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Bio-sourced Monomers and Cationic Photopolymerization: The Green combination towards Eco-Friendly and Non-Toxic Materials

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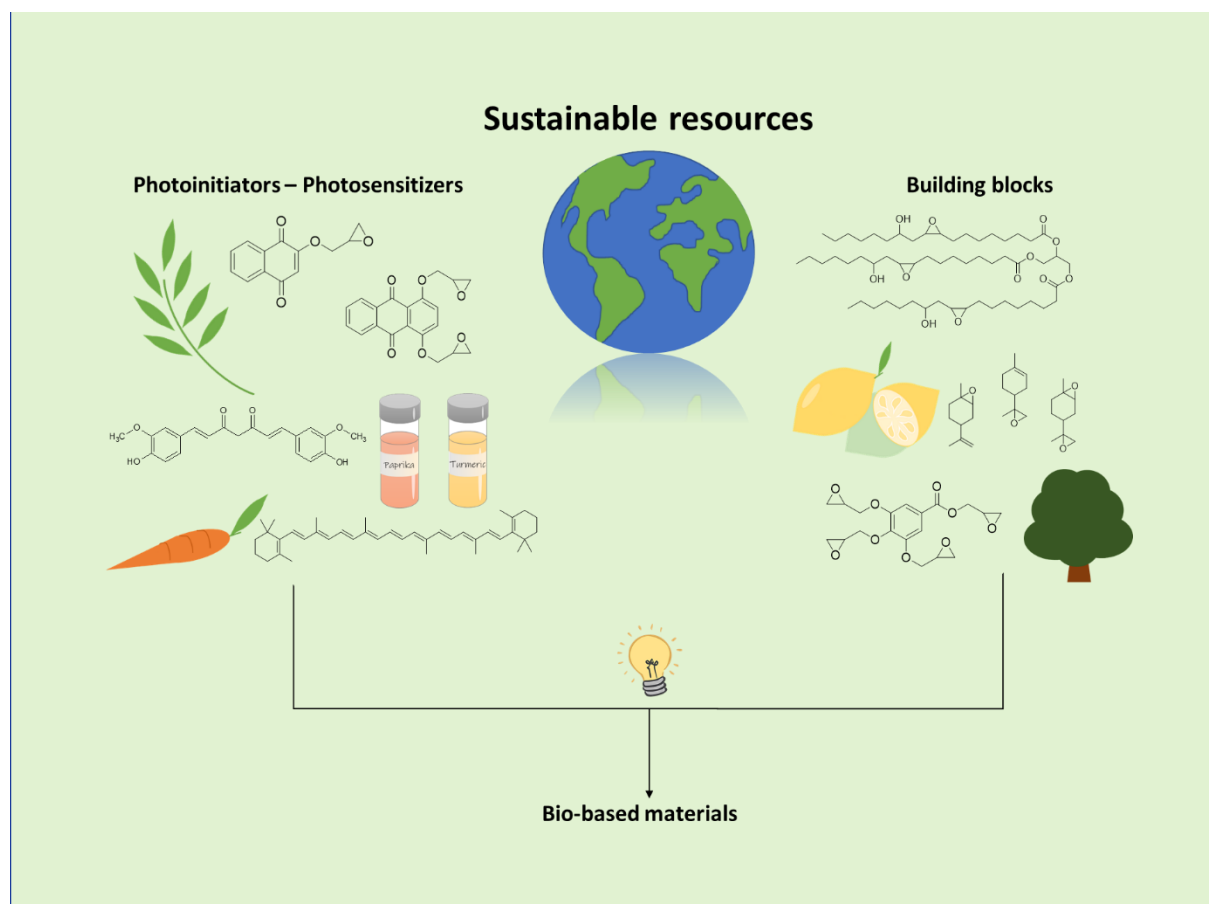
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Graphical abstract



Abstract

Cationic photopolymerization is among the greenest processes used to obtain polymers since light is abundant, inexpensive and allows for rapid and waste-less curing at room temperature. Moreover, in the current search for the reduction of the environmental impacts of polymers, the use of biobased monomers is one of the most crucial stakes. At the crossroads of these domains, biobased monomers photopolymerization offers the best of both. Hence, this review aims at underlying the increasing importance of cationic photopolymerization in combination with bio-based photopolymerizable monomers, and describes the numerous reactive species derived from bioresources that can lead to innovative materials through cationic photopolymerization reactions. This review intends to be a guide to orient academic teams and industries involved in reducing both environmental impacts and toxicity towards the synthesis of environmentally-safe materials. The recent advances on the photochemical systems used, the toxicity of the cationic photoinitiating systems, the reactivity of the new epoxy bio-sourced monomers, their thermomechanical properties as well as the applications of the targeted materials will be described.

Keywords: epoxy monomers; bio-based polymers; renewable resources; photochemistry; cationic photopolymerization

Abbreviations

33DDS	3,3'-diaminodiphenylsulphone
3HF	3-hydroxyflavone
AESO	Acrylated epoxidized soybean oil
BADGE	Bisphenol A diglycidyl ether
BAPO	Bis-acylphosphine
bFdE	Bis-furan diepoxide
Bis-GMA	Bisphenol A glycidyl dimethacrylate
BPA	Bisphenol A
BPB	Bisphenol B
BPM	Bisphenol M
BPS	Bisphenol S
CHO	Cyclohexene oxide
CMD1-4	Curcuminoid derivatives
CNSL	Cashew nutshell liquid
CP	Cationic (photo)polymerization
CQ	Camphorquinone
DB1	Disperse blue 1
DB3	Disperse blue 3
DDM	4,4'-diaminodiphenyl methane
DETA	Diethylenetriamine
DGEBA	Bisphenol A diglycidyl ether
DGEVA	Diglycidylether of vanillyl alcohol
DGFDC	Diglycidyl furan-2,5-dicarboxylate
DHAQ	Dihydroxyanthraquinone
DMF	Dimethylformamide
DMPA	2,2-dimethoxy-2-phenylacetophenone
DSC	Differential scanning calorimetry
DSO	Dihydroxy soybean oil
DVE-3	<i>Tri</i> (ethylene glycol) divinyl ether
ECD	Epoxidized cardanol derivatives
ECH	Epichlorohydrin
ECHA	European Chemicals Agency
ECLO	Epoxidized cyclohexene linseed oil
ECO	Epoxidized castor oil
EGE	Eugenol glycidyl ether
ELNR	Epoxidized liquid natural rubber
ELO	Epoxidized linseed oil
EMX	Epoxidized fatty acid methyl esters
ENLO	Epoxybornane linseed oil
EPOX	(3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate
EPR	Electronic paramagnetic resonance
ESO	Epoxidized soybean oil
EVO	Epoxidized vegetable oil
FCA	2-furan carboxylic acid
FDCA	2,5-furan dicarboxylic acid
FdE	Furan diepoxide
FDM	2,5-furan dimethanol

FM	2-furan methanol
FmE	Furan monoepoxide
FRP	Free radical (photo)polymerization
FRPCP	Free radical-promoted cationic polymerization
GEC	Glycidyl ether of catechin
HEMA	2-hydroxyethylmethacrylate
HMDA	Hexamethylenediamine
HNQ	Hydroxy-1,4-naphthoquinone
HNQA	Allylated hydroxy-1,4-naphthoquinone
HNQE	Epoxidized hydroxy-1,4-naphthoquinone
HSA	(R)-12-hydroxystearic acid
IBVE	Isobutyl vinyl ether
INA	Ice nucleation active
Iod	Iodonium salt
IPDA	Isophorone diamine
LDO	Limonene dioxide
LED	Light-emitting diode
Lim	Limonene-1,2-epoxide
m-CPBA	Meta-chloroperoxybenzoic acid
MMA	Methyl methacrylate
MN	Micronuclei
MXDA	<i>m</i> -xylylenediamine
NVK	<i>N</i> -vinylcarbazole
OBN	Oil blue N
OPC	Organic photoredox compound
P	Purpurin
PA	Purpurin <i>tri</i> -allyl
PAG	Photoacid generator
PET	Poly(ethylene) terephthalate
PHA	Polyhydroxyalkanoate
PHF	Penta-hydroxy flavone
PHTE	Phloroglucinol trisepoxy
PI	Photoinitiator
PIS	Photoinitiating system
PLP	Pulsed laser polymerization
PmA	Purpurin mono-allyl
POM	Polyoxometalate
PS	Photosensitizer
PSA	Pressure-sensitive adhesives
PVC	Poly(vinyl) chloride
QA	Allylated quinizarin
QE	Epoxidized quinizarin
QUIN	Quinizarin
QZ	Quinizarin
RGDE	Resorcinol diglycidyl ether
RNS	Reactive nitrogen species
ROP	Ring-opening polymerization
ROS	Reactive oxygen species
SOC	Spiroorthocarbonate
TBBPA	Tetrabromobisphenol A
TEEP	<i>Tri</i> (epoxy eugenyl) phosphate
TEGDMA	<i>Tri</i> (ethylene glycol) dimethacrylate

TEOS	Tetraethylorthosilicate
TEP	<i>Tri</i> (eugenyl) phosphate
Tg	Glass transition temperature
THAQ	<i>Tri/tetra</i> -hydroxyanthraquinone
TPO	2,4,6-trimethylbenzoyldiphenyl phosphine oxide
UDMA	Urethane dimethacrylate
γ -TO	γ -terpinene oxide

1. Introduction

For more than 40 years, light-induced polymerization has gained an increasing interest and became the cornerstone of many conventional applications in microelectronics, coatings, adhesives, dental applications and more recently, 3D-photoprinting technology [1–5]. Photochemical reactions have also been highlighted by other valuable but less traditional applications in biomaterials [6], surface grafting [7,8], metal nano and micro-composites [9], (semi)-interpenetrated networks [10], photoresponsive materials [11], light-induced living/controlled polymerizations [12–15], spatially controlled photopolymerizations [16], two-photon polymerizations [17–20] and so forth.

In contrast to thermal-induced polymerization, photopolymerization highlights many striking advantages such as low energy consumption, fast polymerization reactions at room temperature or below, mild experimental conditions without the use of harmful solvents, and spatial and temporal control [5]. By means of photopolymerization, reactions occur in few seconds over hours with thermal process, and notably allow advances in dentistry and biological applications for which elevated temperature is unacceptable. Last but not least, fewer side reactions occur under photo-induced polymerization than in thermal process, which commonly leads to chain transfer reactions.

Two different mechanisms, i.e. free-radical and cationic photopolymerization, dominated most of the academic and industrial investigations in recent years [21]. Free-radical photopolymerization (FRP) is a widely performed technique to synthesize polymeric materials. This type of polymerization is limited to monomers with olefinic double bonds, essentially acrylate and methacrylate monomers, which readily react with photogenerated radicals [21,22]. Although FRP is widely used in industrial applications, oxygen remains an efficient radical scavenger that limits photopolymerization under air. Therefore, the light induced cationic photopolymerization (CP) could be an interesting alternative since it offers some advantages over FRP. A multitude of epoxide or vinyl ether-derived monomers can indeed be prone to CP, which is insensitive to oxygen contrary to FRP [21]. In addition, monomers usually used for cationic processes are known to be less irritating than acrylate and methacrylate-based systems [23–25]. Cationic curing processes are also characterized by a lower shrinkage and a lower residual stress thanks particularly to the use of ring-opening monomers [26,27] and cured materials often offer better abrasion and chemical resistance as well as better adhesion properties on various substrates [21,23,26]. Finally, once it is initiated, cationic photopolymerization can proceed once the light source has been removed thanks to the relatively long-lived Brønsted acid photogenerated by onium salts generally used as photoinitiators (PIs) [24]. This process, usually called the “dark reaction”, allows for improved monomer conversion [25].

Cationic photopolymerization initiated by the decomposition of onium salts under light irradiation was first described by Crivello & Lam in the 1970s [28–31]. A variety of onium salts, including sulfonium [32–36], iodonium [28,37], pyridinium [38–40], phosphonium [41,42], bismuthium [43], anilinium [44], pyrylium salts or others [45–47] have since then been extensively

studied and applied in both academic and industrial environments for the polymerization of various types of monomers. Cationic photopolymerization reactions are however hindered by several factors such as spectral sensitivity of onium salts or the processable thickness of the material layer due to the low penetration depth of UV light [23]. Concerning the spectral sensitivity of onium salts, it does not exceed the mid-UV range as most of these salts effectively initiate cationic photoinduced polymerization reactions when exposed to short and mid-UV wavelengths (200-300 nm range) [21,26,48]. Diaryliodonium salts mostly absorb around 210-250 nm and their absorption spectrum is characterized by a long absorption tail going as far as 370 nm [29]. These absorption properties prevent the efficient use of onium salts for visible light-induced CP processes, which is the reason why there has been a growing interest for the design of photoinitiating systems (PISs) capable of generating acids upon exposition to longer wavelengths in the visible light and near-IR regions by a photosensitization process [26,29,49]. Photosensitizers (PSs) are therefore judiciously combined with onium salts to perform CP reactions. Various classes of PSs can be cited like ketones, phenothiazine derivatives, electron-rich polynuclear aromatic hydrocarbons, metal carbonyls, organometallic as well as metallic salt complexes, silyl derivatives, etc. [48–52]. Surprisingly, few examples of natural biobased dyes used as PSs for CP are described in literature, and even fewer investigations concern the study of the cationic photopolymerization of biobased epoxy or vinyl ether monomers.

