

Marriage of Furans and Vegetable Oils through Click Chemistry for the Preparation of Macromolecular Materials: A Succinct Review

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ABSTRACT: The inevitable future scarcity of fossil resources, coupled with sustainability considerations, have stimulated the use of renewable resources for material synthesis, and highly efficient polymerization methods that meet the requirements of green chemistry have drawn attention to fatty acid-based polymers. Additionally, the polymerization of furan monomers and the exploitation of some of the chemical peculiarities of the furan heterocycle have generated a wide diversity of macromolecular materials. A novel approach is reviewed here, calling upon the combined use of both vegetable oils and their derivatives together with furans, as a promising technique to obtain new materials from two renewable resources. This succinct review provides an overview of the present strategies to produce linear and crosslinked thermally reversible polyadducts through Diels-Alder and other click reactions.

KEYWORDS: Vegetable oils, furans, thiol-ene reaction, Diels-Alder polymerization

1 INTRODUCTION

The predicted shortage of fossil resources, coupled with the instability of their prices, have spurred an impressive expansion of research in the last couple of decades related to alternative chemicals and materials derived from renewable resources. Within this blooming field, the use of vegetable oils, considered one of the most important classes of renewable resources [1], has shown potential for delivering a whole host of products as diverse as pharmaceuticals, coatings, packaging materials, fine chemicals, among others [2].

The structure of vegetable oils is schematically represented by the generic triglyceride formula (Figure 1a), in which R_1 , R_2 and R_3 are fatty acid chains that can mainly vary in length (from C12 to C22) and in the number of C=C unsaturations. In some cases, it is also possible to find other moieties bearing the aliphatic chain, e.g., -OH or epoxy groups, as shown in Figure 1b. A very important feature of vegetable oils is that they are always made up of a mixture of

triglycerides, often with one or two predominant structures making up 70–80% of its composition [3].

The degree of unsaturation of a vegetable oil is perhaps its most relevant characteristic, which can be assessed by measuring their iodine value (IV), which classifies vegetable oils as drying ($IV > 130$), semi-drying ($100 < IV < 130$), and non-drying ($IV < 100$) [4]. This parameter relates to properties like siccativity in coatings, lacquers, paints and inks, i.e., the drying of the oil by atmospheric oxidopolymerization, but also other types of polymerizations and chemical modifications [3].

In general, three main routes are exploited for the preparation of polymers from plant oils (Figure 2) [5]. The first is the direct polymerization of the triglyceride molecule through the double bonds or other reactive functional groups present in the fatty acid chain. The second consists of the chemical modification of the double bonds, introducing functional groups which are easier to polymerize, and the third is the chemical transformation of plant oils into original monomer structures.

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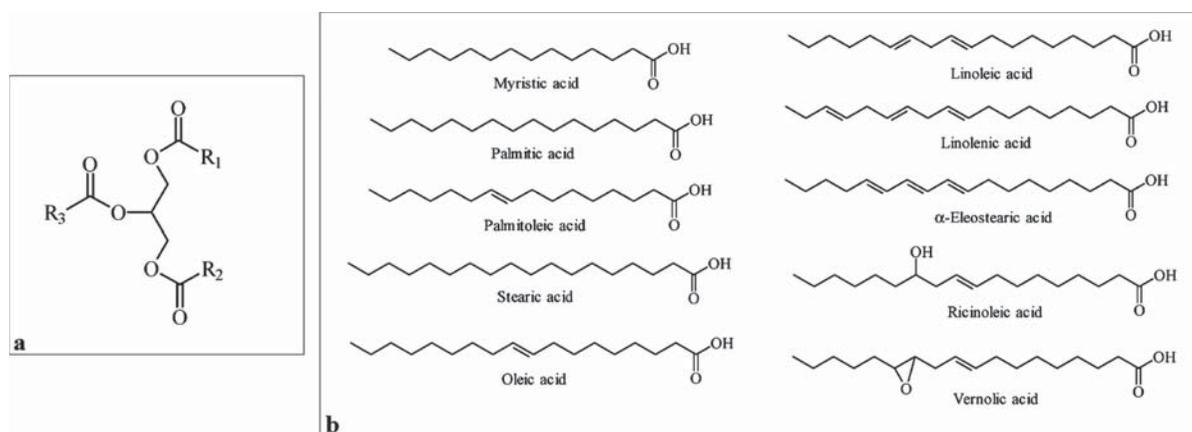


Figure 1 (a) Schematic representation of the structure of vegetable oils and (b) typical fatty acids borne by them [3].

