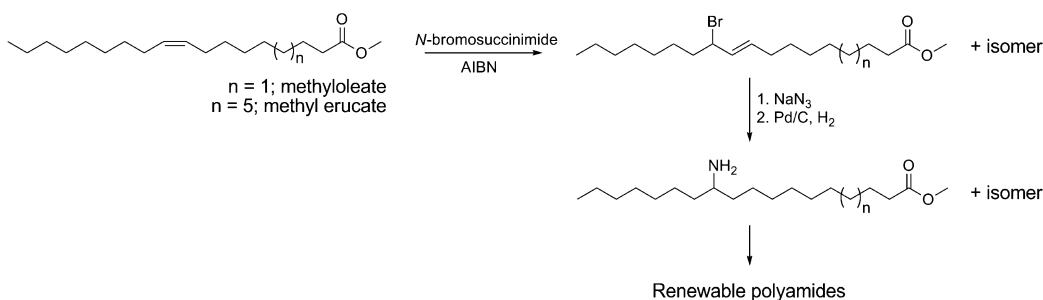


**Scheme 27. Synthesis and Copolymerization of Dithiols Derived from Castor Oil and Limonene<sup>153</sup>****Scheme 28. Monomers Derived from Rapeseed<sup>155</sup>**

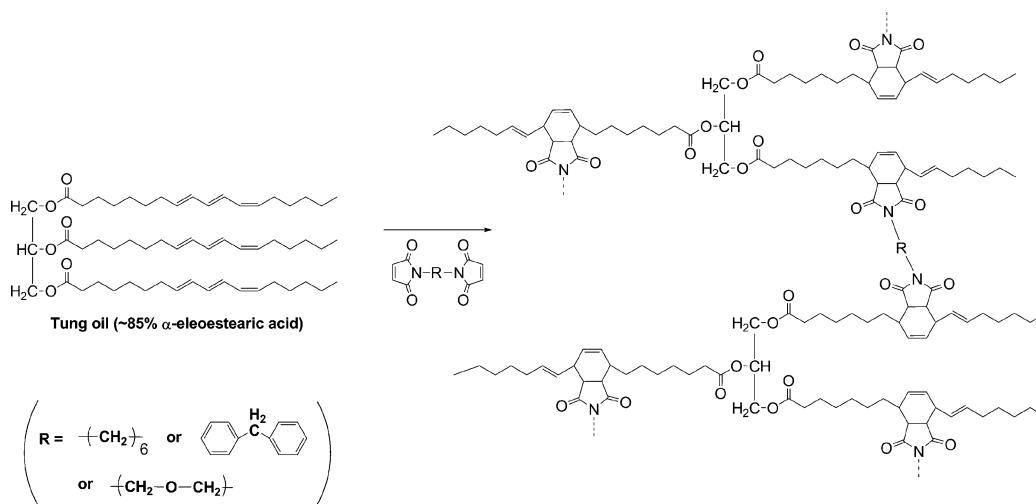
furan–maleimide pair, which opened the way to the preparation of novel materials bearing mendable, recyclable, and thermally reversible properties.

This section is devoted to the specific case of the association between furans and plant oils, a topic based on widening the reactivity associated with triglycerides by the introduction of furan heterocycles into their structures through the DA reaction.<sup>160</sup> As already mentioned, studies conducted by Gandini et al.<sup>46,47</sup> dealt with the DA polymerization of furan- or maleimide-modified 10-undecenoic acid.

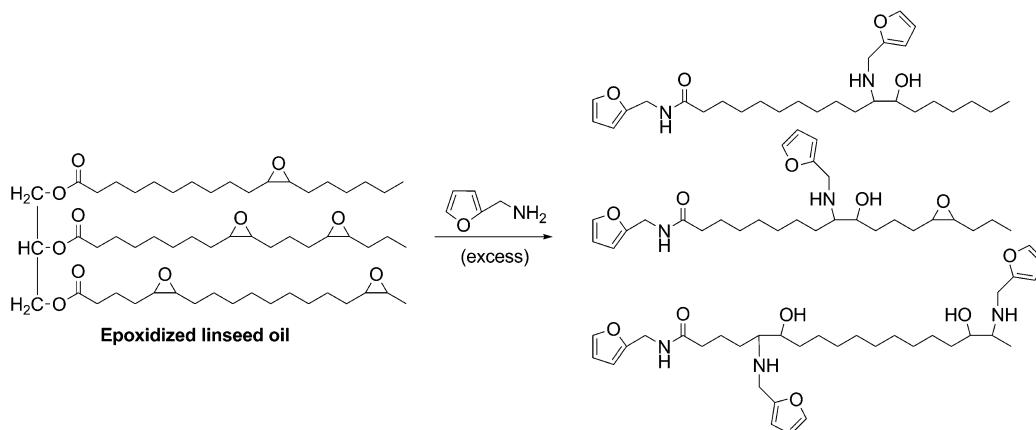
Subsequent investigations called upon the use of pristine triglycerides or their epoxidized derivatives. We used two parallel approaches. In one approach we studied the direct DA polymerization of pristine tung oil (TO), easily obtained from

**Scheme 30. Oxyfunctionalization of Methyl Oleate and Methyl Erucate as Intermediates to AB Monomers for the Synthesis of Renewable Polyamides****Scheme 29. Bromine-Derived Methyl Oleate and Methyl Erucate as Intermediates to AB Monomers for the Synthesis of Renewable Polyamides<sup>157</sup>**

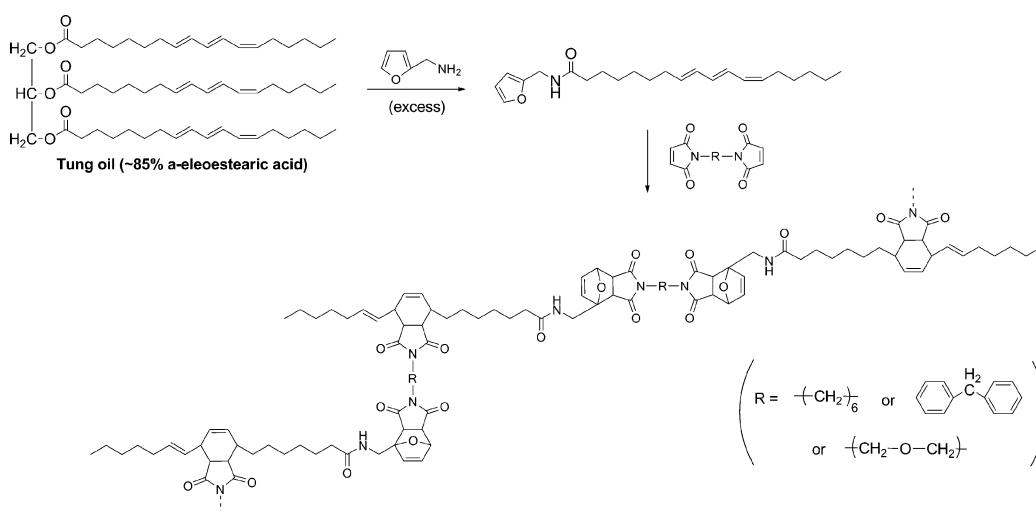
**Scheme 31. Schematic Representation of the Use of TO for the Preparation of Crosslinked Materials via DA Polycondensation<sup>162</sup>**