Nowadays, the recurring use of petro-sourced or non-renewable resources depletes the natural global supplies. The development of new methodologies for the synthesis of innovative materials derived from biomass appears as a real challenge for the scientific community. Additionally, the global political tendencies towards green sustainable chemistry are urging the chemical industries to shift to the use of renewable resources for synthesizing biobased products. As a consequence, the interest in renewable chemistry has tremendously grown in the last few years [53]. Researchers focused their attention on biobased polymers (polyhydroxyalkanoates, sugar, chitosan or triglyceride derivatives) or molecules extracted from foodstuffs, plants or microorganisms [54–56]. However, preliminary treatments (purification, chemical or enzymatic modifications, etc.) are needed to access pure molecules usable in the synthesis of materials. To date, fatty acids, starch or polysaccharides have been widely used but other biobased molecules such as tannins, polyphenols, eugenol, cardanol, lignin and derivatives are under consideration. Fortunately, these families of molecules are easily affordable and biosourced synthons, due to an incredible worldwide production. Nevertheless, and prior to polymerization, pure biosourced molecules should be modified to use them as monomers in polymer synthesis. Thanks to some promising methods of modification, the production of various monomers has been recently outlined [22]. Particularly, the global epoxy polymers production reached 3 million tons in 2017 and their global market increased to US \$21.5 billion in 2015, essentially in the coatings industry. The success of epoxies technology is probably due to their compatibility with many substrates, and the easiness of their synthesis to tailor material properties. Thus, the epoxy monomers synthesis from renewable resources is now a real challenge to reduce non-renewable resource consumption and avoid the use of hazardous chemicals to reduce human toxicity and ecotoxicity impacts. As a result, bisphenol A diglycidyl ether (DGEBA or BADGE), one of the most industrially used epoxy monomers, has recently been banned from food materials since it is considered as a reprotoxic R2 substance leading to some harsh health effects [57–59], including irreversible alterations of the immune and reproductive systems [60]. Therefore, the substitution of DGEBA has mainly implied focusing research on the synthesis of new non-harmful biosourced epoxy monomers with reduced health toxicity.

Therefore, this review not only aims at providing a state of the art on cationic photopolymerization processes applied to photoreactive and bio-sourced epoxy monomers, but also at being a guide to orient academic teams and industries involved in reducing both environmental

impacts and toxicity towards the synthesis of greener materials. The recent advances on the photochemical systems used, the toxicity of the cationic photoinitiating systems, the reactivity of the new epoxy bio-sourced monomers, their thermal/mechanical properties and the applications of the targeted materials will be described.

In the first of the following sections of this paper are described the different strategies for the design of bio-based epoxy monomers and building blocks from tannins and polyphenols, eugenol, cardanol, lignin and derivatives, starch and sugars, vegetable oils and fatty acids, terpenes, terpenoids and resin acids. They represent the main carbon sources for the synthesis of innovative bio-based materials but require preliminary modifications to become photoreactive.

In the following part, an overview of photoinduced cationic polymerization is provided. In particular, the photoinitiation mechanisms involving onium salts through direct light photolysis, free-radical promoted cationic photopolymerization and photosensitized reactions under UV-visible light irradiation are introduced. The photoinduced cationic polymerization of epoxy- and ether-derived monomers are briefly outlined, as well as the recent advances in the design of visible light sensitive onium salts and metal-based photoinitiating systems.

The description of newly developed light sources in the visible and IR range as well as natural solar irradiation conditions are discussed in the third part. An exhaustive overview of abundant, naturally occurring dyes demonstrating photosensitive properties, along with the current use of bio-renewable monomers in the framework of cationic photopolymerization, are also provided in this section. A particular attention is paid not only on the toxicity of both photoinduced resin-based composites and photoinitiating systems, but also on some alternative reactions based on cyclo-addition processes.

Finally, the variety of applications related to the cationic photopolymerization of bio-based monomers are reported in the final section of this review.

2. Strategies for the Synthesis of bio-based Epoxy Monomers

In the following section, a short introduction on epoxy monomers is given. The different strategies for the synthesis of epoxy monomers are discussed in the scope of green chemistry. The focus is put on the large variety of bio-based building blocks as renewable bioresources available for the design of innovative epoxides.

2.1. Introduction on Epoxy resins

Thermosetting polymers represent between 15 and 20% of the total polymer market [61]. These polymers are generally formed from a liquid containing at least one monomer with reactive functions which, through the crosslinking process, irreversibly becomes a solid. This is due to the formation of a three-dimensional network between the monomers by covalent bonds. For this, at least one of the monomers must have at least three reactive functions, or two reactive functions which have the capacity to react more than once with another monomer. Another characteristic of thermosetting polymers is that once the crosslinking reaction is complete, it is no longer possible to change the shape of the material. They are also more resistant to thermal stress, creep and solvents compared to thermoplastic polymers. Among the different types of thermosetting polymers, epoxy

resins represent nearly 70% of the market, with an annual production of around 4 Mt [62]. The global epoxy resin market was around \$21.5 billion in 2016 and it has been estimated that it will reach \$27.5 billion in 2020 and \$37.3 billion in 2025 [63]. The success of this type of resins is due to the excellent mechanical strength of these materials, as well as their high resistance to chemicals, moisture, and corrosion. These resins are composed of monomers or prepolymers which generally have at least two epoxy functions. Epoxides (contraction of epi-, side, and oxide for oxygen and oxidation products) are chemicals with oxygen bridged on a single carbon-to-carbon bond. We also speak of oxacycloalkanes (systematic nomenclature) more often abbreviated as oxiranes. The simplest epoxy is ethylene oxide.

The epoxy functions can react with one another by anionic or cationic polymerization, or even more commonly with reagents containing reactive functional groups with epoxides, such as amines, acids, anhydrides, hydroxyls or thiols. These reactive compounds are generally called hardeners. Epoxy-type adhesive formulations may also contain additives to modulate the reactivity between the components, the final properties of the material or simply to reduce the cost of production.

A large amount of epoxy resins use bisphenol A diglycidyl ether as a monomer containing the epoxy functions. In fact, over 90% of commercial epoxy resin formulations use DGEBA (Fig. 1). Commercial DGEBA monomers usually have values of n between 0.03 and 10. At room temperature, DGEBA is a crystalline solid for values of n close to 0, a liquid up to 0.5 and a glassy solid for $n > 0.5$.

DGEBA is a particularly interesting reagent for the synthesis of epoxy resins, since it confers crosslinked materials remarkable properties. Each part of the molecule influences the properties of the final material. The glycidyl ether functions of DGEBA are fairly reactive functions, which decrease the temperature and/or the crosslinking time compared to other types of epoxy functions. In general, the reactivity of the epoxy functions is as follows: glycidyl ether > terminal epoxide > epoxide in the middle of a carbon chain.

On the other hand, the presence of aromatic rings significantly improves thermal properties. However, DGEBA is synthesized from bisphenol A (BPA) and epichlorohydrin (ECH), as shown in Fig. 1. BPA is a substance which has been classified as reprotoxic 1B by the European Chemicals Agency (ECHA). In addition, this substance is an endocrine disruptor which can mimic hormones in the body and cause deleterious health effects, even at very low dosage [57,59,64]. Moreover, since March 2018, the REACH regulation has severely restricted its use for products intended for consumers. For example, thermal paper containing more than 0.02% BPA cannot be marketed in the EU since January 2020. On the other hand, ECH is also a toxic substance and considered CMR 1B.

Bisphenol A is a product based on the reaction of phenol with acetone under acidic conditions. Its structure is based on two phenols attached in the para position to a carbon bearing two methyl groups. Its structure generally considered to be rigid as well as the high reactivity of its oxirane groups are the main reasons for its wide use in epoxy polymers. BPA production was around 6 million tonnes in 2017 and the growth rate is expected to be 6% per year for the 2019-2024 period. About 66% of the BPA produced is used in epoxy resins, which is the main industry using this compound [65]. BPA-based resins were associated with plastic bottles, aluminium can coatings, dental cements, textiles and food packaging [66]. Unfortunately, BPA-based resins are sensitive to hydrolysis, which can lead to the release of free BPA into the environment. Additionally, when BPA is used as an additive, it is more likely to be released because it does not react within a polymer matrix which is generally more chemically resistant.

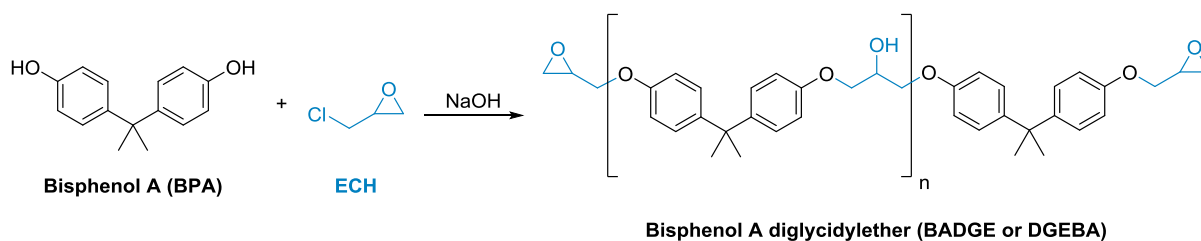


Fig. 1. Synthesis of DGEBA from BPA and ECH.

Despite the thermal/mechanical advantages to use BPA, the latter is now known to have an effect on the endocrine system, and is also suspected of having ecotoxicity on vertebrates, invertebrates and algae [67]. The danger of bisphenol A for health arises from its activity similar to that of the hormone 17β -estradiol, with regard to the α receptor of human estrogens. This activity is mainly due to the chemical structure of BPA, which mimics that of 17β -estradiol (Fig. 2). Several parameters can explain the similar activity of BPA and estradiol. First, the presence of two hydroxy groups leads to an efficient interaction between the receptor and the potential agonist. Additionally, in order to bind within the receptor binding site, the compound must fit within the pocket of the receptor. The size of the pouch is 440 Å and the size of 17β -estradiol is 245 Å, which allows it to fit inside the pouch. The presence of the two hydroxyl groups, the size of the molecule and the distance between the hydroxyls are of prime importance. Some research has also shown that the hydrophobic nature of the middle part of the molecule (for example, the two methyl units of BPA), also has a great influence on the interactions between the compound and the receptor (Fig. 3) [68].

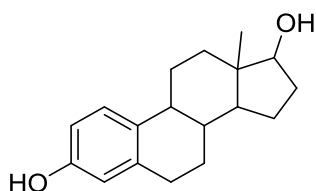


Fig. 2. Chemical structure of 17β -estradiol.

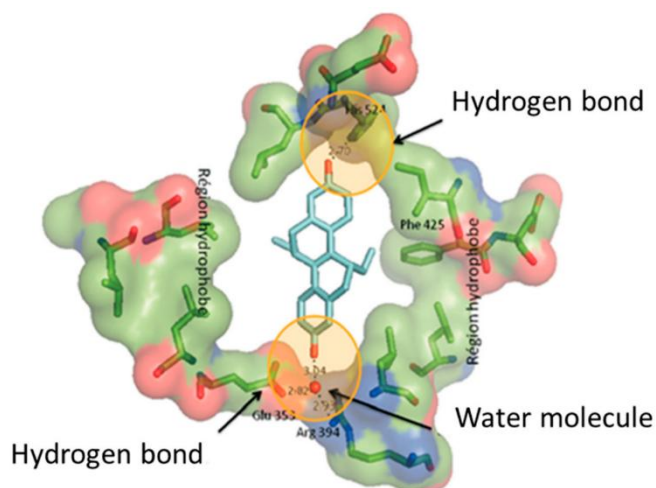


Fig. 3. X-ray structure of the pocket of ER α . Reprinted from Ng et al. [68].

The health risk has led regulators to act to reduce the exposure of populations to BPA. In particular, the European Union has introduced several limitations on the use of BPA-based products. BPA has now been banned in the manufacture of baby bottles since 2011 [69]. In France, the marketing of food packaging in contact with BPA has been banned since 2015 [70]. The European Chemicals Agency, under the Reach Regulation, placed BPA on the SVHC candidate list, as a reproductive toxicant and endocrine disruptor [71]. The European Commission has also introduced a limitation on the use of BPA in thermal paper, limited to 0.02% starting from January 2020 [72].

Some regulations have also restricted the use of BPA in several states in the United States and Canada. Some alternatives to BPA are also being evaluated, as their chemical structure is very close to BPA and endocrine activity is expected to be similar. Above them all, bisphenol S (BPS, Fig. 4) is considered suspect by regulators. For example, in the text of the commission's regulations banning the use of BPA above 0.02% in thermal papers, it is stated that “special attention should be paid to a possible substitution trend towards BPS”, and that “the Agency should communicate any additional information to the Commission so that it can examine whether a proposal to restrict BPS [...] is necessary given that, unlike BPA, the health risk associated with BPS in thermal paper has not yet been rated.”. BPS is also on the Endocrine Disruptor Review List, which means the substance is being evaluated for its potential endocrine disrupting activity, although no results have yet been published [73].

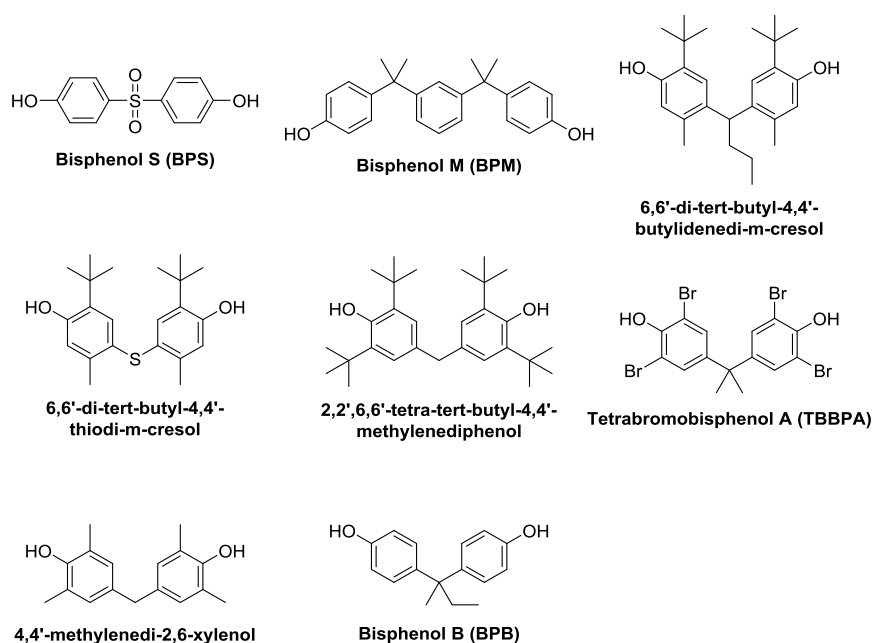


Fig. 4. Structures of bisphenols present on the list of evaluation of endocrine disruptors.

Other bisphenols are also included in the endocrine disruptor assessment list, such as BPM, 4,4'-butylidenebis (6-tert-butyl-m-cresol), 6,6'-di-tert-butyl-4,4'-thiodi-m-cresol, 2,2', 6,6'-tetra-tert-butyl-4,4'-methylenediphenol, TBBPA, 4,4'-methylenedi-2,6-xylenol and BPB (Fig. 4). Inclusion on the list does not mean that endocrine disrupting properties are evaluated, however, for these substances there may be a risk of further regulatory limitations on their use.