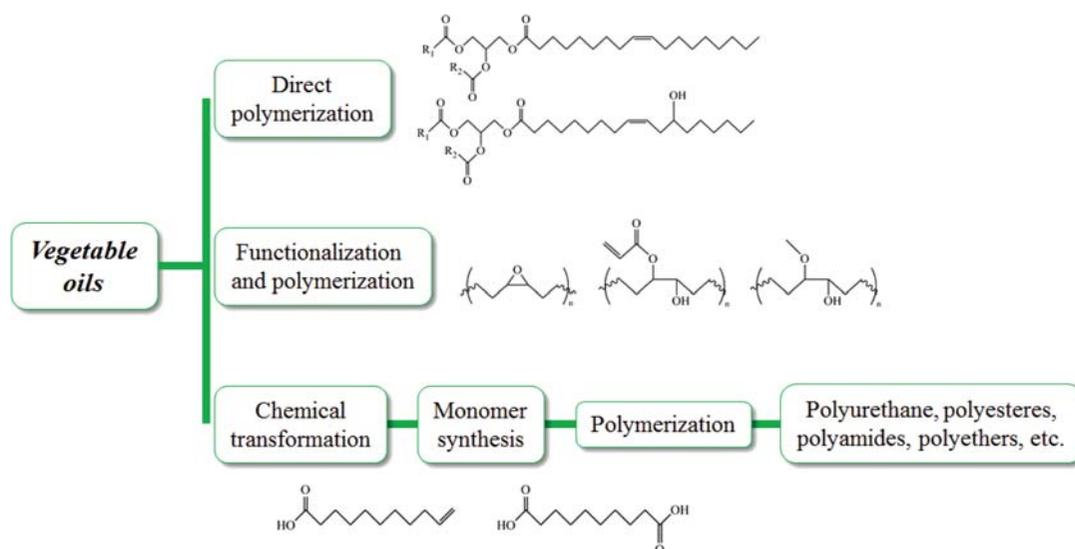


Figure 2 Three possible routes for the synthesis of plant oil-based polymers [5].

Concurrently, the chemistry of furans and its derivatives has been widely studied, and research in this field proved their unquestionable potential to provide entry to a whole family of monomers derived from the two first-generation furan compounds, i.e., furfural (F) and 5-hydroxymethylfurfural (HMF), directly obtained from sugars or polysaccharides, and hence a variety of macromolecular structures with different properties [6]. Furfural provides entry to monomers suitable for chain growth, whereas HMF is the ideal precursor to monomers for step growth, and hence their combined exploitation can simulate all the current fossil-derived counterparts [7–9].

The marriage of vegetable oils and furan derivatives relies on the fact that despite the former structures contain functional groups such as double bonds or epoxy moieties, their reactivity towards polymerization is often limited. Thus the introduction of

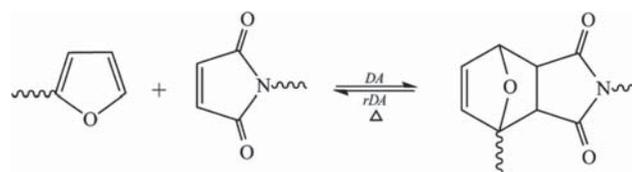


Figure 3 The DA/rDA equilibrium between growing species bearing furan and maleimide end groups.

furan heterocycles into their molecules gives access to a large range of novel polymers with original properties through fairly straightforward and efficient processes, particularly through the Diels–Alder (DA) click reaction [10]. The originality of this [4+2] cycloaddition between a conjugated diene and a dienophile, apart from its click connotation, is its reversible character, illustrated in Figure 3, which shows the specific case of the coupling of a furan ring (the diene) with a

maleimide complementary moiety (the dienophile). The temperature is a key factor in determining the position of the equilibrium, which can be shifted from the predominant adduct formation (DA reaction), at temperatures close to 65°C, to the predominant reversion to its precursors (retro-DA reaction), above 100°C [10, 11].

This brief review aims to describe the state of the art of the association between vegetable oils and furans to produce thermo-reversible linear and crosslinked polymers thanks to the versatile DA/rDA click reaction. The first part is devoted to the synthesis of monomers from isolated fatty acid molecules, using another click mechanism, namely the thiol-ene reaction, and their polymerization, whereas the second describes the use of the crude plant oils to prepare monomers and polymers therefrom.

2 DOUBLE CLICK STRATEGY APPLIED TO THE REVERSIBLE POLYMERIZATION OF FURAN/VEGETABLE OIL MONOMERS

The purpose of this investigation was to append furan moieties to molecules issued from triglycerides through thiol-ene coupling and then polymerize these

furan-bearing monomers using their Diels-Alder polycondensation with complementary maleimide functions. The plant oil derivatives used for the study of bifunctional monomers [11] were based on undecenyl acid (UA), an industrial commodity obtained from the pyrolysis of castor oil used as a precursor to the synthesis of Nylon-11. The undecenyl compounds were used as substrates to append two terminal furan (A) heterocycles or both furan (A) and a maleimide (B) end-groups, calling upon the thiol-ene reaction in conjunction with more classical chemical condensations.

Figures 4, 5 and 6 illustrate schematically how these monomers were synthesized. The protection of the AB monomer with the maleimide function masked by its DA adduct with furan was indispensable in order to avoid its premature polymerization during its synthesis and/or storage [11].

The ensuing AA, AA' and protected AB monomers were then polymerized via the DA reaction (Figure 3), the former with different bismaleimides (BB), the latter on its own, after deprotection by heating it at ~100 °C to remove the furan through the retro-DA reaction. Figure 7 illustrates the mechanism of all these DA polycondensations. Various bismaleimides were used in order to prepare polymers with different glass transition temperatures [11].

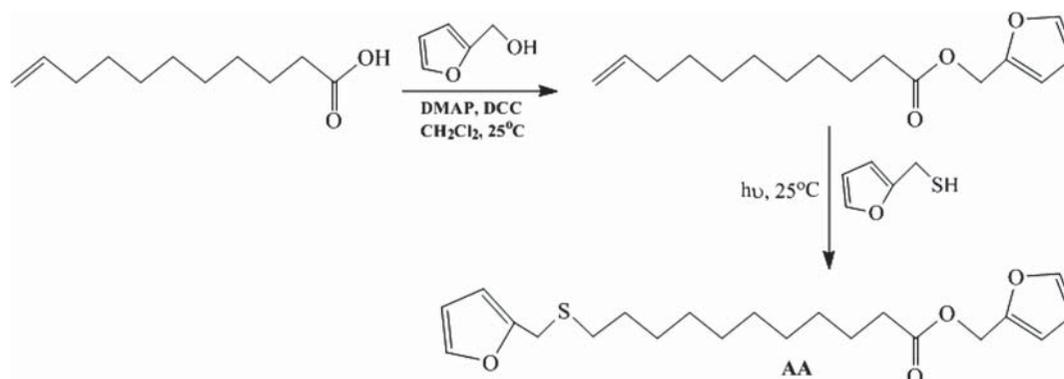


Figure 4 The synthesis of one of the AA monomers.