**Scheme 32. Double Insertion of FA onto Epoxidized LO by Aminolysis and Oxirane Ring Opening<sup>163</sup>**



**Scheme 33. Schematic Representation of the Use of TO for the Preparation of Linear Materials via DA Polycondensation<sup>162</sup>**



the seeds of tung tree (*Vernicia fordii*) nuts, for the synthesis of crosslinked materials. This was possible thanks to the three conjugated double bonds of its main fatty acid,  $\alpha$ -eleostearic acid, which acts as a “diene” in DA reactions with maleimides. The other approach called upon the DA polymerization of

chemically modified tung and linseed (LO) oils, which gave rise to linear and crosslinked materials.

The use of crude TO as a dienic monomer in the DA polymerization with an aromatic commercial BMI was first reported in a study involving drastic temperature conditions,

which led to inevitable side reactions.<sup>161</sup> Our system was broadened with three different BMIs to obtain products with different properties, under milder conditions (80 °C).<sup>162</sup> Scheme 31 illustrates the mechanism of this nonlinear DA polycondensation.

The materials were isolated with glass transition temperatures ( $T_g$ ) ranging from −10 to +75 °C, depending on the relative flexibility of the BMI (R, Scheme 31), while the TGA tracings indicated the onset of mass loss at about 350 °C.

It is important to mention that, in contrast to the thermally reversible furan–maleimide DA reaction, the structure of the adduct in this case is not reversible, at least within practically accessible temperatures. Therefore, despite being an interesting material generated by a direct and environmentally benign click reaction, once the polymer is formed, it cannot be reconverted into its monomers.

The second strategy was related to the polymerization of chemically modified LO and TO. We initially examined the possibility of preparing DA macromonomers from commercial epoxidized LO by appending two or more furan rings in its structure via the reaction with furfurylamine (FA).<sup>163</sup> This strategic, solvent-free, and catalyst-free reaction allows the insertion of furan moieties by two different mechanisms, i.e., (i) through ring opening of the oxirane groups and (ii) through the aminolysis of the glyceride ester groups (Scheme 32).

These monomers were then submitted to DA polymerizations with a commercial aromatic BMI as the dienophile. The thermoreversible nature of these materials was confirmed by their aptitude to depolymerize at ~110 °C through the retro-DA reaction, indicating potential applications as coatings and adhesives, with the unique feature associated with thermoreversibility.

In the same context, we also evaluated the viability of the reaction of TO and FA using the same approach (Scheme 33).<sup>162</sup> This method is similar to that described above involving epoxidized LO; however, the three conjugated double bonds at the fatty acid chains of TO are inert to the presence of FA, and only aminolysis takes place. These trienes are therefore preserved for further use as dienic moieties in the subsequent DA polymerization reactions.

The ensuing polymers had  $M_w$  values ranging from 20 to 40 kDa with polydispersity values always close to 2, indicating that all the structures were in fact linear macromolecules. Their  $T_g$  ranged from 30 to 105 °C, depending on the structure of the BMI used.

This strategy is being pursued and must be viewed as work in progress.

### 3.3. Concluding Remarks

The succinct outlook presented here is hopefully sufficient to highlight the very broad potential provided by organic and polymer chemistry for the elaboration of a growing variety of macromolecular materials based on both pristine and chemically modified VOs. This is not a quiet field, since all its actors are seriously engaged in making it prosper.

## 4. THERMOPLASTIC STARCH: CHEMICAL MODIFICATION AND THERMOREVERSIBLE MATERIALS BY REACTIVE EXTRUSION

Whereas starch has been a natural material utilized for centuries in glue compositions, textile impregnation, and other industrial applications, as well as a food component, thermoplastic starch (TPS)<sup>164–170</sup> emerged in the 1990s as a new and promising

biodegradable polymer. TPS converted starch into one of the few renewable commodity plastics that can be processed in the melt, which justifies the growing interest that both academia and industry place in its further development.<sup>170</sup>

Starch is constituted by two main macromolecular components, namely, linear amylose and branched amylopectin,<sup>171–173</sup> and can be considered a polymer made up of anhydroglucose ( $\alpha$ -D-glucopyranosyl) units. In its native state, starch is composed of partially crystalline granules with different aspects and sizes, which vary from 0.5 to 175  $\mu$ m, depending on the source.<sup>174</sup> These granules are insoluble in cold water, which helps in their isolation and purification.

The majority of the strategies for the use of starch as a raw material for thermoplastics are (a) conversion to monomeric raw materials such as lactic acid and ethylene or use as media for bacterial growth to produce polymers, such as poly(hydroxyalkanoate)s (PHAs), (b) conversion to low molecular weight hydroxylated compounds, such as dextrans and glycolized products, both used as monomers for polyurethane synthesis, or modified by grafting to give new polymers, and (c) use without any severe modification, as filler in other plastics or processed with plasticizers as TPS, thus retaining its macromolecular structure.

In those strategies the degree of starch modification can include (a) its complete chemical destructuring, leading to polymers that are completely different from the starting material, allowing the possibility of producing a wide range of structures using the biorefinery concept, but at high costs. Alternatively, severe modifications can be applied (b) while keeping its basic monomeric structure with costs that are still high, thus limiting the range of applications of the ensuing materials. A more economic process (c), in which starch is used as granules or modified by continuous physical processes such as extrusion, can also be applied. TPS pertains to the latter approach, whose simplicity and low cost of production justify its success in the past two decades. Recently, new materials have been derived from TPS using reactive extrusion (REX) in a process that can be considered intermediate between the two preceding (b and c) strategies. This approach combines the simplicity of TPS production with the possibility of tuning starch properties by adjusting the extension and kind of reaction in TPS-REX processing.

When a starch aqueous slurry is heated above 60–70 °C, the crystalline structure is lost to produce a paste through a process termed gelatinization.<sup>175,176</sup> A similar process of gelatinization, conducted in the absence (or with low concentration) of water in the presence of a high-boiling liquid plasticizer, gives rise to TPS. This process requires conditions of high shear in extruders or intensive mixers typically designed for thermoplastics.<sup>164–168,170,177</sup>

The two traditional TPS drawbacks are its water sensitivity and poor mechanical properties,<sup>178–180</sup> and much research has been devoted to their minimization, mainly by blending with other polymers and preparing composites.