2.2. Design of New Epoxy Bio-based Building Blocks

The high toxicity, the negative effects on health and the environment and the petro-sourced nature of the reagents necessary for the synthesis of DGEBA mean that currently many researchers in both the academic and industrial fields are looking for fewer toxic and more environmentally friendly alternatives. Thus, research work enabling the development of biobased epoxy resins is booming and has already led to the marketing of certain (partially) biobased epoxy resins.

2.2.1. General Synthesis of Epoxy Monomers

Epoxy monomers are generally obtained by epoxidation or oxidation. The most used reaction for the synthesis of epoxy monomers is based on the epoxidation of hydroxy-like molecules (for instance phenols derivatives) by epichlorohydrin (Fig. 5). The reaction generally involves that the oxirane ring is opened during the reaction with the hydroxyl and is then recycled at the end of the reaction.

In all reported routes, ECH is used in significant excess and the reaction is performed in an aqueous solution of sodium hydroxide (NaOH). The literature [61] clearly demonstrates that the reaction between the phenate ion (ArO^-) (**1'**) and ECH (**2**) is divided into two competitive mechanisms as depicted in Fig. 5: the one-step nucleophilic substitution ($\text{S}_{\text{N}}2$, mechanism A) with the cleavage of the C-Cl bond and a two-step mechanism based on the ring opening of ECH (**2**) with ArO^- (**1'**) (mechanism B) followed by intramolecular cyclization ($\text{S}_{\text{N}}\text{i}$) of the corresponding alcoholate (**4**). However, glycidylation of phenols needs first the synthesis of the phenate group with NaOH, which can entail some inconveniences such as limited yields, moderate purity of products and poor reaction selectivity (mechanism B vs mechanism A giving directly **3**). Indeed, 1-chloro-3-aryloxypropan-2-ols (**5**) by-product could be yielded in a non-negligible amount.

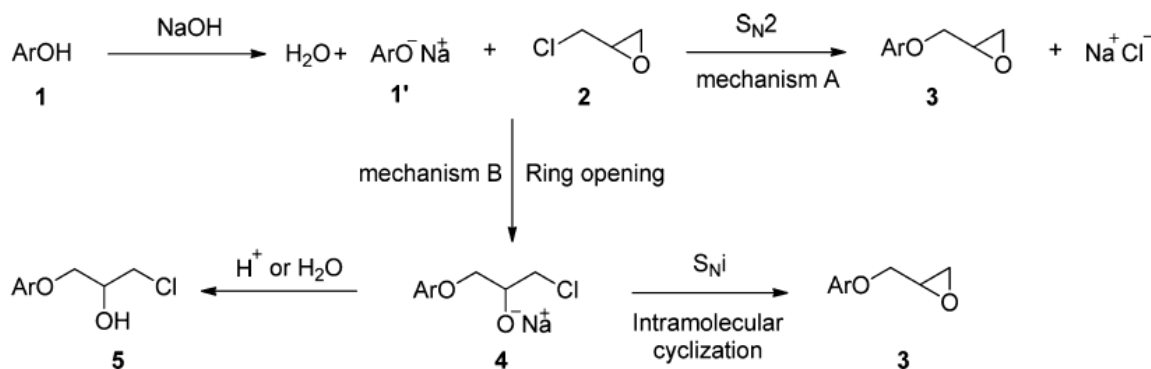


Fig. 5. Mechanisms of epoxidation of phenols with epichlorohydrin, owing to R. Auvergne et al. [61].

Another interesting route of epoxy monomer synthesis consists in oxidation of double bonds present in the structure of a compound by an oxidizing agent (peracetic acid, perbenzoic acid, etc.) (Fig. 6). Here, literature reports particularly the use of meta-chloroperbenzoic acid (m-CPBA) and methyl(trifluoromethyl) dioxirane generated *in situ* from 1,1,1-trifluoroacetone and oxone. The efficiency of each reagent is similar [74].

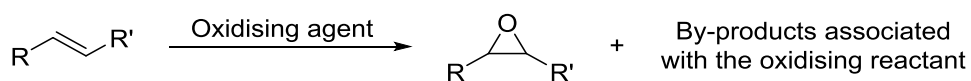


Fig. 6. Epoxidation reaction of an unsaturated reactant.

Many other examples of new epoxy biosourced monomers are described in the following section according to the synthetic routes previously described.

2.2.2. Biosourced DGEBA

As mentioned earlier, DGEBA is synthesized by the reaction between BPA and ECH. BPA is a product synthesized by the condensation reaction of phenol with acetone, catalysed by a strong acid such as hydrogen chloride. On the other hand, ECH is usually synthesized from allyl chloride, which is obtained by the reaction between chlorine and propylene, a petro-sourced reagent [75]. However, ECH can be produced from bio-based glycerol (Fig. 7) [76,77]. An example of a commercial biobased ECH is Epicerol[®] marketed by the Solvay group.

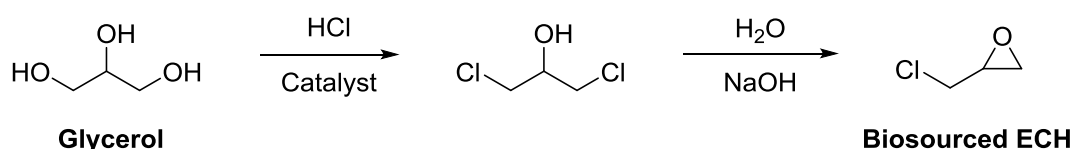


Fig. 7. Synthesis of biobased ECH.

Bio-based ECH can therefore be used for the synthesis of DGEBA by its reaction with BPA (Fig. 1). The resulting DGEBA will therefore be partially biobased, with a carbon content from biomass of 28% at most (depending on n).

Bio-based DGEBA is a commercial product synthesized by several companies. For example, the company Spolchemie, based in the Czech Republic, has a range of EnviPOXY[®] products in its catalogue with a bio-based carbon content of up to 28%. The viscosities of these DGEBA vary between 8,000 and 16,000 mPa.s. On the other hand, the French company Sicomin markets partially biobased DGEBA under the name GreenPoxy[®]. In its catalogue, we can find DGEBA with a biobased carbon content of 28%, synthesized with biobased ECH, and up to 56%, probably using a mixture with partially biobased BPA (derived from phenol and bio-based acetone). The advantage of biobased DGEBA is that the reactivity and properties of the obtained crosslinked materials are the same as those of petro-sourced DGEBA, since it shares the same structure as its petro-sourced counterpart. On the other hand, and for this same reason, biobased DGEBA, as well as its precursors, biobased ECH and possibly biobased BPA, have the same toxicity and CMR characters as their petro-sourced counterparts. Other solutions using fewer toxic reagents and resulting in more environmentally friendly products should therefore be considered for the synthesis of bio-based epoxy resins.

2.2.3. Tannins and polyphenols

Tannins are polyphenols that are very common in nature. It is the second most important source of natural phenols, and the third most important source of compounds extracted from biomass, and their production on an industrial scale amounts to 160,000 tons per year [78,79]. These are non-dangerous natural molecules which have antiallergic, anti-atherogenic and antimicrobial

properties thanks to their antioxidant properties [80–85]. These properties are the consequence of the presence of several phenol groups in the chemical structure, which can be very varied. Moreover, they are classified according to their structure: hydrolysed tannins (ellagitannins or gallotannins), condensed tannins, complex tannins and phlorotannins. Among the different types of tannins, it is hydrolysed tannins and condensed tannins which are generally used for the preparation of epoxy monomers.

Gallotannins are composed of gallic acid groups grafted onto polyols, while ellagitannins result from the oxidative coupling of at least two gallic units of gallotannins. Condensed tannins are obtained by polymerization of flavanols [86]. Depending on the substituents, different flavan-3-ols exist and can be polymerized. Among these compounds, catechin and gallic acid, derived from condensed tannins, are the most studied compounds for the synthesis of epoxy monomers. Yet despite the high bioavailability of tannins and polyphenols and the existence of several patents that claim the use of tannins as precursors of epoxy monomers, there are currently no commercial epoxy resins made from tannins on the market. Nevertheless, it seems important to detail the work that has been carried out so far and to describe the properties of the epoxy resins obtained.

2.2.3.1. *Tannic acid*

Tannic acid has many phenolic hydroxyl functions in its structure (Fig. 8). Therefore, these functions can, in principle be epoxidized with ECH to obtain an epoxy monomer with very high functionality. In contrast, only 5 of the 25 phenolic hydroxyl groups of tannic acid can be glycidylated due to side reactions and steric inhibition of the hydroxyl groups [87]. In this work, epoxidized tannic acid was crosslinked with diethylenetriamine (DETA) and showed lower reactivity than DGEBA crosslinked with the same hardener because of its relatively high molecular weight. It must therefore be crosslinked at high temperatures (≥ 100 °C) to increase the miscibility of the components. On the other hand, the use of epoxidized tannic acid gives the materials cytocompatibility and antioxidant activity. The material also showed good thermal stability due to the high density of aromatic groups and a fairly high Tg (140 °C). Interestingly, tannic acid is soluble in water, so it shows great promise in the manufacture of water-based epoxy materials with increased green attribute, or for the development of new functional materials such as epoxy foams with water as the solvent or foaming agent.

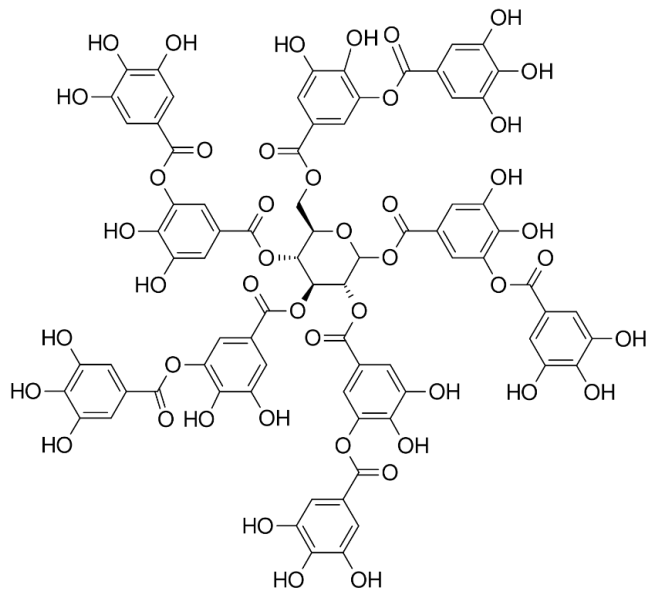


Fig. 8. Structure of tannic acid.

2.2.3.2. Catechin

Catechin is one of the main components of tannins and one of the most studied natural polyphenols for the synthesis of new epoxy resins. It can be epoxidized by two different routes, either by the O-glycidylation reaction with ECH (Fig. 9), or by alkylation with an unsaturated halogen compound followed by its oxidation [88]. However, this reaction gives rise to a by-product having a benzodioxane group which then decreases the average epoxy functionality [89]. Catechin-based synthesized epoxy resins (GEC) mixed with DGEBA were crosslinked with cycloaliphatic amines. The materials thus obtained exhibited good thermal and thermomechanical properties, with T_g and elastic moduli similar to those obtained with epoxy resins based on commercial DGEBA ($T_g = 202\text{ }^\circ\text{C}$, E (vitreous) = 2.40 GPa and E (cauchoutic) = 0.014 GPa for 50% DGEBA/50% GEC vs $T_g = 209\text{ }^\circ\text{C}$, E (glassy) = 2.81 GPa and E (cauchoutic) = 0.019 GPa for 100% DGEBA). Even if the crosslinking of these materials was carried out for 24 h at $60\text{ }^\circ\text{C}$, the reactivity of this resin should be similar to that of DGEBA since the epoxy functions of the epoxidized catechin are glycidyl ether functions, and therefore the complete crosslinking could probably take place at room temperature for 7 days (depending on the hardener). The percentage of bio-based carbon could be 44% and up to 100% if the synthesis is carried out with bio-based ECH.

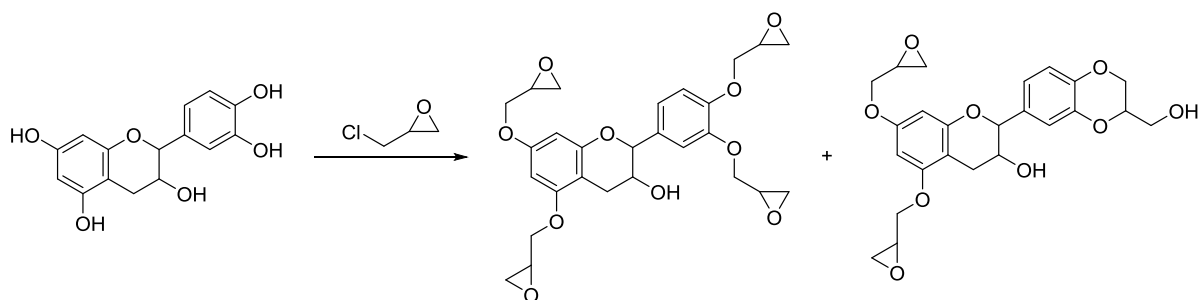


Fig. 9. Products of O-glycidylation reaction of catechin with ECH.

2.2.3.3. Gallic acid

Gallic acid is found in most astringent plants such as galls, sumac, witch hazel, tea leaves, oak bark, etc. Thanks to its chemical structure, which includes three phenolic hydroxyl groups and a carboxylic acid, it can be functionalized in several glycidyl ether groups using ECH to obtain epoxy resins [90]. In this case, the addition of ECH occurs on the carboxylic acid group and on at least one phenolic hydroxyl group in the presence of an ammonium-type phase transfer catalyst in an anhydrous medium (Fig. 10). The resulting epoxy resin was crosslinked with methylhmic anhydride and benzyldimethylamine for 3 h at 100 °C then 15 h at 150 °C. The resulting materials were compared with a commercial epoxy resin, and the results showed a higher deflection temperature under load for materials derived from gallic acid.