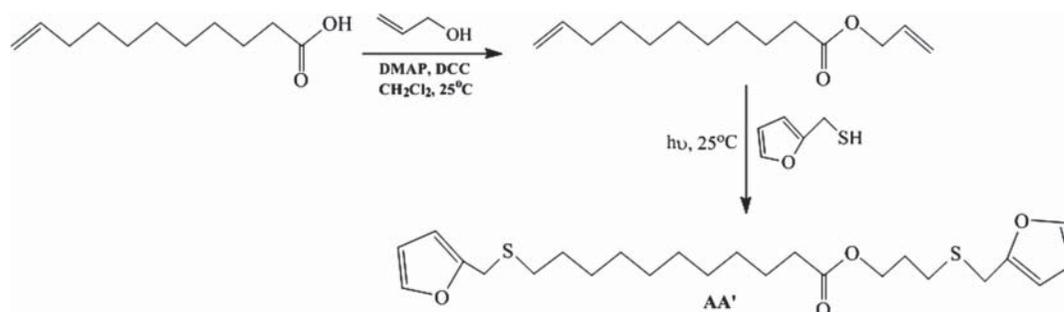


Figure 5 The synthesis of another AA monomer.

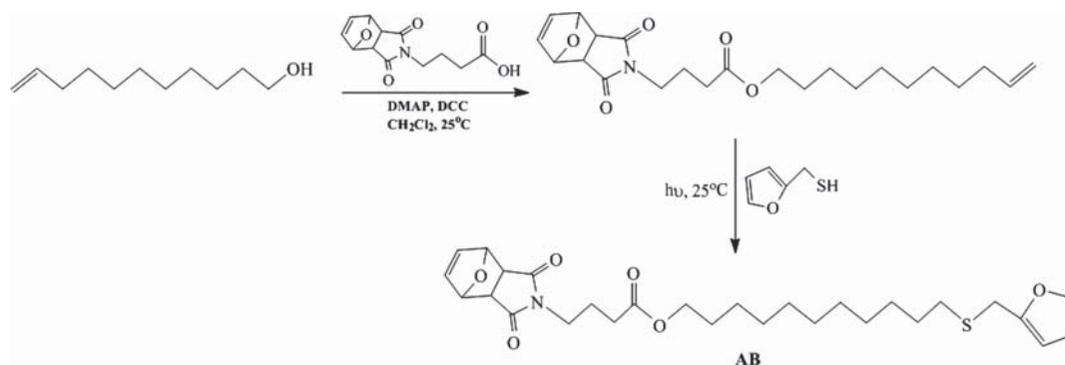


Figure 6 The synthesis of a protected AB monomer.

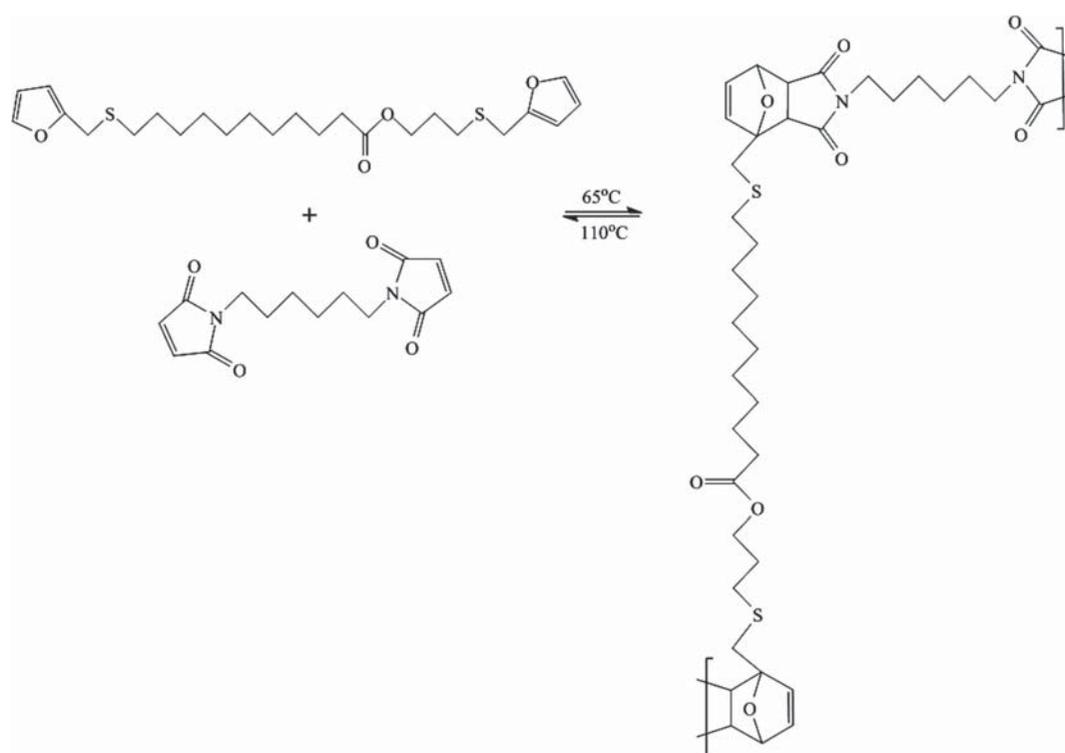


Figure 7 A typical thermally reversible linear DA polycondensation, here with bisfuran AA' and hexamethylenebismaleimide.