The first approach, the polymer blending of TPS with natural and, especially, with synthetic polymers, was the basis of relevant commercial products and is still the subject of intense research.<sup>166,181–195</sup> In several studies involving blends, chemical modification of starch was used to increase TPS compatibility with other polymers, such as poly(lactic acid) (PLA), poly(ethylene), poly(caprolactone) (PCL), poly(butylene succinate) (PBS), poly(butylene succinate-co-adipate) (PBSA), poly(hydrobutyrate)s (PHBs), and Ecoflex BASF

poly(butylene adipate-co-terephthalate) (PBAT). At the beginning of the third millennium, commercial products based on blends of TPS and other polymers such as ethylene vinyl alcohol copolymers (EVOH) were launched, proving the viability of starch as a base for biodegradable thermoplastic polymer compositions.<sup>184</sup>

The compatibility between TPS and nonpolar polymers such as natural rubber (NR) was significantly improved by the oxidation of NR with KMnO<sub>4</sub>, producing rubber chains with pendant OH groups.<sup>196</sup> The blends were prepared by extrusion, and scanning electron microscopy revealed a more homogeneous distribution of the NR phase and an improvement in water resistance and in the brittleness.

The second approach for TPS modification was based on the addition of fillers to produce composites with inorganic fillers,<sup>197,198</sup> natural fibers,<sup>199–207</sup> nanofillers,<sup>208,209</sup> nano-whiskers of cellulose,<sup>210</sup> starch nanocrystals,<sup>211</sup> and cellulose microfibrils,<sup>212</sup> among others.

After a large number of studies were published and patents filed on blends and composites of TPS, a new strategy was adopted based on the chemical modification of starch obtained in general through REX, intended to increase its compatibility with other polymers or with fillers, or to modify the properties of TPS itself by increasing both the water resistance and mechanical properties. Recent reviews on this subject were published recently.<sup>213–218</sup>

It is important to note that the use of starch in plastics is not new and that, before the studies on TPS, starch in its native granule form was used in thermoplastics as a filler,<sup>150</sup> or as a thermoplastic material prepared by grafting starch with vinyl monomers<sup>165,219</sup> and gelatinized with other water-dispersible polymers,<sup>220,221</sup> providing potentially interesting materials which have however a limited use due to rather poor properties or high costs.

In the following paragraphs, new emerging processes for TPS modification are discussed via REX and crosslinked thermoreversible starches which can also be prepared by REX.

One important target of TPS modification is intended to improve its compatibility with other polymers. Reactive blending is a successful technique to improve the compatibility of immiscible polymers. These modifications are produced directly during the blending process by the incorporation of reactive compounds, such as diisocyanates,<sup>185,195,222</sup> organic acids,<sup>223–227</sup> maleic anhydride and peroxides,<sup>228,229</sup> and vinyl polymers with titanates, sodium carbonate, and zinc acetate,<sup>230</sup> or by the previous modification of TPS by REX, as, for example, in the preparation of maleated TPS by TPS processing in the presence of maleic anhydride,<sup>231</sup> which is then blended in a second extrusion step.

#### 4.1. Intensive Starch Modification by REX of TPS

A new approach emerged recently that can be considered as an intermediate strategy, in which starch is used as a pristine material for the preparation of new monomers, or used without any chemical modification as in TPS. This approach combines the advantages of direct modification of starch during TPS processing and the use of starch to produce building blocks for the synthesis of new materials. One process for intensive starch modification, based on its depolymerization, followed by repolymerization, was described recently,<sup>232</sup> in which intensive depolymerization was carried out by the use of citric acid during TPS preparation by extrusion,<sup>228,229</sup> leading to a significant reduction in molar mass, while in the same extrusion

process a polymerization agent was added, namely, MDI. The conditions are such that in the first step depolymerization dominates and in the second polymerization takes place preferentially. The idea was to produce a different polymer from the starting material, which can be considered a copolymer of urethane and starch segments. Glycerol or other hydroxyl-containing compounds, added as plasticizers, will also react, making the system rather complex. The notable advantage here is the possibility of tuning the outcome by using as variables the extent of depolymerization, the degree of polymerization, and the type of depolymerization and polymerization agents. Thus, a thermoplastic starch sample prepared with corn starch and 30 wt % glycerol with a Young's modulus of 27 MPa and an ultimate tensile strength of 3.5 MPa has reduced values of 5 and 0.6 MPa after depolymerization and, after depolymerization followed by polymerization in a single step, ends up with values of 27 and 5 MPa, clearly showing the recovery of the initial properties.<sup>232</sup> It is important to note the fact that even if the properties after processing are similar to the original ones for a given TPS composition, the final product is a novel material with a lower tendency to crystallize and is more compatible with aliphatic polyesters and other biodegradable polymers.

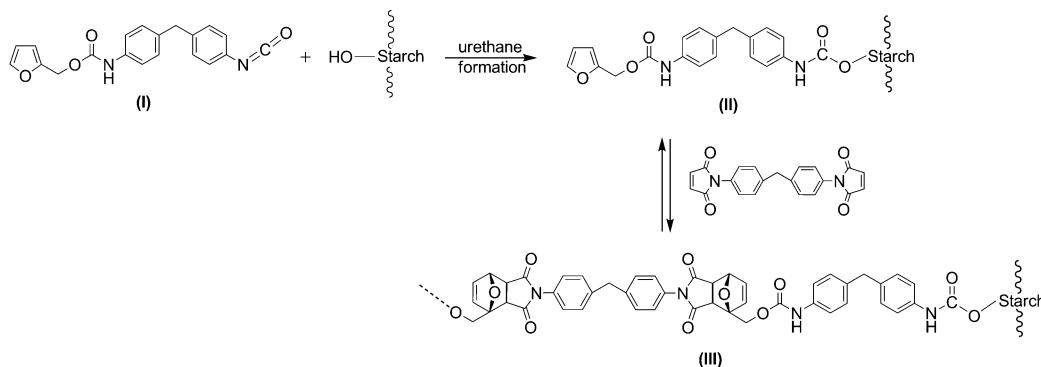
#### 4.2. Thermoreversible Crosslinked Starch from TPS

**4.2.1. Crosslinked Starch and TPS.** Crosslinked starches have been extensively used for a long time in the food and textile industries and for adhesives.<sup>233</sup> They are produced as slurries by the reaction of bi- or multifunctional reagents, keeping the granule structure, but increasing the resistance to gelatinization and providing a better high-viscosity stability of the required suspensions.<sup>229</sup> Few studies deal with crosslinked starches in compositions of TPS or produced from TPS. Das et al.<sup>234</sup> describe the crosslinking of blends of starch/poly(vinyl alcohol). Low moisture absorption films were produced from gelatinized starch and a solution of PVA by casting and using different crosslinkers such as borax, formaldehyde, epichlorohydrin, and ZnO. The effect of post-crosslinking of thermoplastic starch/poly(vinyl alcohol) blend films produced by casting was studied by Liu et al.<sup>235</sup> The films were prepared in a glutaraldehyde aqueous solution and then crosslinked by heating. Kaewtatip and Thongmee<sup>236</sup> studied the effects of the addition of crosslinked starch granules on the TPS properties. The material produced was a composite that maintained the thermoplastic properties of TPS, but with enhanced hydrophobicity and mechanical properties.