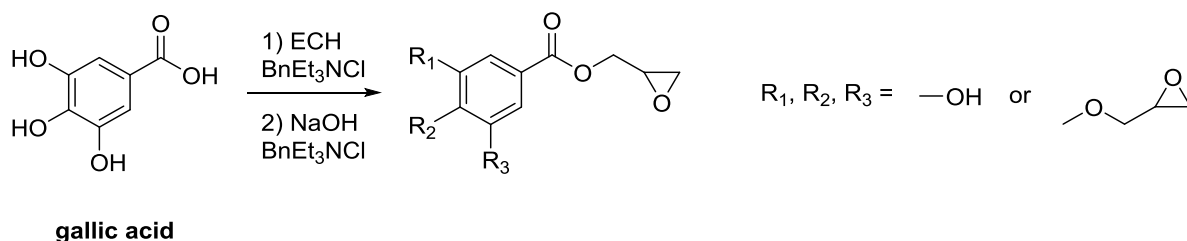


Fig. 10. O-glycidylation of gallic acid with ECH.

Another method to obtain an epoxy resin from gallic acid is to combine gallic acid with allyl bromide, then partially and/or totally oxidize the allyl groups with the enzyme lipase B in the presence of hydrogen peroxide and caprylic acid [91]. The tetraepoxide monomer could be isolated and then crosslinked with IPDA. The material so synthesized has a remarkably high Tg (233 °C) as well as a very high charring rate. The epoxidation reaction can also be performed with m-CPBA [92]. This method gives rise to a mixture of tetra-epoxy (75%), tri-epoxy (23%) and di-epoxy (2%) compounds as shown in Fig. 11. The crosslinking of this resin with IPDA, the Jeffamine D230 and N,N'-dimethylbenzylamine produces materials with relatively high Tg (between 98 and 158 °C) and mechanical properties similar to those obtained with DGEBA using the same hardeners, but with material brittleness significantly higher (elongation at break of 1.4% and 6.1% for epoxidized gallic acid and IPDA and Jeffamine D230, respectively, compared to 1.7% and 8.6% for DGEBA and IPDA and Jeffamine D230, respectively). Even if in this work the crosslinking was carried out for 1 h at 120 °C then 1 h at 150 °C, it should in principle take place at room temperature because the epoxy

functions are glycidyl ether groups. Charring rates at 600 °C are quite high (between 18.1 and 29.5%) depending on the hardener. On the other hand, this monomer has a relatively low level of bio-based carbon (37%), since allylation is carried out from allyl bromide, a petro-sourced compound with high toxicity.

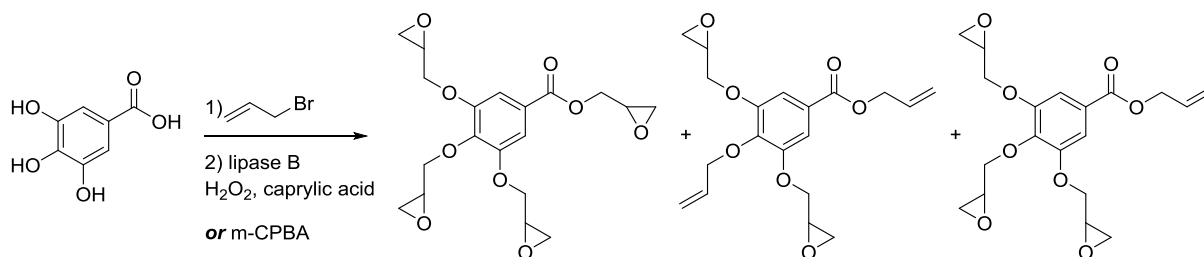


Fig. 11. Synthesis of an epoxidized monomer from gallic acid by allylation and epoxidation.

2.2.3.4. Resorcinol

Resorcinol is a dihydroxybenzene (aromatic ring with two phenolic hydroxyl groups in the ortho position). It can be obtained by distillation of natural resins, such as galbanum or asafoetida. The two phenolic hydroxyl functions can react with ECH in the presence of NaH to form resorcinol diglycidyl ether (Fig. 12) [89,93]. If the ECH used is bio-based, this monomer has a bio-based carbon content of 100%, otherwise the bio-based carbon content will be 50%. Crosslinking with diamines such as HMDA or bio-based amines synthesized from limonene and eugenol gives rise to bio-based epoxy resins showing good thermal stability (T_g between 60 and 80 °C) and mechanical properties comparable to DGEBA-based materials [94]. This monomer is manufactured by the Huntsman® Company under the names ERY SIS® RDGE and RDGE-H. This monomer has glycidyl ether groups, which are fairly reactive groups with respect to amines, and which should therefore allow its crosslinking at room temperature. On the other hand, this monomer is considered to be CMR.

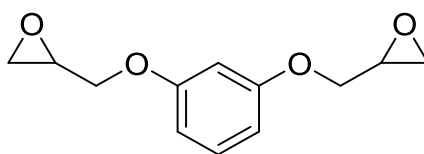


Fig. 12. Structure of resorcinol diglycidyl ether.

The synthesis of several resorcinol-based monomers has also been published, such as the monomer depicted in Fig. 13 [95]. The resorcinol derivative has two aromatic rings in its structure, which gives the so-formed materials good thermal stability and high T_g values. Various patents show the synthesis of crosslinked epoxy polymers from epoxy monomers based on resorcinol (or phloroglucinol), previously epoxidized by reaction with ECH [96,97].

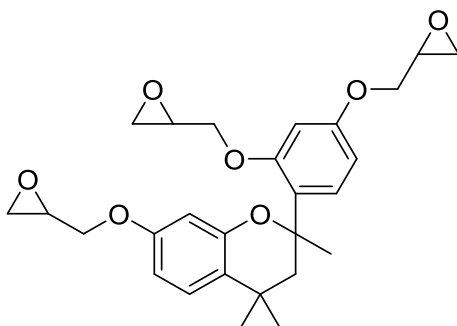


Fig. 13. Structure of a resorcinol-based triglycidyl ether monomer.

2.2.4. Cardanol

Cardanol is a yellowish, viscous phenolic lipid found in cashew nutshell oil (Cashew NutShell Liquid or CNSL). It is a renewable natural source of phenols obtained from a by-product of cashew (*Anacardium occidentale*). It is used as a precursor to several chemicals, materials and fuels [98]. CNSL annual production was around 1 Mt in 2009 [99]. The CNSL constitutes between 18 to 27% of the total mass of the cashew nut [100,101]. CNSL represents one of the largest sources of bio-based phenolic compounds today. It is mainly composed of anacardic acid (3-n-pentadecylsalicylic acid) and small amounts of cardanol (3-n-pentadecylphenol), cardol (5-n-pentadecylresorcinol) and methylcardol (2-methyl-5-n-pentadecylresorcinol) (Fig. 14). These components have an aromatic ring with one or two hydroxyl function (s) and an aliphatic chain of fifteen carbons. This aliphatic chain can be saturated, monoolefinic (C8), diolefinic (C8, C11) and triolefinic (C8, C11, C14), with an average value of two unsaturations per molecule. Heat treatment of CNSL induces partial decarboxylation of anacardic acid, which is completed by subsequent purification via distillation. The result of this decarboxylation is a yellow oil containing about 90% of cardanol, with a low percentage of cardol and methylcardol [102]. Cardanol is a mixture of four meta-alkylphenols which differ in the degree of unsaturation of the aliphatic chain: 3% 3- (pentadecyl) phenol, 42% 3- (8-pentadecenyl) phenol, 17% 3- (8,11-pentadecadienyl) phenol and 38% of 3- (8,11,14-pentadecatrienyl) phenol, of predominantly cis conformation [103].

The presence of an aromatic part (phenol) and a long aliphatic chain with unsaturations gives cardanol remarkable properties and makes it a promising candidate for the substitution of petro-sourced phenolic derivatives. CNSL can therefore be considered as a versatile and valuable raw material for the production of polymers and represents an excellent natural alternative to phenols derived from petrochemicals [104]. In addition, cardanol improves the properties of coatings such as chemical and mechanical resistance, anticorrosion and flexibility [105]. The presence of unsaturations in its aliphatic chain allows the introduction of epoxy groups. In fact, a patent filed by Cardolite® Corporation claims the commercial use of epoxy cardanol [106], and PPG Industries also claims in another patent the use of cardanol mixed with BPA to obtain crosslinked epoxy biobased polymers [107]. The epoxidation of unsaturations can be carried out enzymatically in the presence of acetic acid in toluene [108]. On the other hand, most of the epoxy functions generated are found in the middle of the aliphatic chain and are not very reactive functions, which implies that the polymerization will not take place at room temperature and/or not with amines.

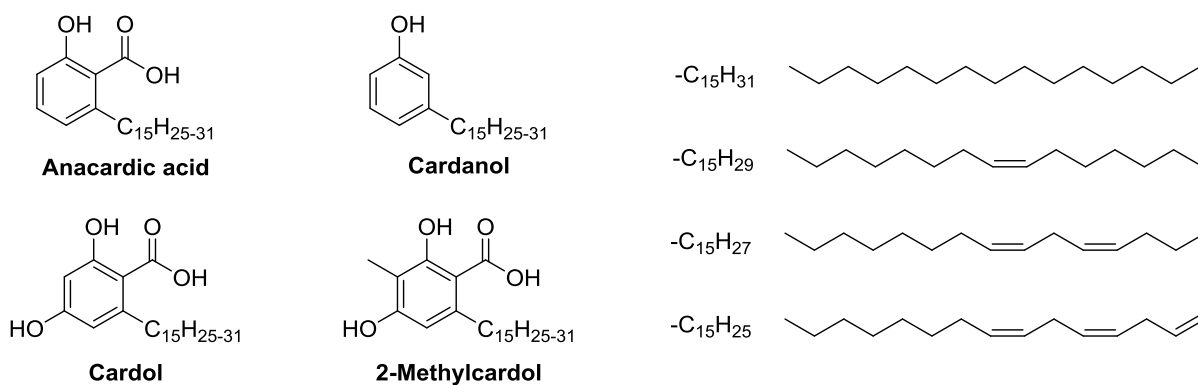


Fig. 14. Chemical structures of components of CNSL.

On the other hand, cardanol has a phenolic hydroxyl function in its structure and it can therefore be easily functionalized with an epoxy group by direct reaction with ECH (O-glycidylation). This phenolic glycidyl ether function is more reactive and allows polymerization at room temperature. This product is marketed by Cardolite[®] Corporation under the name NC-513 (Fig. 15). But the presence of a single epoxy function in the monomer makes it primarily intended for use as a reactive diluent and not as an epoxy resin.

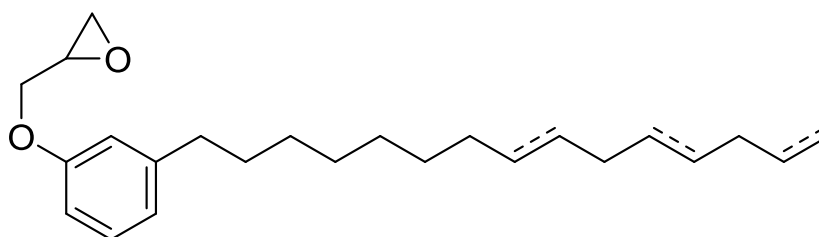


Fig. 15. General structure of monoepoxidized cardanol (Cardolite[®] NC-513).

The synthesis of di-glycidyl cardanol was carried out by a two-step reaction. First, a phenol function is introduced on the aliphatic chain of cardanol by reaction with phenol in the presence of strong acids such as tetrafluoroboric acid (HBF_4) [109]. The second step is to combine the resulting diphenol with ECH through the O-glycidylation reaction. Cardanol di-glycidyl is also marketed by Cardolite[®] Corporation under the name NC-514.

2.2.4.1. Cardolite[®] NC-514

NC-514 is a potential candidate for the substitution of DGEBA as an epoxy resin. It has good reactivity, similar to DGEBA, thanks to the presence of epoxy functions of the phenolic glycidyl ether type. It also has good thermal stability due to the presence of aromatic groups. On the other hand, the presence of a long aliphatic chain gives the crosslinked materials using this resin remarkable flexibility, as well as good chemical or moisture resistance. The resin, brown in colour, has a fairly high viscosity, of the order of 25,000 mPa.s, and a density of $1.07 \text{ kg}\cdot\text{dm}^{-3}$.

Analysis of NC-514 by ^1H NMR shows that most of the aliphatic chains of NC-514 monomers present in the resin are saturated (95%), but there are 5% of chains with C11 unsaturation (Fig. 16). On the other hand, even though the O-glycidylation reaction was quantitative, 30% of the epoxy groups are already open and are no longer reactive [110].

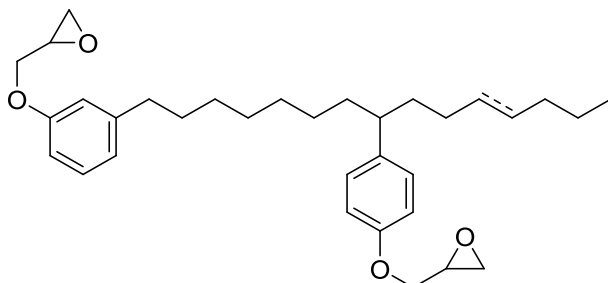


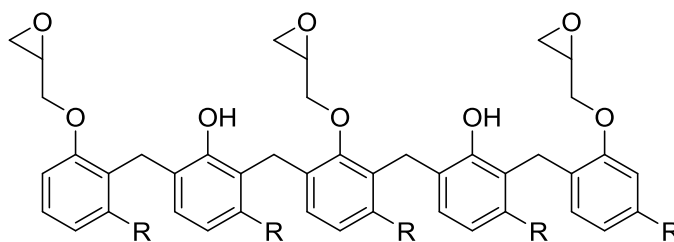
Fig. 16. Idealized structure of diglycidyl cardanol (Cardolite® NC-514).

Several scientific publications have analysed the materials which use this epoxy resin in their composition [111–114]. For example, for a series of materials made with NC-514 as epoxy resin using isophorone diamine (IPDA), the T_g values obtained are between 41 and 50 °C [110]. For a material using DGEBA as epoxy resin and crosslinked with the same hardener (IPDA), the T_g is 158 °C. This strong decrease in T_g relative to DGEBA is due to the long aliphatic chain of NC-514 which softens the polymer network. The gel rate, which is related to the crosslinking rate of the material, is also lower for materials synthesized with NC-514. Even if the materials of this publication were crosslinked for 5 h at 120 °C then for 30 min at 170 °C, NC-514 exhibits good reactivity thanks to the phenolic glycidyl ether functions, and the crosslinking could be complete at room temperature after 7 days (depending on the hardener used). The percentage of biobased carbon is not indicated in the technical data sheets of Cardolite® Corporation. This percentage can vary between 64% and 100%, depending on whether the ECH and the phenol that Cardolite® Corporation uses is bio-based or not. In the case of petro-sourced phenol and ECH the percentage of biobased carbon would be 64%. If one of these two components is bio-based and the other is not, the percentage of bio-based carbon would be 82%. On the other hand, if the ECH and the phenol used for the synthesis of NC-514 are biobased, we will obtain a product with 100% biobased carbon.