Reactions, carried out at 65°C, were followed by UV spectroscopy and revealed a progressive decrease in the optical density of the maleimide peak at ~300 nm (due to the loss of its conjugation system upon adduct formation), accompanied by a corresponding increase in the viscosity of the medium. The concomitant changes in the ^1H NMR spectra displayed a gradual decrease in the intensity of the maleimide and furan proton resonances at a rate similar to that of the UV spectra evolution and the parallel surge of the peaks associated with the three sets of protons attributed to the adducts. Typically, several days were necessary to

reach high conversions. The polymers, isolated by precipitation in petroleum ether and vacuum drying, gave Tg values ranging from ~ -40 to 0°C and Mw from 7000 to 17000 with SEC tracings suggesting the presence of cyclic oligomers, including the corresponding dimers, through the appearance of individual peaks within the distribution curves [11].

The polymers were then submitted to the corresponding retro-DA depolymerization at 110°C (Figure 3), followed by UV and ^1H NMR spectroscopy. These processes were characterized by the reverse pattern with respect to the polycondensations,

consisting of the gradual increase in the maleimide peak at 300 nm, the concomitant decrease in the adduct resonance intensities and the corresponding growth of the furan and maleimide counterparts, together with the decrease in viscosity of the solutions. Within a few days, the spectra revealed the presence of the starting monomers, thus confirming the thermo-reversible character of these systems. These regenerated monomers could in turn be re-polymerized by heating at 65°C, emphasizing the reproducibility of these cycles of events [11].

The next systems investigated within this approach were nonlinear DA polycondensations in which trifunctional monomers (Figure 8) were coupled with difunctional complementary counterparts or self-polymerized, if they bore both furan and maleimide

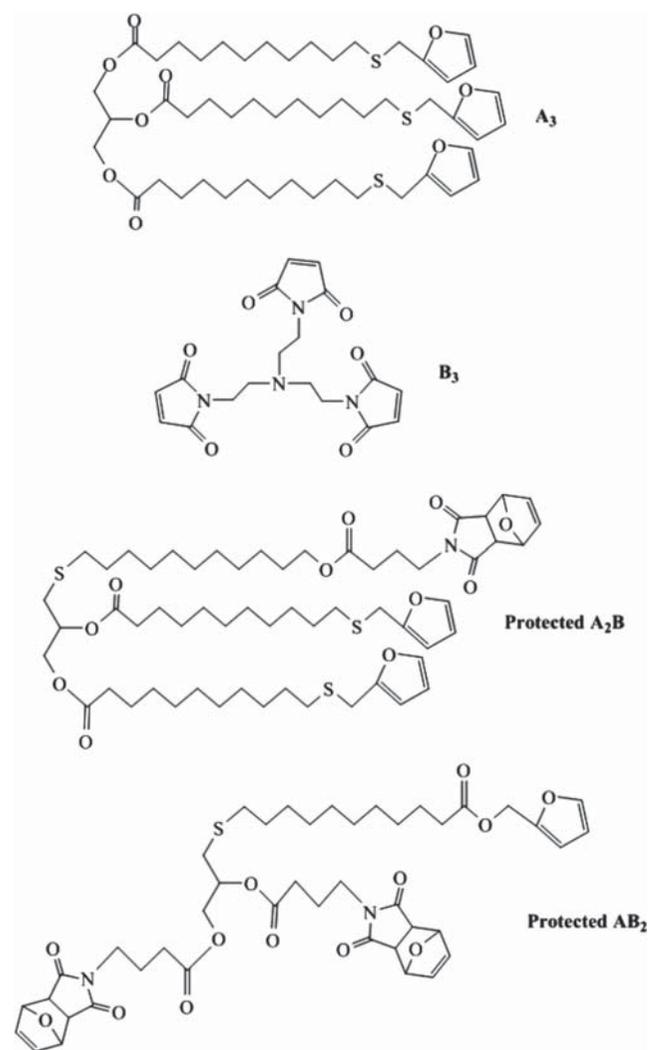


Figure 8 The trifunctional monomers used in the nonlinear DA polycondensations.

moieties [7]. Figures 9–11 show the synthetic pathways used to prepare the trifuran monomer A₃, the AB₂ and the A₂B protected monomers, respectively, again calling upon different applications of the thiol-ene click reaction. The aliphatic trismaleimide was synthesized for this study [7]. The bifunctional monomers used here were hexamethylenebismaleimide and the A₂ difuran, as prepared in the previous investigation [11] (Figure 4).

The DA polycondensations were carried out and followed as described above for their linear counterparts and displayed the same trends and qualitative features, except for the much steeper viscosity increase, including the formation of gels in certain instances [7].

Different B/A ratios were applied in order to explore the behavior of both the non-crosslinking branching systems and reactions leading to networks. Figure 12 shows the principle of one of these thermoreversible nonlinear polymerizations leading to gel formation under appropriate B/A initial ratios. Of course, when monomers A₂B and AB₂ were used, they self-polymerized after the appropriate deprotection and only gave hyperbranched products, since these structures cannot crosslink. Figure 13 shows one such system [7].

All these polymers were thoroughly characterized and then submitted to the retro-DA reaction, which always produced a progressive depolymerization all the way to the initial monomers [7].

3 USE OF PRISTINE PLANT OILS AND FURANS FOR SYNTHESIS OF MONOMERS AND POLYMERS

3.1 Direct Polymerization of Pristine Tung Oil

As mentioned above, the internal unsaturations of some vegetable oils can be activated through a free radical or a cationic polymerization mechanism [12, 13].