Thermoplastic starch was crosslinked by irradiation with aromatic additives blended during processing,<sup>237</sup> using cinnamyl alcohol, *p*-methoxybenzyl alcohol, benzenedimethanol, cinnamic acid, coumaric acid, and ferulic acid. The materials were characterized by gel formation due to grafting of functional moieties onto the starch backbone that occurs only in the absence of glycerol. This effect was attributed to the interactions of glycerol which interfere in the reactions of the aromatic additives used for starch modification.<sup>237</sup> Starch films produced by casting gelatinized starch with citric acid (CA) were cured by baking at 105 or 150 °C for minutes,<sup>238</sup> and the gel content, which increased with increasing CA concentration and temperature, was used to quantify the extent of crosslinking.

**4.2.2. Thermoreversible Crosslinked Starch Obtained from TPS.** Crosslinked thermoplastic starch can be an effective way to improve the properties of TPS-based materials, in

**Scheme 34.** Reaction of FA–MDI (I) with Starch To Give Grafted Starch (II) and DA and Retro-DA Reactions between the Furan-Modified Starch and Bismaleimide To Give Product III<sup>239</sup>



particular its resistance to moisture. However, a crosslinked material will show the difficulties inherent to its macromolecular structure, in particular further processing and recyclability. In a recent study, a novel furan-modified thermoreversible crosslinked thermoplastic starch (TR-CTPS) was developed, in which the crosslinking mechanism is based on the thermoreversible furan–maleimide adduct formed by the DA reaction.<sup>239</sup> This new concept allows the processing of TPS with the crosslinking agent 1,1'-(methylenedi-4,1-phenylene)bismaleimide in the usual form, since at the processing temperature the crosslinking reaction cannot occur because the retro-DA predominates.<sup>13,14</sup> After processing, when the temperature decreases below about 60 °C, the DA coupling becomes predominant, leading to a crosslinked insoluble material. If heated again to temperatures above 110 °C, the retro-DA occurs and a thermoplastic material is regenerated. Scheme 34 shows the structures of furfuryl alcohol (FA)–4,4'-methylenediphenyl diisocyanate (MDI) (I), grafted starch (II), and the product (III) resulting from the DA/retro-DA reactions between the furan-modified starch and the aromatic BMI.

This thermoreversible TPS network opens the way to new starch-based materials for novel applications with higher water resistance and enhanced mechanical properties.

## 5. ADVANCES IN NANOCELLULOSE DEVELOPMENTS AND APPLICATIONS

Cellulose fibers constitute the basic structural element of wood and annual plants. In wood, cellulose fibers are associated with lignin and hemicelluloses, giving rise to an exemplary composite possessing one of the highest mechanical properties in nature.<sup>3</sup> Cellulose has been part of the development of human society at all ages in a progressively more sophisticated fashion and continues to provide exciting materials.

Cellulose is of great interest in many research areas, especially because of its mechanical properties and functionality. The morphology of cellulose is also very important as a material, since it can be disassembled into nanofibers, used, among other exploitations, to prepare new cellulose-based composites, while its hydroxyl functions allow chemical modifications to be carried out.<sup>240</sup>

The three types of nanocelluloses, i.e., cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC), and bacterial cellulose (BC), represent an advance in cellulose technology, with progress in scaling up the production of NFC and CNCs.<sup>241</sup> Nanocellulose demand is increasing mainly for application in the reinforcement of polymeric matrixes,

nanopapers, hydrogels, and additives for paper and cardboard. With respect to its preparation, NFC is generated by the separation of the individual elementary nanofibrils from the cellulose fiber by mechanical treatment, chemical treatment, or the combination of mechanical and chemical treatments of pulp.<sup>242</sup> CNCs represent the crystalline phase of cellulose, and it is obtained by the acid dissolution of its amorphous phase.<sup>243</sup> BC is the pure nanocellulose produced by living organism such as molds, tunicates, and bacteria.<sup>244</sup> In the case of BC produced by bacteria from the *Gluconacetobacter* genus, it is secreted in the form of nanofibrils, free from lignin and hemicelluloses, which assemble to form a physical network in the shape of an aqueous membrane. It finds applications in numerous areas, particularly in the biomedical field.

The hydroxyl functionalities of cellulose are readily open to chemical reactions allowing its modification, either in the bulk or at the surface of its fibers. Whereas the bulk reactions are mostly used to prepare thermoplastic materials such as cellulose esters and ethers, thus altering drastically the properties of the natural fibers, the surface modification does not modify their morphology, thus maintaining their mechanical and thermal features.<sup>1</sup> The purpose of this latter approach, extended recently to nanocelluloses,<sup>245</sup> is to introduce specific moieties which will give the surface novel aptitudes, such as the compatibilization with a matrix in a composite, or the possibility of further chemical reactions in the elaboration of novel materials. A typical example of this modification is the extensively used oxidation of cellulose fibers with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical that generates oxidized NFC bearing carboxylic groups at their surface which facilitate their preparation and stability against self-association.<sup>246</sup>

### 5.1. Developments and Perspectives in the Chemical Modification of NFC, BC, and CNCs

**5.1.1. Nanofibrillated Cellulose.** NFC is the most abundant among nanocelluloses, and hence, research associated with their applications and chemical modifications has developed more rapidly than with BC and CNCs. The grafting of functional groups at the surface of NFC has been extensively studied. Among the covalent modifications, esterification, etherification, silylation, sulfonation,<sup>247</sup> and polymer grafting are the most important reactions, whereas noncovalent modifications include the physical adsorption of electrolytes or polyelectrolytes.<sup>1,248</sup>

**5.1.2. Bacterial Cellulose.** Cellulose synthesized by microorganisms, such as BC, is an alternative source of

nanocellulose for many applications.<sup>244</sup> In its native state, BC is a membrane hydrogel, a unique morphology in nature, almost impossible to artificially copy. BC is produced as highly pure cellulose containing 96–98 wt % water. In nature, it is synthesized as a survival protective barrier for microorganisms against environmental hostility such as competitors and sunlight.<sup>245</sup> The membrane is composed of long entangled fibers with a very low width (~50 nm in diameter), available at low cost with a stable production in the food industry of Southern Asia.<sup>241</sup> The production of BC is of great interest because the biotechnological approach to its production is totally green and the product is easily separated and purified. BC has been studied for application in biomedical materials and products based on a natural polymer from renewable resources. Among the numerous applications in the biomedical field, many reports have been published concerning its use inside the body.<sup>250,251</sup> Its use as an additive for special papers has been successfully demonstrated,<sup>252</sup> as well its use as a substrate for electronic devices<sup>253,254</sup> or other substrates in substitution for conventional paper.