2.2.4.2. Cardolite® NC-547

It is also possible to obtain a cardanol-novolac prepolymer from the condensation reaction of cardanol with formaldehyde catalysed with *p*-toluene sulfonic acid at 120 °C for 7 h [115]. Subsequently, the epoxidation is carried out with ECH in a basic medium. This novolac epoxy resin is also marketed by Cardolite® Corporation under the name NC-547 (Fig. 17). It has a higher viscosity than NC-514 (between 20,000 and 50,000 mPa.s) and a slightly lower density (0.94 kg.dm⁻³). The materials obtained with this epoxy resin are hydrophobic and very flexible elastomeric materials, even at low temperatures. The tensile strength is lower and the T_g higher than that obtained with NC-514 due to the higher aromatic density of NC-547 [112]. The reactivity is similar since it also contains phenolic glycidyl ether functions and may optionally be completely crosslinked at room

temperature for 7 days. The rate of bio-based carbon is between 92 and 97%, depending on whether the ECH used for its synthesis is bio-based or not.



NC-547

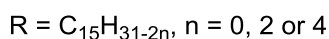


Fig. 17. Chemical structure of Cardolite® NC-547.

2.2.5. Eugenol

Eugenol is a phenolic compound found in a wide variety of plants such as cloves, cinnamon, basil, pepper, oregano, thyme and nutmeg, among many others [116–119]. Clove oil contains a high concentration of eugenol, which is responsible for its characteristic aroma. Even though eugenol can be obtained from lignin, commercial eugenol is mainly obtained from clove oil, but it is also extracted from cinnamon leaves, bark and basil oils, which also contain high concentrations of this molecule.

Since eugenol is a bio-based phenolic monomer that can be functionalized with one or more epoxy groups, it is a potential candidate to replace DGEBA as an epoxy resin. It is formed by an aromatic ring comprising two reactive groups (phenolic hydroxyl and allyl), which allows the functionalization of the molecule (Fig. 18). There are two possibilities for introducing an epoxide function into eugenol: by epoxidation of the allyl group or by introduction of a glycidyl ether group on the phenolic hydroxyl group.

The epoxidation of the allyl group of eugenol is generally carried out with *m*-CPBA [120–122]. This reaction is carried out after a prior protection step or after a prior functionalization of the phenolic hydroxyl group to prevent the formation of by-products. On the other hand, the reaction of *O*-glycidylation of the phenolic hydroxyl group of eugenol with ECH produces eugenol glycidyl ether (EGE) [123–128]. The functionalization of the two positions by epoxidation and *O*-glycidylation must be carried out with a specific order as shown in Fig. 18. It is important to first perform the epoxidation of the allyl group (following a preliminary protection step of the phenolic hydroxyl group), then perform the *O*-glycidylation reaction [129].

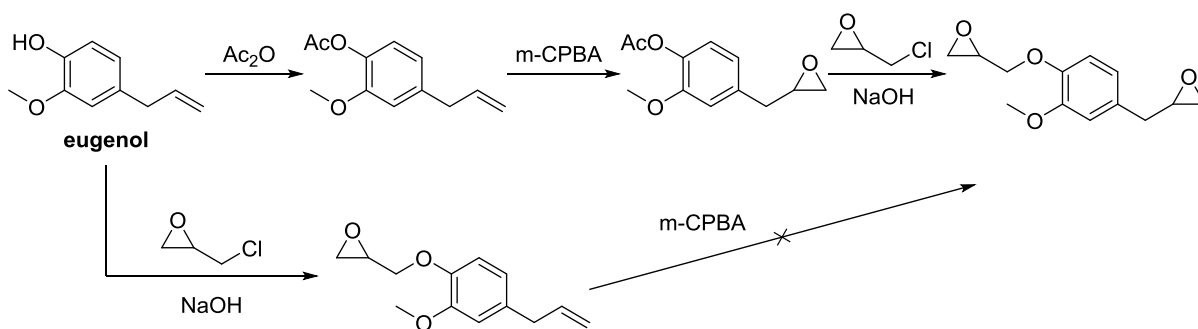


Fig. 18. Epoxydation and O-glycidylation of eugenol.

The resulting epoxy resins, crosslinked with petro-sourced and bio-based anhydrides and a catalyst at 150-200 °C, were compared to a commercially available epoxy resin (DER[™] 353) crosslinked with the same curing agents. The authors concluded that the two materials exhibited similar thermal and mechanical performance. The T_g values obtained for these materials were above 100 °C. Eugenol diepoxide can be completely bio-based if synthesized with bio-based ECH, otherwise the bio-based carbon content would be 77%. The disadvantage of this epoxy resin is the different reactivity between the two existing epoxy groups. As previously mentioned, the glycidyl ether group has a higher reactivity than the epoxide formed by epoxidation of the allyl group, which will likely react more slowly at room temperature. However, despite numerous scientific papers or patents in the literature dedicated to epoxy resins synthesized from eugenol, there are no commercial epoxy resins synthesized from eugenol to date.

In the literature, other authors have developed some epoxy monomers derived from eugenol based on the di- or trimerization of eugenol via its phenolic hydroxyl function with an aromatic diacyl chloride [130], an aromatic dichloride [131] or by the formation of cyanurate ring [122], thus avoiding the use of ECH. In this case, the crosslinking was carried out with 4,4'-diaminodiphenyl methane (DDM) and with 3,3'-diaminodiphenylsulfone (33DDS). The resulting materials were compared with epoxy resins obtained from DGEBA and the same curing agent, respectively. The results showed that epoxy resins derived from eugenol have comparable or even improved thermal and mechanical properties, in addition to other improved properties such as higher charring rate and lower flammability. However, the reactivity of the epoxy functions, even if it remains correct since they are epoxy functions at the end of the aliphatic chains, is probably lower than that of DGEBA since it is not a glycidyl phenolic ether function.

Alternatively, the synthesis of a triepoxidized monomer, namely tri(epoxy eugenyl) phosphate (TEEP), from eugenol can be carried out using phosphoryl phosphate trichloride [121]. This monomer was then cured by epoxy-amine reaction with an aliphatic diamine (Jeffamine[®] EDR-148) and with an aromatic diamine (m-xylylenediamine, MXDA). Both materials exhibit good thermal and mechanical properties, as well as high carbon yields and therefore have potential application as flame retardant materials (Fig. 19).

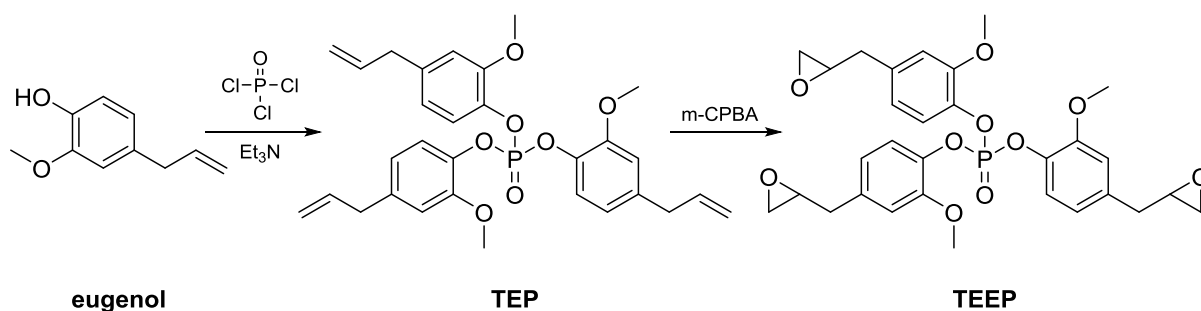


Fig. 19. Synthesis of tri(epoxidized eugenyl) phosphate (TEEP).

2.2.6. Lignin and derivatives

2.2.6.1. Lignin

Lignin is one of the main components of wood, along with cellulose and hemicellulose. It is considered to be one of the most abundant aromatic biopolymers in plants [128]. The presence of a large number of functional groups in its structure (Fig. 20) allows the introduction of various functional groups such as epoxies. However, there are only a few publications on the use of lignin as an epoxy monomer [132–136]. In the literature we mainly find three processes that describe the epoxidation of lignin [137].

The first method aims to increase the content of phenolic groups in lignin with phenol and BPA [138–142]. Then, the phenol functionalized lignin can react with ECH to form introductory glycidyl ether groups. The second method consists in combining lignin with aliphatic di-epoxy compounds in DMF at 80 °C [143,144]. The crosslinking of an epoxy resin formed from kraft lignin and polyethylene glycol diglycidyl ether and crosslinked with poly(azelaic anhydride) gives rise to a material with T_g below 0 °C [145]. The third process is based on oxypropylation, which is the reaction between lignin and propylene oxide, thus forming hydroxyl groups. These hydroxyl groups are then transformed into glycidyl ether groups by reaction with ECH. Crosslinking of this epoxy resin with aromatic diamines forms materials with T_g values of 80–200 °C, depending on both the type of lignin and the degree of oxypropylation [146].

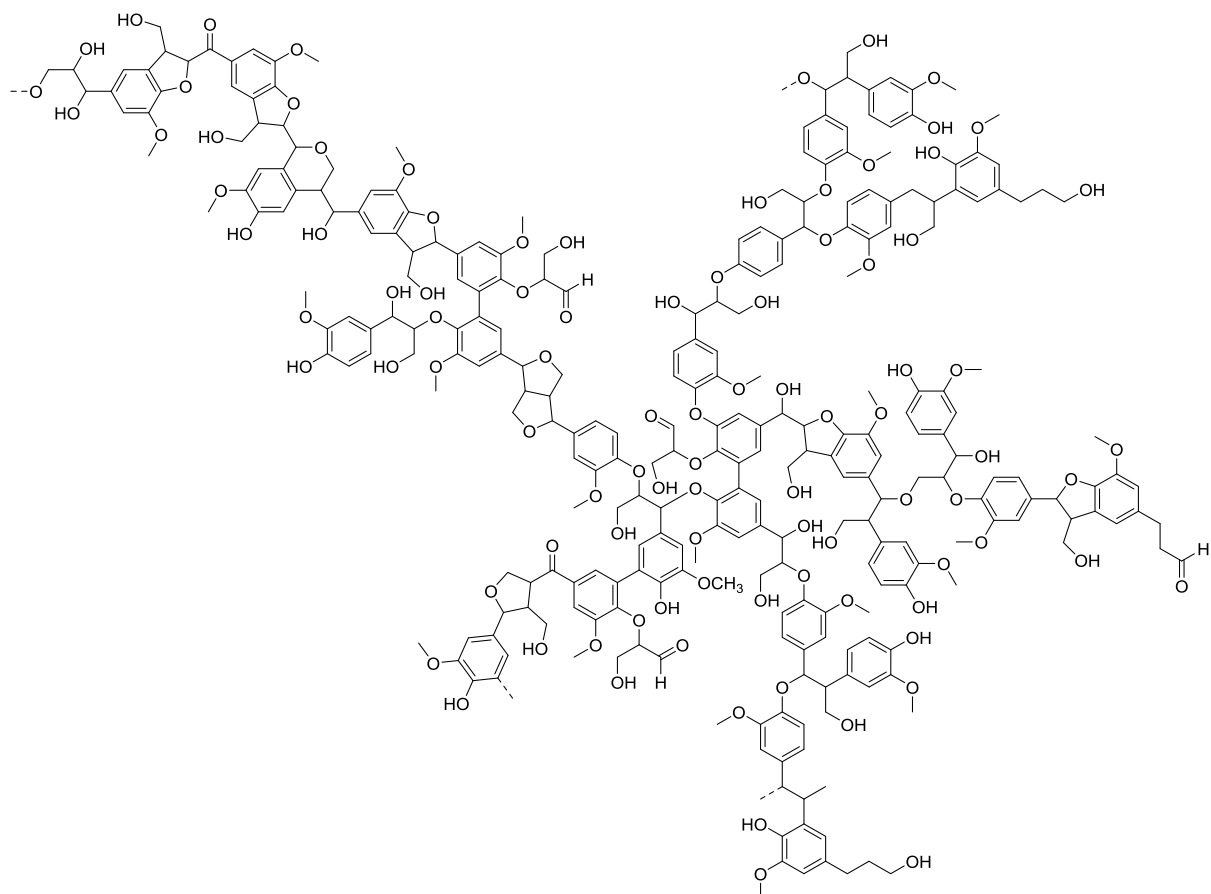


Fig. 20. General chemical structure of lignin.

2.2.6.2. Vanillin and derivatives

Vanillin is an aromatic aldehyde having a phenolic hydroxyl group. This is the molecule that gives the characteristic aroma to vanilla. This molecule can be extracted directly from the vanilla pod, but it can also be obtained via synthesis from petro-sourced precursors or from lignin. This molecule has an aromatic ring with a phenolic hydroxyl group and an aldehyde. These reactive functional groups allow the functionalization of vanillin to obtain epoxy monomers. Vanillin can be easily converted into vanillic acid, vanillic alcohol and 2-methoxyhydroquinone. These three molecules can react directly with ECH to produce the three diepoxy monomers with glycidyl ether functions (Fig. 21) which can be used to prepare bio-based epoxy resins [147,148]. In this case, the three epoxy resins were crosslinked with isophorone diamine (IPDA) at 100 °C for 1 h, then at 125 °C for 1.5 h and finally at 160 °C for 1 h. The thermomechanical properties of these polymers were subsequently compared with those obtained with DGEBA/IPDA, obtaining fairly similar results (T_g , modulus of elasticity, thermal stability and crosslinking density), in particular for vanillic acid diepoxy, which exhibits excellent thermomechanical properties. In addition, given that these monomers have epoxy functions of the glycidyl ether type, the crosslinking reaction can in principle take place at room temperature. The level of biobased carbons will depend on the vanillin derivative and if the ECH used for the O-glycidylation reaction is biobased or not (54-100% biobased carbons).