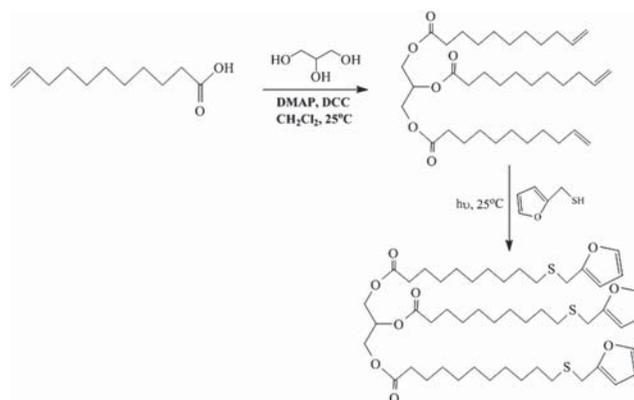
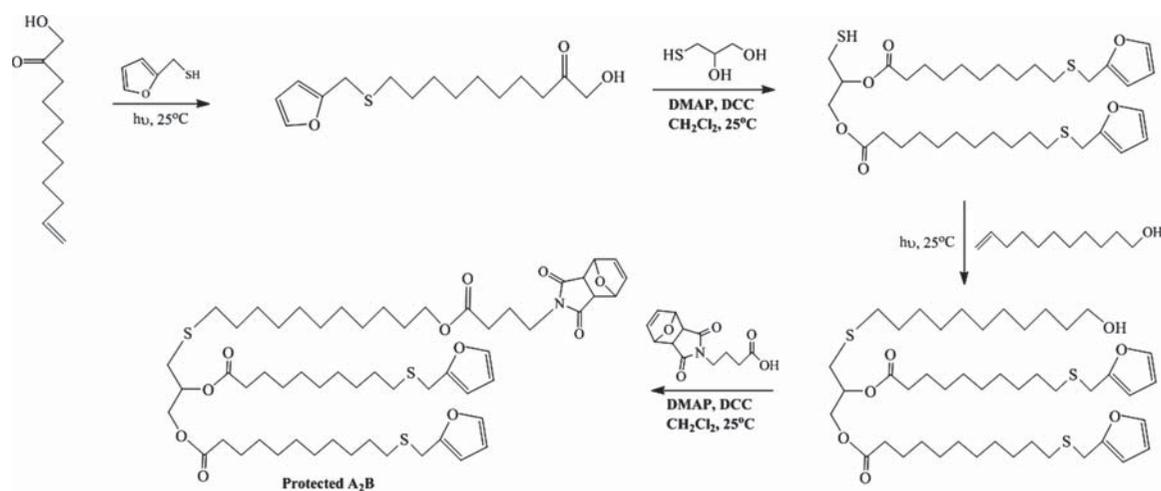
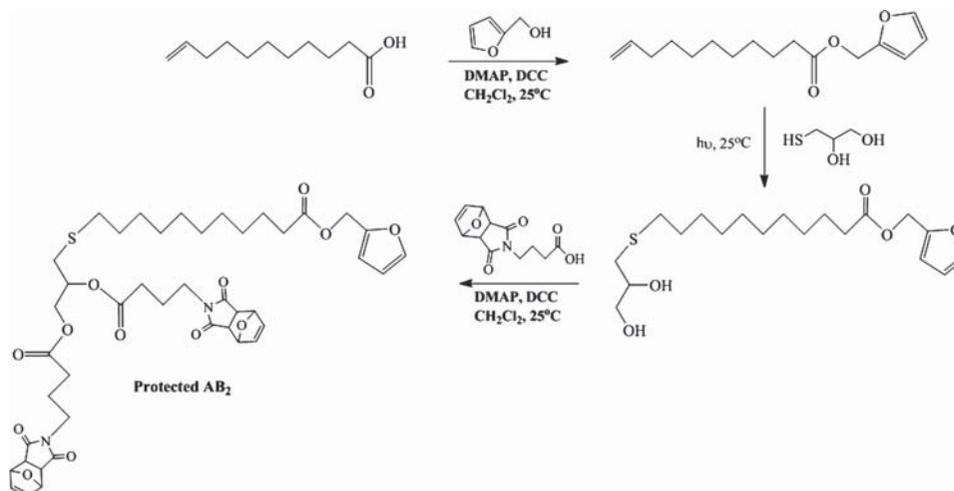
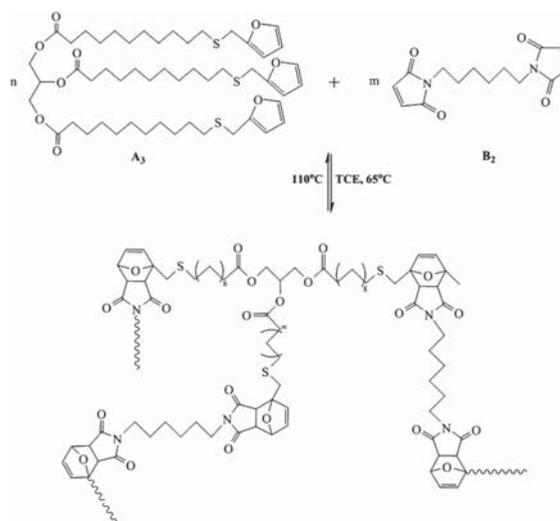


Figure 9 Synthesis of the trifuran monomer.

Figure 10 Synthesis of the protected A_2B monomer.Figure 11 Synthesis of the protected AB_2 monomer.Figure 12 The thermoreversible nonlinear DA polycondensation of $A_3 + B_2$ leading to gel formation.