The chemical modification of BC is similar to the NFC modification methods. The preservation of the structure and morphology of the membrane depends on the reagents and reaction conditions, and special attention has been paid to avoid degradation of the membrane structure and to ensure a homogeneous surface modification.

**5.1.3. Cellulose Nanocrystals.** The functionalization of CNCs required rather laborious steps from their preparation and purification to the actual surface treatment. A new approach has been developed to save time and purification steps, based on the simultaneous hydrolysis and functionalization, in which the reagent for hydrolysis is also capable of chemically modifying the CNCs, as in the case of organic acids.<sup>255</sup> The method was successfully applied to 2-propynoic acid, 4-pentenoic acid, 3-mercaptopropionic acid, and 2-bromopropanoic acid, which decorated CNCs with triple or double bonds, thiols, and bromoester groups, respectively. The average yield was 50–60 wt %, the particle dimensions were 180–200 nm length × 13–18 nm diameter, the crystallinity degree was 65–80%, and the degree of surface substitution varied from 0.06 to 0.27.

Figure 2 shows films prepared from nanofibers of NFC, BC, and TEMPO-modified NFC (ToNFC). Figure 3 shows the



Figure 2. Films of (from left to right) NFC, BC, and ToNFC.

morphology of BC, NFC, ToNFC, and CNCs acquired by scanning electron microscopy.

### 5.2. Nanocellulose Hydrogels

The inherent hydrophilicity of cellulose renders it a valuable raw material for biodegradable, biocompatible, and renewable hydrogels. Cellulose hydrogels are physical gels of its ethers and esters displaying high stability above their lower critical solution temperature (LCST). Cellulose association with ions such as ionic liquid<sup>256</sup> and poly(*N*-isopropylacrylamide) (pNIPAM),<sup>257</sup>

generates thermosensitive hydrogels thanks to the electrostatic interactions of its positive charges with the negative counterparts from the hydroxyl and carboxyl groups of cellulose. Cellulose hydrogel hybrid materials with synthetic polymers such as poly(acrylonitrile)<sup>258</sup> show tunable properties, but their crosslinking with hazardous agents such as epichlorohydrin or glutaraldehyde is a problem. An interesting approach to solve this drawback is the use of the copper-catalyzed 1,3-dipolar cycloaddition click reaction, in which the reaction in an aqueous medium calls upon tosyl cellulose as the starting material.<sup>259</sup> The preparation involves the coupling of carboxymethyl 6-deoxy-6-aminopropargyl cellulose and carboxymethyl 6-azido-6-deoxy cellulose (both prepared from tosyl cellulose in water), in the presence of copper(I) catalyst and ascorbic acid. This simple and flexible system generates self-sustainable materials with tunable mechanical properties, driven by the ensuing crosslink density.

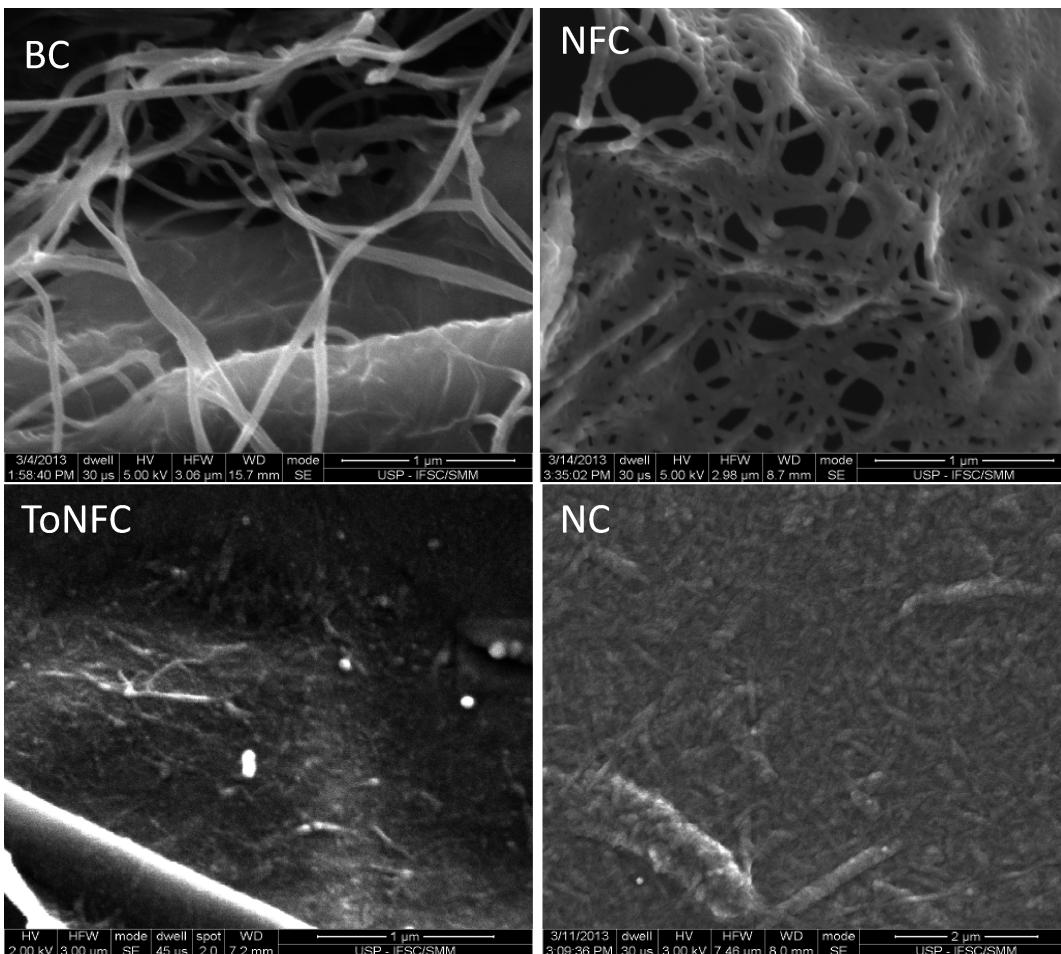
As already mentioned, the most radical advance in soluble cellulose development is the preparation of ToNFC, which exhibits improved mechanical properties and controllable abundance of surface carboxylic groups.<sup>260</sup> The possibilities of further surface chemical modifications using the carboxylic functionality include the generation of amide moieties in aqueous media using the reagents 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) as coupling agents,<sup>261,262</sup> both water-soluble, for the grafting of cysteine,<sup>263</sup> tryptophan,<sup>264</sup> and polyethylene glycol (PEGylation),<sup>261,265</sup> hydrophobization by grafting octadecylamine and also by amidation of an alkylamine,<sup>266</sup> and formation of an alkylketene dimer by esterification.<sup>266</sup>

ToNFC is a transparent gel (Figure 4) formed by individual cellulose nanofibers with a high aspect ratio<sup>267</sup> (3–4 nm in width and a few micrometers in length).<sup>268</sup> The presence of the carboxylic negative charges at the surface of the individual fibers keeps them apart by electrostatic repulsion. The low diameter of the individual fibrils gives rise to a smoother film compared to the NFC or BC counterparts (Figure 2). The viscosity of ToNFC is high at acidic conditions ( $\text{pH} \approx 3.5$ ) and decreases with increasing pH, while obviously decreasing with increasing temperature.<sup>269</sup> It can also be modulated by adding charged molecules.