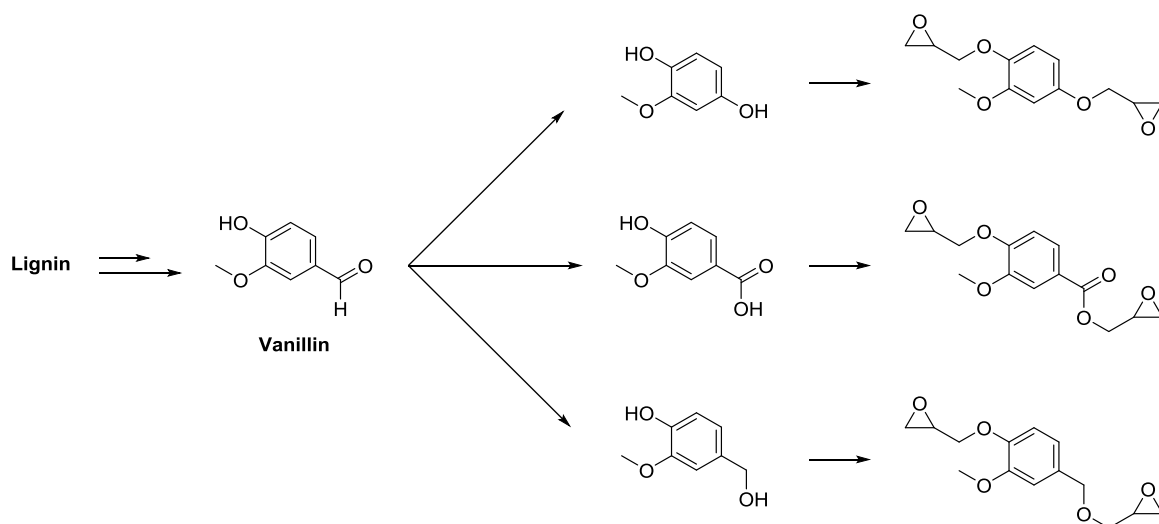


Fig. 21. Synthesis of epoxidized vanillin derivatives from lignin.

Another study shows the preparation of a diepoxide monomer from vanillic acid using a coupling, allylation and epoxidation strategy (Fig. 22) [91]. The synthesis of this monomer is carried out by the reaction between two molecules of vanillic acid and one of 1,5-dibromopentane. Subsequently, the phenolic hydroxyl groups can react with allyl bromide followed by a chemo-enzymatic oxidation reaction in which some of the allyl groups are transformed into glycidyl ether functions, resulting in a mixture of diepoxidized products and monoepoxidized derivatives. This synthetic method avoids the use of ECH, which is toxic and CMR. However, it uses DMF as a solvent (CMR) in the allylation step, and the halogen compounds used in this synthesis (1,5-dibromopentane and allyl bromide) are toxic, CMR and petro-based compounds.

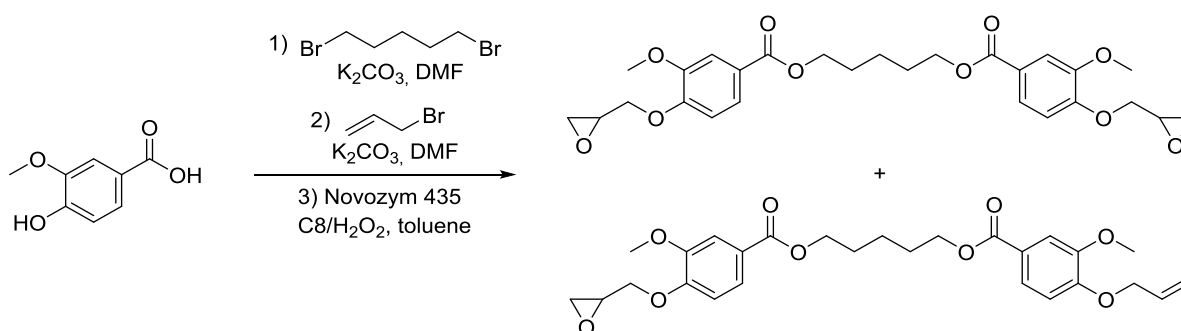


Fig. 22. Synthesis of pentan-1,5-diyl bis (3-methoxy-4-(oxiran-2-ylmethoxy) benzoate) by coupling, allylation then epoxidation by chemo-enzymatic route.

2.2.7. Starch and sugars

2.2.7.1. Glycerol

Glycerol (or glycerine) is a simple polyol which can be obtained from sugars but also from vegetable oils. It is used as a sweetener, in particular in pharmaceutical compositions. Glycerol can be epoxidized by reaction with ECH to form poly(glycidyl ether) glycerol (Fig. 23). Since it has a secondary alcohol that is less reactive in its structure, the introduction of glycidyl ether functions with ECH is mainly carried out on primary alcohols. This synthesis requires an excess of ECH, which results in the presence of chlorine atoms in the resins and the possible subsequent formation of hydrogen chloride (HCl). On the other hand, an advantage of poly(glycidyl ether) glycerol is the possibility of forming oligomers like for DGEBA to generate poly(glycerol)-poly(glycidyl ether). This makes it possible to modulate the viscosity of the resin as a function of the molecular mass of the oligomers. Several studies report the synthesis of polymers from glycerol poly(glycidyl ether) and poly(glycerol)-poly(glycidyl ether), which are moreover commercially available (Nagase Chemtex® DENACOL™ EX-313 and EX-512, respectively) [149,150]. The resulting polymers, crosslinked with two bio-based hardeners, showed interesting mechanical properties but Tg values below 60 ° due to the absence of aromatic groups. The bio-based carbon content will be at least 33% for diglycidyl ether glycerol and can be up to 100% if the ECH is bio-based.

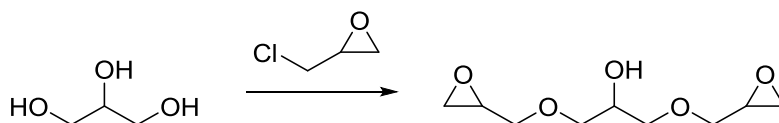


Fig. 23. Synthesis of epoxidized glycerol.

2.2.7.2. Sorbitol

Sorbitol is a polyol used as a sweetener and is produced from starch, resulting from the depolymerization of biomass (Fig. 24). For this, the starch must first be hydrolysed to generate D-glucose [151]. Then D-glucose is hydrogenated to generate sorbitol. Since glucose can be produced from starch, but also from cellulose or lignin by chemical transformation, it is one of the most abundant natural resources.

The Huntsman® Corporation markets a tetra-functional epoxy resin based on sorbitol. This epoxy resin, called ERISYS® GE-60, is a viscous liquid (between 8,000 and 18,000 mPa.s) with epoxy functions of the glycidyl ether type. The crosslinking reaction should therefore take place at room temperature thanks to the reactivity of these functions. In contrast, the thermal stability of the crosslinked material is inferior to materials made from DGEBA (5% mass loss at 249 and 261 °C for resins crosslinked with Jeffamine EDR-148 and Jeffamine D-230, respectively) due to the absence of aromatic groups, but the mechanical properties of the materials obtained are fairly correct [152,153].

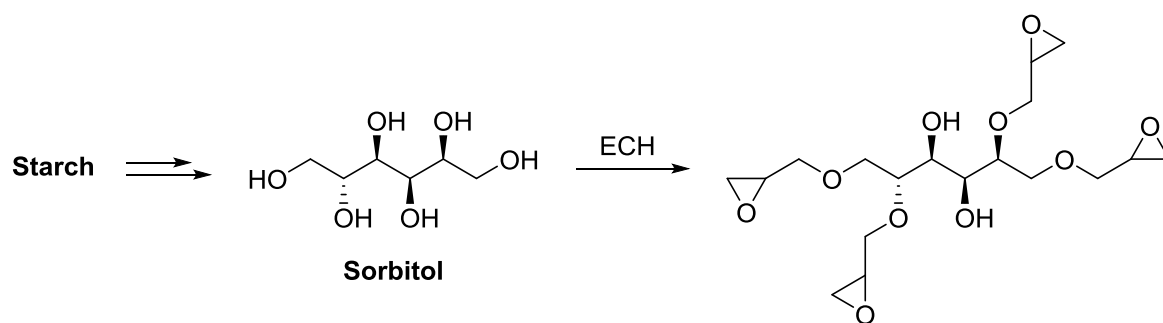


Fig. 24. Synthesis of epoxidized sorbitol (ERISYS® GE-60) from starch.

The bio-based carbon content depends on the bio-based nature of the ECH used for the O-glycidylation of sorbitol. Depending on this, the percentage of biobased carbon will be 33% or 100%, but neither the percentage nor the source of the ECH used for the synthesis of this resin is indicated in the technical data sheet of the product.

2.2.7.3. Isosorbide

Isosorbide is a diol with a structure based on two fused furan rings obtained by dehydration of sorbitol [154]. It is a non-toxic, chiral molecule that provides stability to polymers such as polyesters, polycarbonates and polyurethanes [155]. Due to the versatility of its hydroxyl groups, isosorbide is used in several fields of application such as pharmaceuticals, detergents, cosmetics, or as a stabilizer or plasticizer [156]. There are different methods allowing the synthesis of the isosorbide diglycidyl ether as well as its oligomers, as shown in Fig. 25 [157–162].

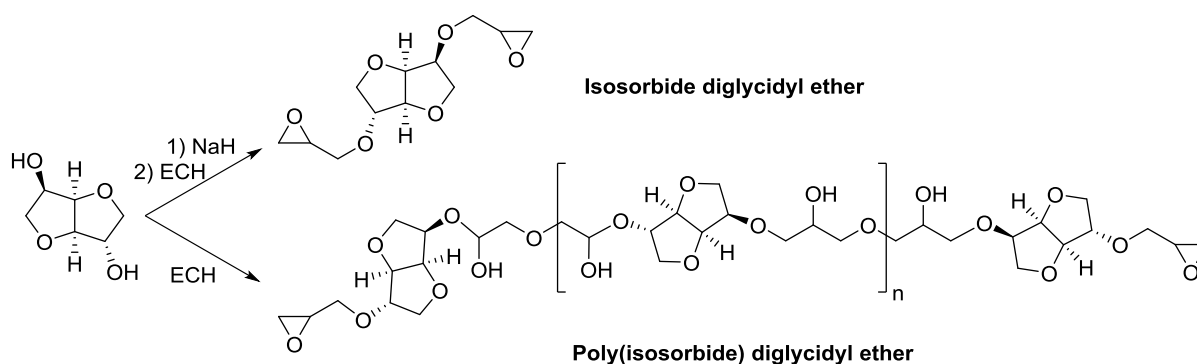


Fig. 25. Synthesis of isosorbide diglycidyl ether and du poly(isosorbide) diglycidyl ether.

The first method is a two-step reaction that involves generating isosorbide alcoholate in the presence of NaH and its subsequent reaction with ECH in the presence of a strong base. This method is selective because it only leads to the diglycidyl ether of isosorbide. The second method, quite similar to the synthesis of DGEBA, consists of combining isosorbide directly with ECH in aqueous medium in the presence of a strong base, which generates oligomers of the isosorbide diglycidyl ether [163,164]. As with DGEBA, the possibility of obtaining oligomers makes it possible to modulate

the viscosity of the resin. Isosorbide diglycidyl ether can also be obtained by the allylation reaction of isosorbide with allyl bromide, followed by an oxidation step [161]. This synthetic method avoids the use of ECH, but instead uses allyl bromide (toxic, CMR and petro-sourced) and m-CPBA (very strong oxidizer). Moreover, due to the large amount of m-CPBA required, this synthesis has not been developed industrially.

Diglycidyl ether isosorbide has fairly reactive glycidyl ether groups, which should allow crosslinking with an amine at room temperature. On the other hand, this resin provides materials with fairly good rigidity and thermal stability thanks to its structure, but inferior to DGEBA-based materials [161]. The isosorbide-based resins crosslinked with diethylenetriamine (DETA) showed T_g values of about 60 °C, lower than those of DGEBA/DETA because of the absence of aromatic groups in the isosorbide-based resins. However, they show similar or even better tensile and impact strength than DGEBA-based materials. The bio-based carbon content of this monomer will be at least 50% and will be higher in the case of oligomers. It can even be 100% if the ECH used for its synthesis comes from glycerol.

Bis-isosorbide diglycidyl ether can also be obtained by combining isosorbide with a large excess of ECH and with sodium hydroxide [164]. The resulting resin was then cured using an aliphatic amine (Jeffamine T403). The properties of this materials were compared to those of a material synthesized with DGEBA (EPON 826) and crosslinked with the same hardener. As in the previous case, the mechanical properties of the material made with isosorbide were similar and even superior to that of DGEBA, with 40% higher impact resistance. In contrast, the T_g was lower than that of DGEBA (48 °C and 90 °C, respectively).

2.2.8. Vegetable oils and fatty acids

Vegetable oils are mixtures of triglycerides from plants. These are therefore substances rich in biosourced hydrocarbons. Usually, they are extracted from the seeds of oil plants. Vegetable oils are generally liquids at room temperature. Currently, it is the most widely used renewable resource in the chemical industry [165,166]. The triglycerides found in vegetable oils have three ester bonds which can be hydrolysed to form glycerol and three fatty acids. Fatty acids represent about 95% of the total weight of triglycerides. Vegetable oils are made up of a wide variety of fatty acids which composition varies depending on the oil, but most fatty acids have naturally occurring functional groups such as unsaturations, hydroxyl groups, and sometimes even epoxy groups. Low reactivity natural carbon-to-carbon double bonds can be easily converted into epoxy groups (Fig. 26). Epoxidized vegetable oils are generally used as plasticizers or stabilizers for the synthesis of poly(vinyl chloride) (PVC) or for paints and coatings [167]. They can also be used to replace conventional epoxy resins such as DGEBA to synthesize crosslinked epoxy-type polymers. Vernonia oil, extracted from the *Vernonia galamensis* plant, is a vegetable oil rich in vernolic acid, which naturally contains an epoxy group in the aliphatic chain (Fig. 27) [168].