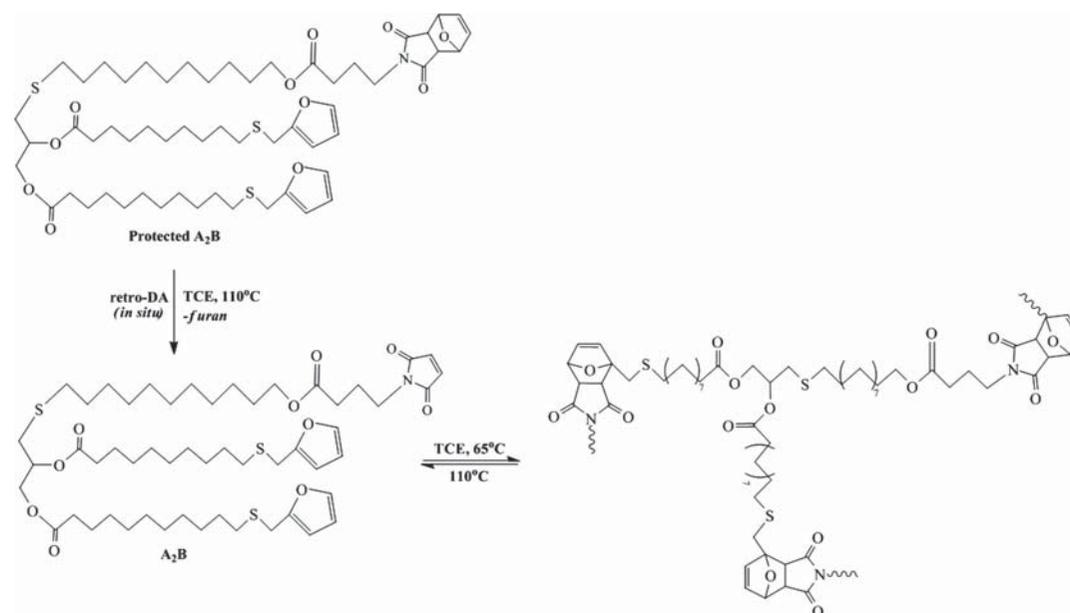


Figure 13 The DA self-polycondensation of A_2B giving a hyperbranched structure.

In the former context, linseed oil (LO) and tung oil (TO), mostly composed of, respectively, linolenic and α -eleostearic acids (Figure 1b), have been used in paints, inks and coatings, due to their drying properties associated with atmospheric oxidopolymerization. Alternatively, the cationic copolymerization of these C=C double bonds, catalyzed by boron trifluoride diethyl etherate, leads to thermosetting polymers ranging from rubbers to hard plastics with a variety of oils, with petroleum-based comonomers such as styrene, divinylbenzene and dicyclopentadiene [14]. These processes can, however, be relatively inefficient because of low reactivity, and that is the main reason why the overwhelming majority of studies involve methods for the copolymerization of chemically modified triglycerides and fatty acids.

The direct utilization of crude plant oils without further treatment in polymer synthesis is nevertheless of high practical significance, since the derivatization steps require additional reagents, generate waste, and should therefore be minimized or avoided if greener procedures are desired.

Tung oil is a peculiar triglyceride structure in which each chain bears three conjugated unsaturations. Although its use in this context has been much less important to date than that of such oils as soybean, castor and linseed, a number of studies have been devoted in recent years to new approaches toward the polymerization of pristine TO or of monomers derived from its chemical modifications [15]. These include materials based on (i) TO, styrene [16] and

divinylbenzene [17], (ii) the cationic polymerization of the oil [18], (iii) monomers derived from the introduction of carboxylic groups onto the oil structure using its DA reaction with maleic anhydride [16, 19], and (iv) TO-based polyurethanes [20]. The use of TO as a dienic monomer in the DA polymerization with a bismaleimide was first reported in a study [21] which, however, applied very drastic temperature conditions to promote the couplings and led to side reactions. Recently, we investigated a more systematic approach to this system using milder conditions (80°C) which avoided side reactions, using a selection of bismaleimides in order to obtain products with different properties [15]. Figure 14 shows the mechanism of this nonlinear DA polycondensation.

In this study, it was possible to produce crosslinked polymers with glass transition temperature ranging from -10°C to 75°C , depending on the relative flexibility of the different bridging units in the bismaleimides (R, Figure 4). As for their thermal stability, the TGA tracings showed the onset of mass loss at about 350°C with a gradual descent to 550°C [15].

The radical structural change associated with the formation of the adduct in this case is responsible for the fact that the retro-DA reaction does not take place, at least within practically accessible temperatures, in contrast with the furan/maleimide combination discussed above. In other words, the present triene-maleimide DA system possesses the characteristic features of a click chemistry reaction, albeit without the additional advantage of thermal reversibility, and

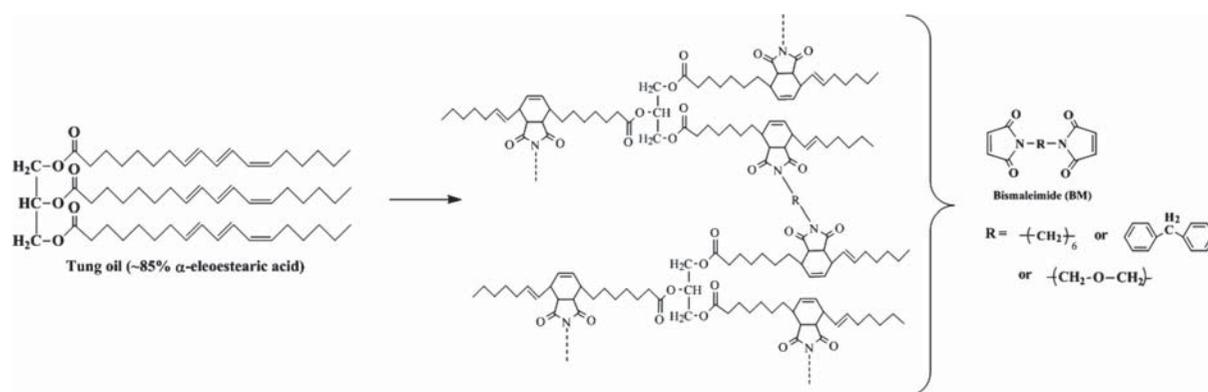


Figure 14 Schematic representation of the use of crude TO to produce Diels-Alder-based polymers.

therefore the materials described above cannot be deconstructed by heating [15].