### 5.3. Pickering Emulsions from Nanocellulose

A promising application associated with the properties of modified nanocelluloses is their use for replacement of surfactants or emulsifiers in the pharmaceutical, health care, and food industries. Emulsifiers are normally the most used compounds for emulsion stabilization, but they can induce irritability in susceptible patients, especially for sensitive skin, and hence, surfactant- or emulsifier-free emulsions have been developed using amphiphilic solid particle stabilizers with micro- or nanometric sizes, called pickering emulsions.<sup>270,271</sup>

Surfactant molecules are usually in rapid dynamic equilibrium between the oil/water interface and the bulk phase, in contrast with the irreversible adsorption shown by solid particles, which leads to extreme stability of the emulsions.<sup>272</sup> Pickering emulsions can be prepared using inorganic particles such as silica<sup>273</sup> or calcium carbonate,<sup>274</sup> but biobased particles are more interesting for the development of environmentally friendly materials and biocompatible additives for health care and cosmetics,<sup>275</sup> as well as for possible applications that demand high amounts of emulsifier. The first biobased



**Figure 3.** SEM micrographs of BC, NFC, ToNFC, and CNCs.



**Figure 4.** Never-dried ToNFC suspension at 0.6% wt.

Pickering emulsion was starch chemically modified with hydrophobic moieties such as octenylsuccinic anhydride,<sup>276</sup> which represented an advance in the development of pickering emulsions from renewable resources for the food industry. In this context, the chemical modification of cellulose for the development of emulsion stabilizers represents a further advance in materials science, but with wider applications than those of the modified starch, because of their properties.

Chemically modified cellulose nanofibers or nanocrystals have shown good properties for pickering emulsion preparation. To act as an emulsifier and stabilize amphiphilic structures

in emulsions, the hydrophilic surface of cellulose must be chemically modified, giving rise to amphiphilic counterparts at the surface of its nanofibers.<sup>277</sup> Nanocellulose pickering emulsions are also useful for the stabilization of multiple emulsion systems as in the case where water/oil (w/o) and oil/water (o/w) emulsions exist simultaneously.<sup>275</sup> The stabilization of double emulsion systems requires at least one hydrophobic emulsifier for the w/o phase and its hydrophilic counterpart for the o/w phase. The esterification with hydrophobic lauroyl chloride at the surface of NFC or CNCs generated cellulose-based stabilizers for the oil–water interface in simple water-in-oil emulsions, while the combination of the lauroyl-modified and unmodified nanocelluloses provides oil-in-water-in-oil double emulsion stabilization.<sup>275</sup>

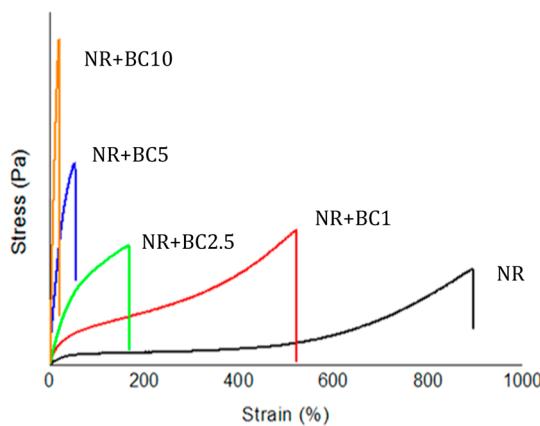
The grafting of pNIPAM at the CNC surface via surface-initiated single-electron transfer living radical polymerization generated brushes with a thermoresponsive behavior. The material was capable of responding to the effect of ionic strength because of the ionic character of pNIPAM.<sup>278</sup> In that study, pickering heptane-in-water emulsions containing 0.05–0.5 wt % pNIPAM-g-CNCs were stable for four months thanks to the LCST of pNIPAM, but were broken when heated above that temperature.

The stabilization of emulsions free of surfactants by solid particles offers high resistance to coalescence and controllable stability, i.e., attractive benefits for health care and cosmetic applications.

#### 5.4. Composite Materials Based on Cellulose and Nanocelluloses

In composite sciences, the use of nanofibers to reinforce polymeric matrixes has gained attention in the past few decades, because of the possibility of replacing conventional fibers such as glass, carbon, and plastic fibers by a totally renewable, biodegradable, low-cost, and ubiquitous material. Nanocomposites based on nanocelluloses and macromolecular matrixes are materials with highly enhanced mechanical properties, even at very low loadings, which differentiate them from ordinary cellulose fillers. In addition, cellulose fibers can provide improved properties, compared with those obtained with conventional fibers. Chemically modified cellulose fibers or nanofibers bearing surface apolar groups are well-known to improve the compatibility of cellulose with nonpolar matrixes such as polyolefins.

CNCs, BC, and NFC have been extensively studied as reinforcements for polymer matrixes. Synthetic and natural polymers, elastomers, thermoplastics, and thermosets all respond very well to the incorporation of nanocelluloses regarding the improvement of their mechanical properties, as evidenced by the increased Young's modulus of the ensuing composites. An elastomeric matrix studied in this context is natural rubber, which, when reinforced with BC, shows a spectacular improvement of its mechanical properties, which increases by increasing the amount of incorporated nanofibers, as shown in Figure 5. The Young's modulus of vulcanized



**Figure 5.** Tensile tests of natural rubber and its BC-based composites with 1, 2.5, 5, and 10 wt % BC.

natural rubber,  $\sim 1 \times 10^4$  Pa, increased from  $2.5 \times 10^5$  to  $6 \times 10^5$  Pa, when loaded with 5 and 10 wt % milled BC, respectively.<sup>279</sup> The other interesting feature associated with this entirely renewable composite was the progressive shift of material consistency from purely elastomeric to highly rigid, as the BC content was raised, as clearly illustrated in Figure 5.