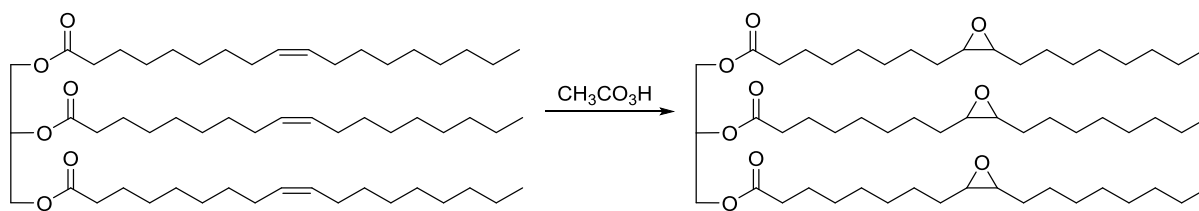


Fig. 26. Formation of a tri-epoxy from the triglyceride of oleic acid.

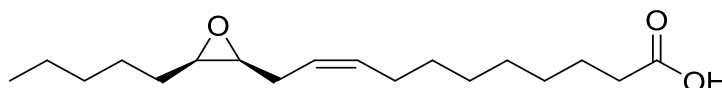


Fig. 27. Chemical structure of vernolic acid.

Arkema® is one of the main industrial producers of epoxidized vegetable oils, with the development of Vikoflex™ products based on epoxidized soybean oil and linseed oil. These oils have bio-based carbon levels of 100% or close to 100%. In addition, their synthesis does not require the use of ECH since the unsaturations can be directly transformed into epoxy functions with an oxidant. However, epoxy resins synthesized from vegetable oils have poorly reactive epoxy functions because these functions are located in the middle of the aliphatic chain, or in the best case at the end of the chain. This explains why these epoxy resins do not crosslink at room temperature. In order for them to crosslink, acids are generally used as a high temperature hardener, in particular because amines could lead to amidification side reactions on the nearby esters. However, if the functionalization is carried out at the end of the chain, the reactivity is similar to epoxy resins (glycidyl ether), especially when the crosslinking reaction is carried out with anhydrides [168]. In general, the use of epoxidized vegetable oils leads to very (too) flexible materials, compared to the use of DGEBA.

2.2.9. Terpenes, terpenoids and resin acids

Terpenes, terpenoids and resin acids are a class of natural biomass rich in hydrocarbons. Many plants and trees (especially pines and conifers) produce this type of molecules.

2.2.9.1. Limonene

Limonene is a terpene found in the peels of citrus fruits. Its world production is estimated between 50 and 75 million tonnes per year [169]. It is used in industry as a perfume and as a solvent for coatings. Thanks to the presence of two unsaturations in its chemical structure, it is possible to obtain monoepoxide and diepoxide monomers via the oxidation of the double bonds with simple oxidants such as hydrogen peroxide or m-chloro perbenzoic acid (Fig. 28) [170]. Moreover, these monomers are commercially available and are generally used as reactive diluents in epoxy resins.

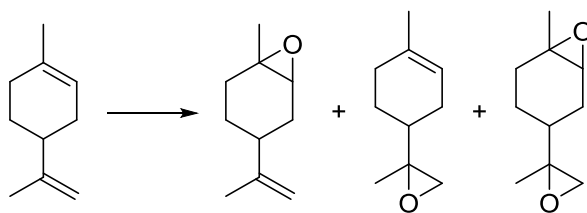


Fig. 28. Epoxydation of limonene.

Epoxydized limonene is a molecule with 100% biobased carbons and does not require the use of ECH for its synthesis. However, the epoxy functions of limonene, and in particular the endocyclic epoxy function, are relatively unreactive. Therefore, the polymerization reaction does not normally take place at room temperature.

2.2.9.2. Colophane

Rosin is the main component of pine resin, which consists of approximately 70% rosin, 15% turpentine, and 15% debris and water [171]. This is the non-volatile solid fraction of the resin. Its global production was around 1.23 Mt in 2019 [172]. Rosin is made up of three types of tricyclic molecules: abietane, primarane and isoprimarane. For many years, rosin and its derivatives have been used for the production of soaps, inks, coatings, adhesives and rubber additives, but recently there has been increasing interest in rosin acids as chemical raw materials for polymers or other chemicals.

It is possible to obtain epoxy monomers from rosin, for example by converting rosin to maleopimaric acid and then to the corresponding triglycidyl ester by reaction with ECH, aqueous sodium hydroxide and tetrabutylammonium bromide (Fig. 29) [173]. For the crosslinking of the epoxy resin obtained, the authors used the precursor of the triglyceridic ester, maleopimaric acid. The material thus obtained exhibits excellent thermomechanical properties, with a T_g at 164 °C and a flexural modulus of 2200 MPa. These values are lower but similar to the values obtained with materials made with DGEBA. In contrast, impact strength and elongation at break were lower, compared to materials derived from DGEBA.

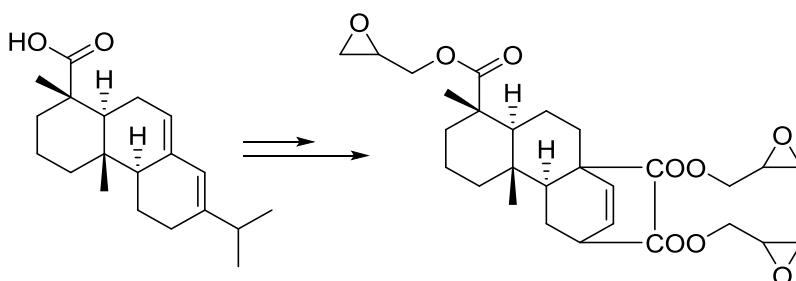


Fig. 29. Chemical structure of abietic acid and a tri-epoxy monomer obtained from this acid.

Several epoxy resins made from pine oil, and therefore rosin, are available on the market.

2.2.9.3. Commercial products

Recently, industrial companies have proposed commercial epoxy monomers that are (at least) partially biobased. Some of them are only based on petrosourced monomers that have been epoxidized with biobased ECH, whereas others are derived from renewable resources. Hereby are mentioned some of the most common. SUPER SAP® ONE is an epoxy resin made from pine oil (rosin) by Entropy Resins®, an American company. According to the manufacturer, it cures at room temperature (25 °C) in 7 days with Super Sap® ONF (Fast) Hardener. The pot life of the mixture is 15-20 min. The mixture, with 31% bio-based carbon content, has a fairly low viscosity (500 mPa.s). The crosslinked material obtained from this mixture has excellent mechanical properties according to the manufacturer, and the resin intended applications are coatings. EPOBIOX® is also a commercial epoxy resin made from pine resin, and therefore rosin, by Amroy Europe Oy, a Finnish company. This resin has 70% biobased carbon and allows vertical gluing. AMPRO™ BIO is an epoxy resin made from rosin by the Swiss company Gurit®. This resin contains between 40 and 60% biobased carbon. According to the manufacturer, it crosslinks at room temperature and has a fairly short pot life (23 min) when mixed with AMPRO™ Fast Hardener. The Tg of the materials obtained are between 44 and 47 °C depending on the crosslinking time. Resoltech® 1800 ECO is an epoxy resin made from rosin by Resoltech, a French company based in Rousset (13), France. This resin has 33% biobased carbon when cured with 1804 ECO hardener. The Tg of the crosslinked material is 50 °C after 14 days at 23 °C, and it goes up to 94 °C after thermal cycling at high temperature. The viscosity of the mixture is quite low (258 mPa.s).

The development of biobased epoxy resins allowing the substitution of the diglycidyl ether of bisphenol A remains very difficult, because many synthetic bisphenols, whose structures are very similar to BPA, appear to have comparable activity with regard to human hormone receptors. Widely used compounds reported in the literature, such as resorcinol, face the same problems. University researchers have focused a lot on compounds that can be extracted from bioresources, because their chemical structures are more complex and some of them have low toxicity profiles. These compounds are extensively studied because their chemical structures provide new properties. However, these structures also provide different thermomechanical properties to epoxy materials, so it can be difficult to find a unique alternative to DGEBA. Thus, natural phenols are particularly interesting because they can present a promising alternative to DGEBA. Many of the epoxy compounds described are still in the early stages of research, but some are already on the market, such as NC-514. Researchers are now also focusing on evaluating the endocrine activity of new compounds, in order to provide the most useful information to the community, and in particular to industrial researchers, when they need to select the right substitute for their intended applications. This review aims at focusing first on the properties of interest for each potential bio-based substitute for DGEBA. In addition, a literature review of biological assays on the endocrine activity of these new monomers has been added, in order to shed light on the potential application limitations of the use of such compounds. Some of these substitutes are now clearly not recommended as substitutes for DGEBA, but others have promising low toxicity profiles. However, evaluation of endocrine activity is not always performed by researchers, even when they claim to find DGEBA alternatives. Beyond the renewable carbon content or the toxicity of these monomers, the curing conditions are crucial. Photopolymerization is one of the greenest polymerization processes. One of the challenges is to determine the reactivity of these biobased epoxy monomers toward photopolymerization.

3. Cationic Photopolymerization: principles, mechanisms and perspectives

The following section aims at providing an overview of photoinduced cationic polymerization processes. Different photoinitiation mechanisms are discussed and the cationic photopolymerization of typical epoxy and ether vinyl monomers are introduced. Recent advances in the design of visible light sensitive photoinitiating systems based on onium salts, organometallic complexes and other metal-based systems are also outlined.

3.1.1. An overview of photoinitiated cationic polymerization

Among polymerization methods traditionally used in polymer sciences, light possesses distinct advantages: it is not only abundant, inexpensive and non-invasive, hence a relatively green source of energy, but it also allows for rapid curing, room-temperature conditions, non-polluting and solvent-free systems, potential use of natural and renewable raw materials as well as spatial and temporal control [5,23,26,174].

Photoinduced cationic polymerization has already been exhaustively described in the literature by several outstanding reviews [5,21,23–25,48,174–176]. The aim of the following sections is to give an overview of cationic photoprocesses along with their mechanisms before presenting the recent strategies investigated in the scope of visible light-induced cationic photopolymerization.

Unlike free-radical promoted photopolymerization, molecular oxygen does not inhibit photoinitiated CP [21]. In addition, monomers usually used for cationic processes, including epoxides and cyclic ethers, vinyl ether-based monomers, trioxanes, lactones, alkenes, thiiranes and oxazolines [25,174], are known to be less toxic or irritating than acrylate and methacrylate-based systems, their alternative radical polymerization monomers [23–25]. Cationic curing processes are also characterized by a lower shrinkage and a lower residual stress thanks particularly to the use of ring-opening monomers [26,27] and cured materials often offer better abrasion and chemical resistance as well as better adhesion properties on various substrates [21,23,26]. Last but not least, once it is initiated, cationic photopolymerization can proceed once the light source has been removed thanks to the relatively long-lived Brønsted acid photogenerated by onium salts generally used as photoinitiators [24]. This process, usually called the “dark reaction”, allows for further monomer conversion [25].

Cationic photopolymerization initiated by the decomposition of onium salts under light irradiation was first described by Crivello & Lam in the 1970s [28–31]. A variety of onium salts, including sulfonium [32–36], iodonium [28,37], pyridinium [38–40], phosphonium [41,42], bismuthium [43], anilinium [44], pyrylium salts [177,178] or others [45–47] have since then been extensively studied and applied in both academic and industrial environments for the polymerization of various types of monomers.

Onium salts are composed of two entities: a cationic centre consisting of a heteroatom and organic moieties and an inorganic metal complex counteranion [23,48]. Chemical structures of the most common onium salts are depicted in Fig. 30. If the cationic part of the salt is responsible for its

UV-absorption properties, it is the anionic part, usually BF_4^- , PF_6^- , AsF_6^- and SbF_6^- , that controls the strength of the acid photogenerated during the photolysis. The nucleophilicity along with the strength of the associated photogenerated proton increase with the size of the counteranion [23,24].

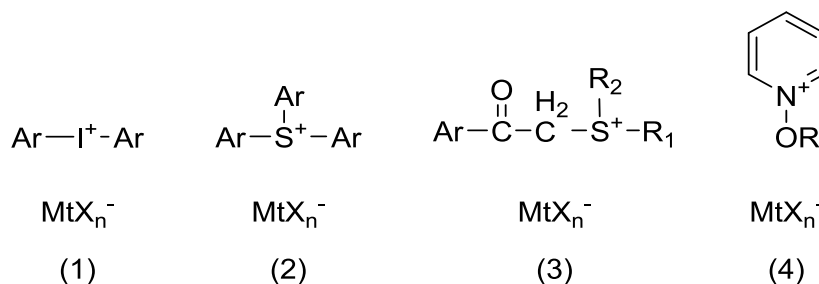


Fig. 30. General chemical structures of diaryliodonium (1), triarylsulphonium (2), dialkylphenacylsulfonium (3) and *N*-alkoxy pyridium (4) salts.

The mechanism of cationic photoprocesses has already been widely reviewed [5,21,23–25,48,49,174–176]. Diphenyliodonium hexafluorophosphate is a typical example of onium salts, the simplified photoinitiation mechanism of which is described in Fig. 31. Briefly, upon UV irradiation, the diphenyliodonium entity undergoes either homolytic or heterolytic cleavage, giving rise respectively to a radical cation/phenyl radical pair or a phenyl cation. If these highly reactive species are able to directly initiate the polymerization process in some cases, they most generally further react in the presence of solvent or hydrogen donor groups to form strong Brønsted acids. Released protonic acids are the actual initiators of the cationic polymerization [25]. Thus, the actual parameter distinguishing a photoinduced active centre from classical polymerization initiators is the use of light to generate the aforementioned active centre. In this respect, onium salts are considered as photoacid generators (PAGs) [23].