3.2 Polymerization of Chemically Modified Linseed and Tung Oils

Among the most interesting chemical modifications of oils and fatty acids, epoxydation occupies a privileged position for the number and variety of studies and applications it has spurred [22–25]. This reaction involves the transformation of C=C alkenyl moieties along the fatty acid chain into oxirane groups using a variety of oxidation systems, although terminal epoxy functions have also been appended to saturated triglycerides [22–25]. Both the epoxidized oils as such and a variety of acrylated and other derivatives have been polymerized and copolymerized to give materials with different promising properties and, as a consequence, some of these novel monomers are industrial commodities today [22–25].

Our group recently examined the possibility of preparing DA monomers based on fatty acid derivatives bearing two or more furan rings in their structure, starting from commercial epoxidized oils [26] by exploiting their liability to react with furfuryl amine (FA) by two different mechanisms, viz., through the coupling with the oxirane moiety by ring opening and through the aminolysis of the glyceride ester groups, thus generating three fatty-acid monomers in which the furan heterocycles would be present as both furfuryl secondary amine and furfuryl amide moieties. Figure 15 shows the two parallel reactions developed in the specific case of the reaction of industrial epoxidized linseed oil (ELO) with FA. The only previous report on a similar system described the zinc chloride catalyzed ring opening of the oxirane moieties of epoxidized soybean oil (ESO) induced by diethylamine, under experimental conditions that

purportedly minimized aminolysis [27]. Zinc perchlorate has also been reported to accelerate the reaction between primary amines and 1,2-disubstituted epoxides [28], but the catalyst was not previously tested on epoxidized oils.

These two parallel reactions for the furan insertion were confirmed by ^1H NMR, FTIR spectroscopy and mass spectrometry [26]. Whereas the aminolysis reached completion in the chosen conditions, some of the oxirane rings were still present at the end of these reactions, probably because of steric hindrance associated with the presence of two contiguous oxirane rings.

Depending on the amount of oxirane groups in the fatty acid chain of the pristine oil, the final macromonomer will bear two or three furan moieties in their structure. However, the structures bearing three furan moieties were in a minority, since only some small amounts of gelled material were found in the reaction medium at the end of the process. This observation was corroborated by ^1H NMR spectroscopy, which showed that the integration of the appropriate peaks agreed with an average incorporation of just over two furan rings [26].

These monomers were then submitted to a study of their DA polymerizations using the commercial aromatic 1,1-(methylenedi-4,1-phenylene) bismaleimide, as the complementary monomer. The ^1H NMR spectra of the ensuing polymers indicated that the DA polycondensation had indeed taken place, since the furan and maleimide proton signals had been replaced by the characteristic counterparts for the corresponding DA adducts. The GPC of these polymers gave average Mw values ranging from 35 000 to 40 000, with PDIs around 5, which clearly indicated that some branching reactions had accompanied these largely linear DA polycondensations. The DSC of these materials indicated that they were amorphous, with glass transition temperatures comprised between 80 and 100°C. The

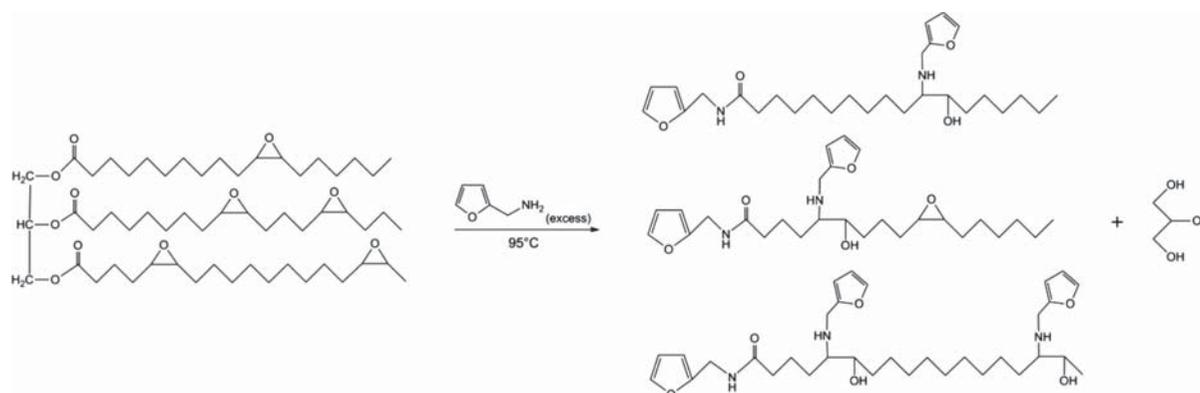


Figure 15 Double insertion of FA onto ELO by aminolysis and oxirane ring opening [26].

TGA tracings showed a thermal stability up to $\sim 250^\circ\text{C}$ followed by a weight loss extending to 700°C with a graphitic residue of about 30% [26], the latter being in tune with the presence of both aromatic and furan structures [29].