The Young's modulus of an acrylic resin ( $\sim 120$  MPa) composed of butyl acrylate and methyl methacrylate increased from about 130 to 360 MPa, when loaded with 1 and 10 wt % BC, respectively, showing the same trend as with natural rubber.<sup>280</sup> The reinforcement of thermoplastics with a low deformation character, such as poly(lactic acid), was less impressive.<sup>281</sup>

The improvement in mechanical properties was also observed in polysaccharide matrixes, such as pullulan and chitosan reinforced with nanofibers. For instance, the Young's modulus of a pullulan–glycerol (7.3 wt %) matrix reinforced

with 20 and 40 wt % NFC increased from 2.5 to 25 MPa,<sup>282</sup> and a similar effect was observed for chitosan reinforced with NFC.<sup>283</sup> For proteic matrixes such as fibroin, the reinforcement mimicked that of the polysaccharide counterparts.<sup>284,285</sup>

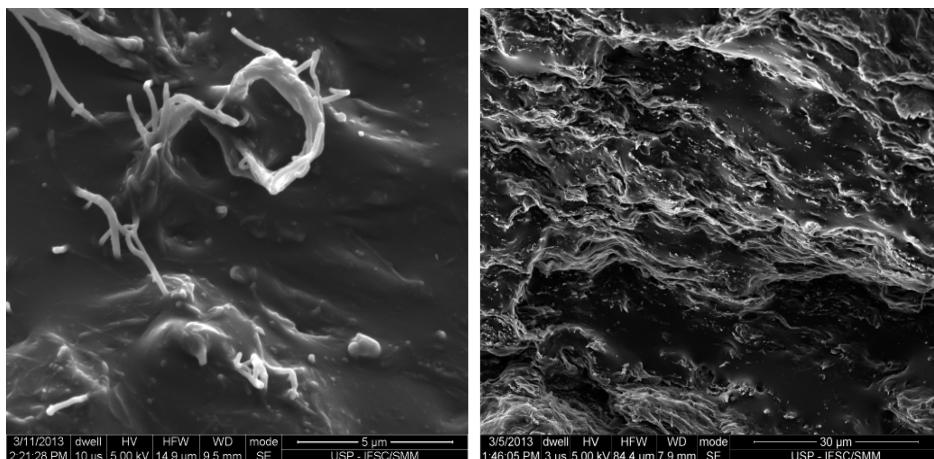
The adhesion of the fibers to the matrix strongly affects the mechanical properties of composite materials. The adhesion of nanofibers (BC, CNCs, and NFC) to polymeric matrixes is normally high, even within polymers of low polarity (Figure 6), probably because of the very low dimensions and high surface-to-volume ratios of these fillers, which generate a percolating network with strong OH-bonded interparticle connections. The use of cellulose as a filler for macromolecular matrixes also stimulates advances in green technologies, as in the case of emulsion polymerization latexes for the preparation of composites, in which only aqueous systems are employed.

A very interesting approach to reinforce cellulose nanofibers, namely, ToNFC, is the use of peptides with a secondary structure as the reinforcing agent for cellulose or other polar polymers. The idea is to reach the reinforcement using the force governed by two different types of molecular interactions: (i) the electrostatic interaction between the peptide and the polymeric matrix and (ii) the force associated with the secondary structure inherent to the peptide, which is also of electrostatic origin. The interaction between the peptide and the matrix increases the tensile strength of the material, while the inherent secondary structure of the peptide is responsible for increasing the elongation at the limit of the peptide strength. This is a promising strategy to increase the tensile strength of the material without decreasing its elongation at break, a new concept in materials science, which has already been tested by our research group in collaboration with other colleagues.

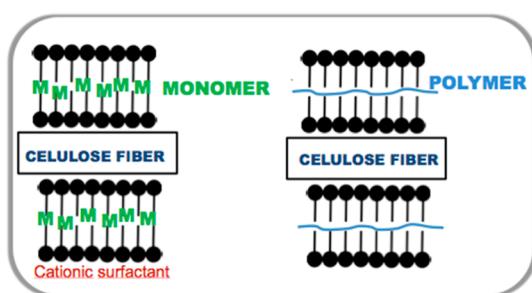
#### 5.5. Sleeving Nanocelluloses by Admicellar Polymerization

As already pointed out, composites based on cellulose and hydrophobic matrixes encounter the classical problem of low interfacial compatibility associated with the high polar character of the fibers, and the problem is even more critical with nanocelluloses, which should remain in suspension, because if dried, they become very hard to redisperse. An alternative strategy to improve the quality of adhesion to the matrix calls upon the *in situ* modification of the surface of the nanofibers in their pristine aqueous suspension by the physical deposition of a thin film of hydrophobic polymer at the surface of the individual nanofibers. The principle of the method, known as admicellar polymerization, involves the formation of a double layer of a cationic surfactant on the surface of the fibers, followed by the incorporation of a hydrophobic monomer in the aqueous medium, Figure 7. After the monomer migration to the surfactant sleeve, the polymerization is carried out using a water-soluble initiator. The modification is thus attained by the physical deposition of the polymer, generated *in situ*, as shown in Figure 8.

The method, first described for conventional fibers,<sup>286,287</sup> also works with success for nanocelluloses.<sup>288</sup> The innovation associated with this process is the direct preparation of modified nanocelluloses in their natural aqueous medium, avoiding the laborious operations used in previous modification approaches, where organic solvents are required. Furthermore, this approach bears strong green chemistry connotations. The incorporation of the sleeved nanofibers into natural rubber confirmed the interest of this physical modification.<sup>279</sup>



**Figure 6.** SEM micrographs of the cross-sections of NR/BC10, broken with a tensile machine at room temperature, observed at two different magnifications. Reprinted with permission from ref 278. Copyright 2012 Elsevier.



**Figure 7.** Admicellar polymerization of a monomer at the surface of cellulose fibers.

### 5.6. Concluding Remarks

The opening assertion concerning the progressively more sophisticated exploitation of cellulose finds here a clear continuity with the advent of nanocelluloses and their rapid development. The scaling up of CNC, BC, and NFC production is very important, since their substrate source is ubiquitous and cheap, and this is already taking place, albeit at different rates. Nanocelluloses are witnessing a rapid ascent as renewable materials, pushing the limits of their future implementations.

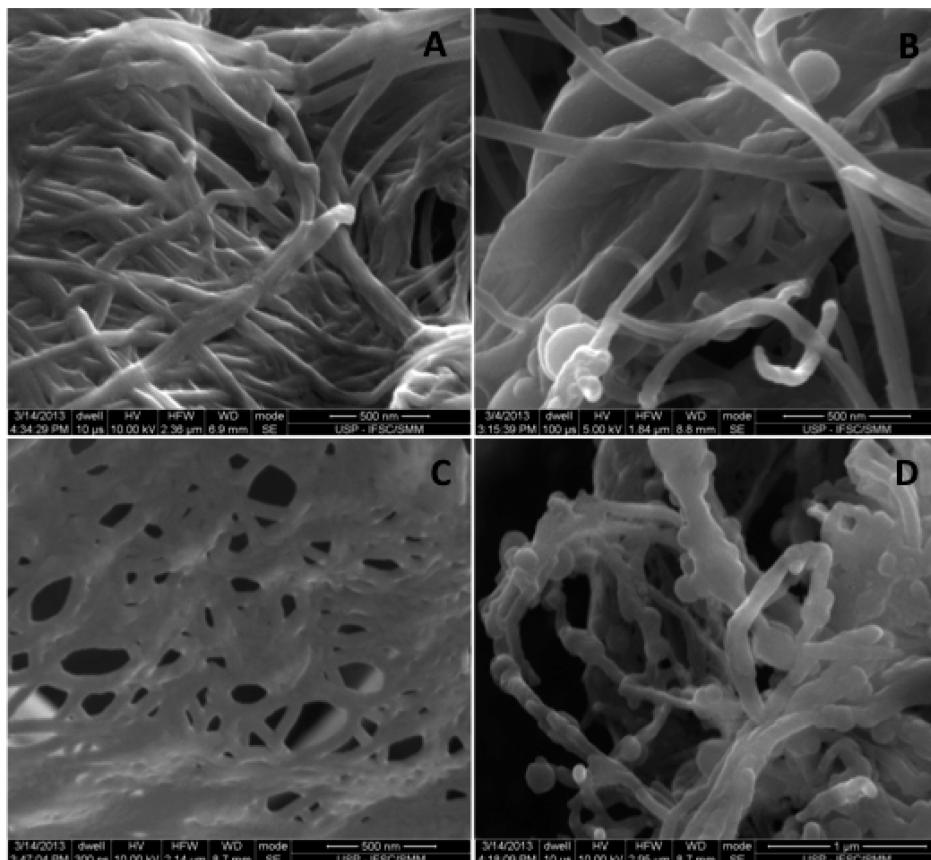
### 6. SUMMARY AND OUTLOOK

This overview of recent advances in the polymer chemistry related to some of the most important renewable resources hopefully highlighted the huge variety of biobased materials that can be obtained from furans, plant oils, starch, and cellulose.

The use of by-now-overexploited terms such as “green” and “sustainable” requires some comments as concluding remarks to clarify our work philosophy when studying polymers from renewable resources. On one hand, green chemistry has been formally enshrined in the classical dodecalogue put forward by Anastas and Warner,<sup>289</sup> but it is rare that even the most scrupulous studies comply exhaustively with these stringent requirements, although progress in that direction is constantly being realized. In the examples related to our investigations discussed here and indeed in most of our research, efforts were systematically made to move forward in the general direction set out by those postulates. Quite apart from the basic issue of using renewable resources, aspects related to minimizing the

use of unsafe reagents, catalysts, and solvents, applying mild reaction conditions, implementing biobased processes, and attaining maximum atom economy, among others, were constantly on our mind, as underlined by the use of the term “green chemistry connotations” to emphasize the incomplete fulfilling of the “official” requirements. In other words, we recognize the limitations still in place in this context, in which our central tenant of exploiting renewable resources was by definition the first priority. This state of affairs is in fact common to most publications in this area, with varying degrees of preoccupation toward complementing the main purpose with green chemistry implementations. The issue of sustainability, on the other hand, cannot be adequately fulfilled merely by the otherwise basic use of renewable resources, because other important aspects must be taken into account. First and foremost among them is of course the ultimate economic competitiveness of any novel polymer destined to replace an equivalent material presently manufactured from fossil resources, unless the former possesses one of several properties with superior performances compared to those of the latter. The successful examples are still scarce, mostly because equally scarce are the processes which have been scaled up to production levels. In the examples discussed in the review, the furan-based PEF represents the most promising situation, precisely because of the positive results related to some of its functional properties, as compared to those of its aromatic and fossil-based PET. The other highly relevant aspect associated with sustainability has to do with the implementation of a satisfactory biorefinery operation when dealing with the need to separate different biomass components, as in the case of lignocellulosic substrates, i.e., the search for the optimized exploitation of each of them. Considerable advances have been made in this area, thanks to the cooperative research involving experts in bioprocesses, monomers and polymers, the isolation of valuable compounds (both standard commodities and unique structures), and sources of alternative energy. These considerations obviously apply to the topics selected for the review, more so for furans and vegetable oils and less importantly for the polysaccharides.

It is clear that further developments are needed, both in novel approaches and in the industrial implementation of the most promising processes, but the outlook is bright thanks to the motivation of the scientific and technological communities



**Figure 8.** SEM micrographs of BC (A) and NFC (C) nanofibers and their respective sleeved counterparts BC–poly(styrene) (B) and NFC–poly(lauryl acrylate) (D) by admicellar polymerization.

involved in this effort to replace progressively fossil resources with sustainable counterparts.

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### Notes

The authors declare no competing financial interest.

### Biographies



For the past 56 years Alessandro Gandini has conducted research and taught chronologically in Switzerland, the United Kingdom, Canada, the United States, Cuba, Canada, France, Brazil, and Portugal, and now in France and Brazil, with invited professorships in numerous other countries. Polymer chemistry, photochemistry, and surface

science have dominated his professional interests, with a progressively growing involvement in polymers from renewable resources, a topic he was one of the first to investigate and promote.



Talita M. Lacerda was born in 1986 in São Carlos, SP, Brazil. She received a B.S. degree in chemistry in 2008 and a Ph.D. degree in chemistry in 2012, both from the São Carlos Institute of Chemistry, University of São Paulo. She joined Professor Alessandro Gandini's research group at the University of São Paulo in 2012 as a postdoctoral researcher. Since then, she has been investigating the development of novel thermoreversible polymers based on vegetable oils and furan derivatives. She also held a postdoctoral position for one year (2013–2014) in Professor Michael A. R. Meier's group at the Karlsruhe Institute of Technology, Karlsruhe, Germany. Her research interests mainly cover the field of synthesis and characterization of novel polymer materials from renewable resources.



Antonio J. F. Carvalho is an associate professor in the Department of Materials Engineering in the São Carlos School of Engineering, University of São Paulo. He received his B.Sc. (chemistry) and M.Sc. (physical chemistry) degrees from the University of São Paulo. During his M.Sc. work, he moved to the Pirelli Corp. in São Paulo, where he worked for 10 years in research and development of polymer materials for cable insulation. He then completed a Ph.D. in materials science at the University of São Paulo (wood fiber composites of thermoplastic starch), and after a postdoctoral experience at the Physics Institute of São Carlos (ionomer copolymers for organic light-emitting diodes), he moved to the Federal University of São Carlos and then to the University of São Paulo in his present position. His research interests include thermoplastic starch, development of nanocomposites from nanocelluloses, blends, and composites of polymers from renewable resources, and surface and interface science.



Eliane Trovatti was born in Brazil. She graduated with a master's degree in pharmaceutical sciences and biochemistry and a Ph.D. degree in biotechnology from São Paulo State University. She was a postdoctoral fellow at the University of Aveiro, Portugal, Wallenberg Wood Science Center, Sweden, and University of São Paulo. Her research interests include biomaterials and materials from renewable resources, the biotechnological process for the synthesis of cellulose from microorganisms, the synthesis of peptides with antimicrobial activity, and the development of composite materials based on cellulose, nanocelluloses, natural rubber, and polysaccharides.

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