The thermoreversible nature of these materials was verified by their aptitude to depolymerize at high temperature through the retro-DA reaction, which was carried out at 110°C . The solution viscosity decreased progressively with time and after 48 hours the ^1H spectrum displayed the reappearance of the resonances attributed to the three furan and the two maleimide protons.

The thorough characterization of the polymers and of the products of their depolymerization reactions is still in progress, together with other polycondensation reactions, including some using a trismaleimide to prepare thermoreversible crosslinked materials, and also some other epoxidized vegetable oils, such as soybean oil. These new materials have potential applications that include coatings and adhesives, with the unique feature associated with the possibility of removing them by a simple heating process due to their unique thermoreversible character.

An additional contribution to this ongoing research effort aimed at finding novel sources and strategies to valorize plant oils as precursors to original macromolecular materials, particularly with the conjunct incorporation of furan moieties, involves the reaction of TO and FA to synthesize macromonomers to be further polymerized with bismaleimides [15]. This method is similar to that described above involving ELO, with two main differences: (i) during the monomer synthesis, only aminolysis takes place, since the three conjugated bonds of TO do not react with FA and are therefore preserved for further use as dienic moieties in the subsequent DA polymerizations, and (ii) the depolymerization reaction involving the triene-maleimide DA system does not possess

the advantage of thermal reversibility, as already mentioned.

Figure 16 shows the monomer synthesis from TO and FA, and its subsequent polymerization with different bismaleimides.

The isolated fatty acid furfuryl amide (TOFA) gave FTIR, ^1H NMR and mass spectra entirely in tune with the expected structure with no evidence of the TO triene moieties having been affected by the reaction. The DSC tracings of TOFA revealed a semicrystalline character, as confirmed by its birefringence under polarized light optical microscopy, with a melting temperature at 63°C upon heating and a crystallization temperature of 30°C upon cooling [15].

After the linear DA polycondensations of TOFA and the three bismaleimides, none of the FTIR spectra of the resulting polymers showed the characteristic furan breathing mode peak around 1000 cm^{-1} or the maleimide peak near 700 cm^{-1} , indicating that near complete yield had been achieved in each reaction. The ^1H NMR spectra of these polymers confirmed the high yield of each polycondensation through the formation of both DA adducts, by the fact that the intensity of the furan characteristic proton resonances became very small, and the same applied to the resonance of the maleimide protons, which were replaced by the corresponding furan-maleimide adduct protons. The TGA tracings indicated that their thermal stability reached about 200°C , after which the loss of mass proceeded gradually up to 500°C . The glass transition temperatures of these materials ranged from 30 to 105°C , depending on the bismaleimide structure, and their GPC gave average M_w values ranging between 20 000 and 40 000 with a PDI always close to two, indicating that all the structures were in fact linear macromolecules [15].

As already mentioned, these polymers incorporated two types of DA adducts, only one of which, the

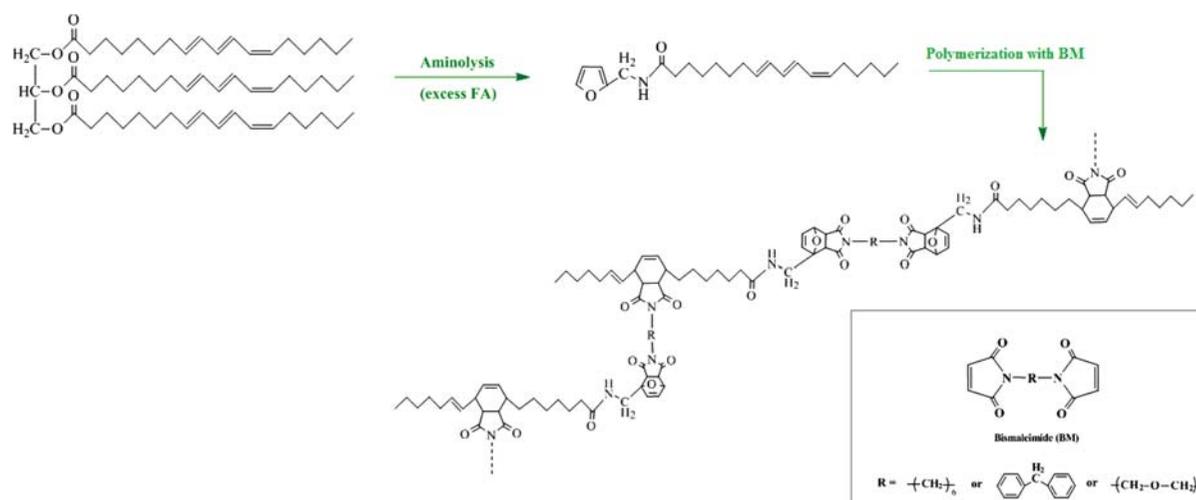


Figure 16 Schematic representation of the use of crude TO synthesized monomers and Diels-Alder-based polymers [15].

furan-maleimide structure, was susceptible to undergoing the retro-DA reaction above about 100°C. The materials were then kept at 120°C and the ^1H NMR spectra after 24 h clearly showed that this thermal treatment had given a high yield of the retro-DA reaction through the reversion of the furan-maleimide adducts, as evidenced by the reappearance of the three characteristic furan proton signals, the concomitant virtual disappearance of the adduct peak and the reappearance of the maleimide proton signal.

4 CONCLUDING REMARKS AND PERSPECTIVES

The working hypothesis based on associating two renewable resources to prepare original macromolecular materials through click chemistry, with particular emphasis on using pristine oils and green chemistry concepts, coupled with the fact that these polymers can be thermally reversible, appears to produce worthwhile results in terms of possible applications in different domains. Further work is therefore warranted to widen its scope.

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