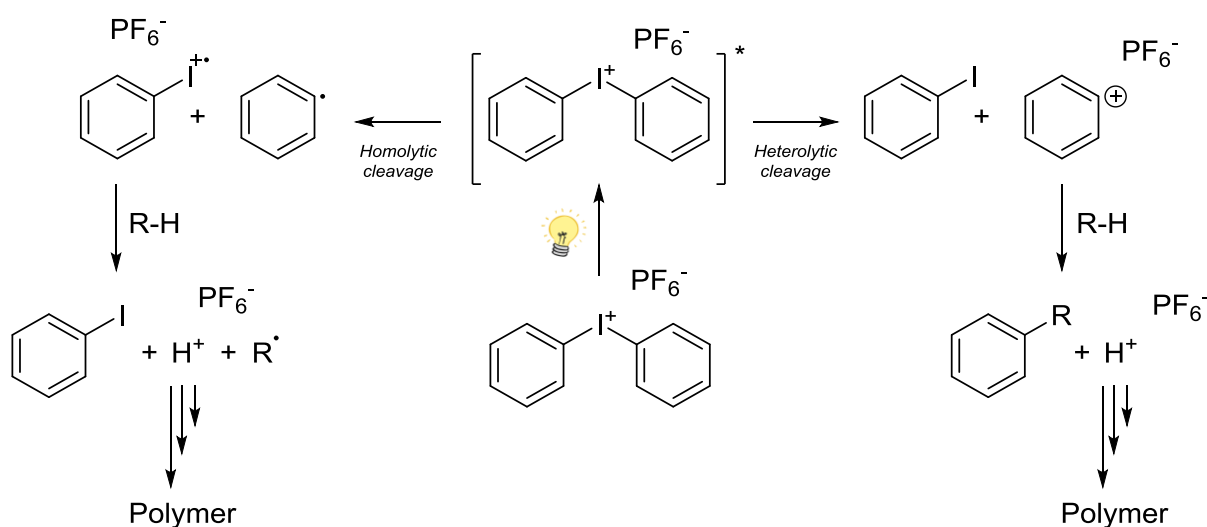


Fig. 31. Mechanism of direct activation of diphenyliodonium hexafluorophosphate under irradiation as a typical example of onium salts.

Diaryliodonium and triarylsulphonium salts bearing anions such as BF_4^- , PF_6^- , AsF_6^- and SbF_6^- are considered as universal cationic photoinitiators since they have the ability to initiate the polymerization of almost every known type of cationically polymerizable monomers upon irradiation [25]. They are the most widely used class of cationic PIs and have reached commercialization whereas dialkylphenacetylsulfonium and N-alkoxypridinium salts are still actively investigated [49].

Most industrial applications of cationic photoprocesses include multifunctional cycloaliphatic epoxy based formulations because of their high curing rates as well as their excellent thermal and mechanical properties, solvent resistance and adhesion to a broad array of substrates [25]. They consist mainly in coatings, composites, adhesives, inks, medical applications and 3D-printing technologies [23–25].

Cationic photopolymerization reactions are however hindered by several factors such as spectral sensitivity of onium salts or the processable thickness of the material layer due to the low penetration depth of UV light [23]. As a matter of fact, as depicted in Fig. 32, the greater the wavelength, the more light penetrates the successive layers of the irradiated material [179].

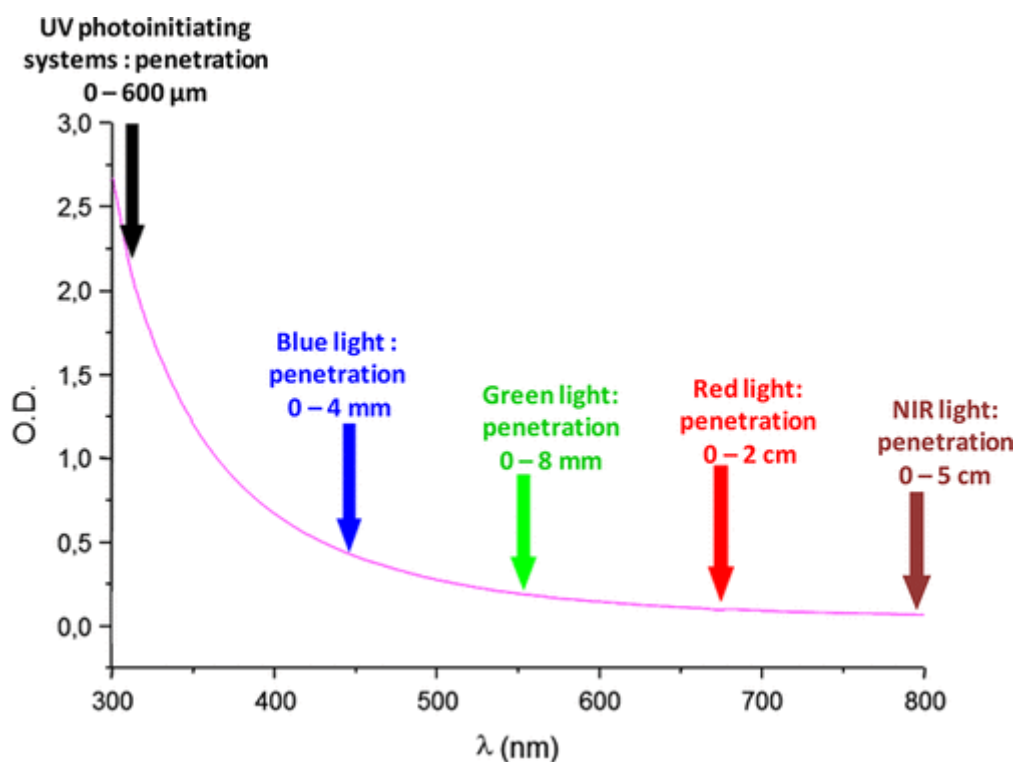


Fig. 32. UV-vis diffusion of light for a polystyrene latex (112 nm of average diameter) and calculated penetrations of selected photons. Reprinted with permission from Bonardi et al. [179]. Copyright 2018 American Chemical Society.

Concerning the spectral sensitivity of onium salts, it does not exceed the mid-UV range as most of these salts effectively initiate cationic photoinduced polymerization reactions when exposed to short and mid-UV wavelengths (200–300 nm range) [21,26,48]. Diaryliodonium salts mostly absorb around 210–250 nm and their absorption spectrum is characterized by a long absorption tail going as far as 370 nm [29]. These absorption properties prevent the efficient use of onium salts for visible light-induced cationic polymerization processes, which is the reason why there has been a growing

interest for the design of photoinitiating systems capable of generating acids upon exposition to longer wavelengths in the visible light and near-IR regions [26,29,49].

In this respect, free-radical promoted cationic polymerization reactions [5,48,175,180–182] as well as photosensitization [49,50,183] have become very attractive alternatives for the development of visible light absorbing PISs.

3.1.2. Free radical-promoted cationic polymerization

Free radical-promoted cationic polymerization (FRPCP) has emerged in the late 70s [181,182] as a way to circumvent some of the issues raised by other approaches, such as appropriate solubility profiles of efficient photosensitizers [174] and the use of high-energy irradiation devices for the direct photolysis of onium salts [48]. The radical species can either be of thermal or photochemical origins [48,181].

The principle of FRPCP relies on the indirect reduction of cationic onium PIs by light-sensitive radical-generating species through electron-transfer mechanisms [48,49,175]. Succinctly, upon irradiation, type I radical PIs undergo direct unimolecular homolytic bond cleavage whereas excited type II PIs interact with hydrogen donor species through photoinduced electron-transfer to give rise to electron-donor free radicals. These radicals, whether they are formed by cleavage (type I) or by hydrogen abstraction (type II systems), are likely to be oxidized by onium salts, resulting in the formation of a cationic species initiating in turn the CP of various monomers.

The spectral sensitivity of such photoinitiating systems can be tuned by selecting a radical PI with adequate absorption properties [48,49]. The richer the radicals electron-wise, the more they are readily oxidized [175]. Examples of FRPCP using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a classical benzoin type I PI and benzophenone as a well-known type II radical PI are described in Fig. 33 and Fig. 34.

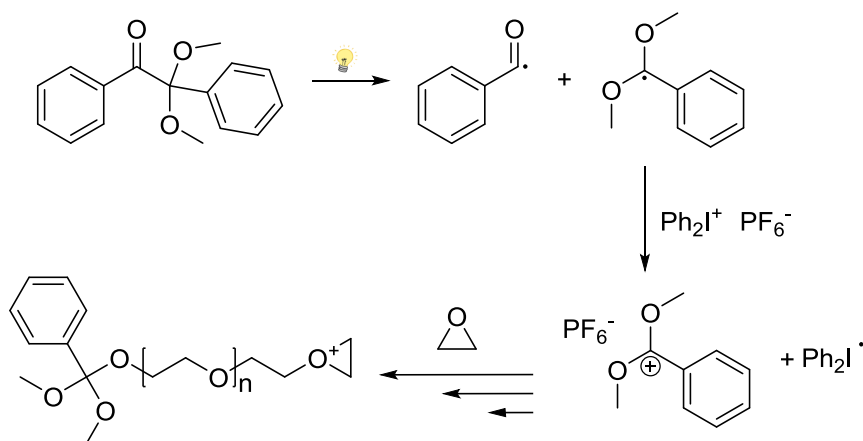


Fig. 33. Mechanism of free radical-promoted cationic polymerization of an epoxide monomer using DMPA as a classical type I photoinitiator.

The efficiency of the whole system is directly associated with the redox potentials of both the free radical and the considered onium salt used in the FRPCP mechanism [175]. It depends notably

on the radical species R^\cdot formation quantum yield and on the ability of the corresponding cation entity R^+ to efficiently initiate the cationic polymerization reaction [184]. Iodonium salts have a higher reduction potential, which make them very suitable candidates for FRPCP, as compared to sulphonium salts, whose use is therefore rather limited in this respect [175].

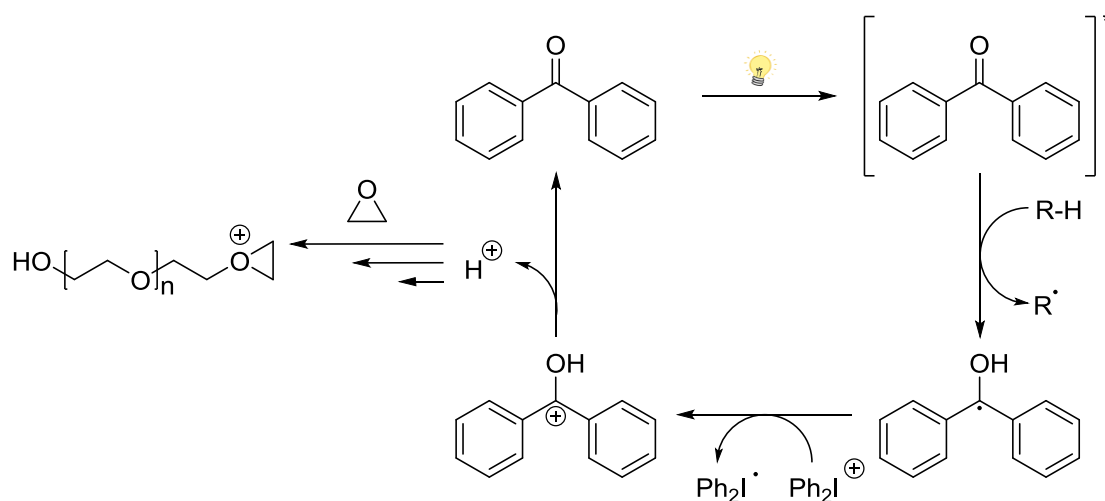


Fig. 34. Mechanism of free radical-promoted cationic polymerization of an epoxide monomer using benzophenone as a typical type II photoinitiator.

FRPCP has attracted strong interests as this technique allows for the use of longer wavelengths as far as the near IR region for photoinduced CP reactions initiated by onium salts [48]. Since the synthesis of visible light absorbing PIs can be expensive and time consuming and the choice of efficient PIS rather limited [49,50], it rapidly represented a promising alternative to conventional cationic photopolymerization techniques since all conventionally used free radical photoinitiators represent suitable candidates for the reduction of onium salts [175,184]. Additionally, the use of free radical PIs also present other advantages such as good solubility in a wide range of commonly used monomers, absorption characteristics covering the UV as well as the visible light regions of the electromagnetic spectrum, commercial availability, excellent dissociation yields and high reactivity of photoinduced radicals [175].

The use of additives and three-component systems for FRPCP conducted under visible light are under intensive investigation as they have shown to greatly enhance cationic photoprocesses via the formation of highly reactive initiating entities [175]. In this regard, photosensitization, silyl radical chemistry, metal based and organic photoredox catalysts as well as amine-based co-initiators are all promising strategies currently studied for the development of efficient visible light FRPCP. Yet, as for conventional FRP reactions, the main limitation of FRPCP remains oxygen inhibition since the peroxidation process (addition of radicals to oxygen) is highly efficient [184–186]. Cationic photoprocesses which usually presents the distinct advantage of not being hindered by oxygen is here slowed down under air for this reason [184].

3.1.3. Photosensitization in cationic polymerization

The concept of photosensitization relies on the use of light absorbing compounds, whose absorption ranges in the near-UV, visible light and even near-IR regions of the light spectrum, as a way to induce the photolytic decomposition of a considered PI and thereby generate highly reactive species effectively initiating the polymerization process (radicals or cations) [49,50]. In the framework of photoinduced CP, photosensitization refers to the process by which a molecule strongly absorbing in the visible light range induces the photodecomposition of cationic PIs, leading to the generation of a strong Brønsted acid which in turn will initiate the CP.

These molecules are referred to as photosensitizers (PSs) and include various classes of compounds: ketones (camphorquinone, benzil, anthraquinones, thioxanthenes, benzophenone, indanedione and acridinedione derivatives, chalcones, naphthalimide compounds, etc.), phenothiazine derivatives, electron-rich polynuclear aromatic hydrocarbons (anthracene, pyrene, perylene and pyrromethene derivatives, carbazoles, quinoxalines, boranil compounds, etc.), metal carbonyls, organometallic as well as metallic salt complexes, etc. [48–52]. Photosensitizers usually possess electron-rich chemical structures with strong absorption characteristics in the near-UV/visible light parts of the spectral range.

PSs allow for the broadening of the spectral sensitivity of cationic PIs from the 200-300 nm range throughout the entire UV region and well into the visible spectral areas [25,49,52]. Intramolecular photosensitization can also occur when using onium salts bearing long wavelength light absorbing groups [49,187]. Via intramolecular interactions, the efficiency of the electron-transfer photosensitization is improved.

In cationic photoprocesses, PISs relying on photosensitization are composed of a PS/PI couple. In FRPCP, they consist in a complex association of at least a PS, a cationic PI and a radical source (usually a radical PI) [49,50]. Upon irradiation, excited photosensitizers can activate and reduce onium salts either by energy-transfer or electron-transfer photosensitization [5,25,49,174].

In energy-transfer photosensitization, the PS acts as an energy carrier and is supposed to be fully recovered at the end of the process. Upon irradiation, the excited PS transfers its energy to the PI provided that the energy of the excited state of the PS is greater than that of the target molecule. Upon satisfaction of this prime requirement, the excited PI undergoes then a photolytic decomposition giving rise to the cationic entity (Fig. 35a) [5,49].

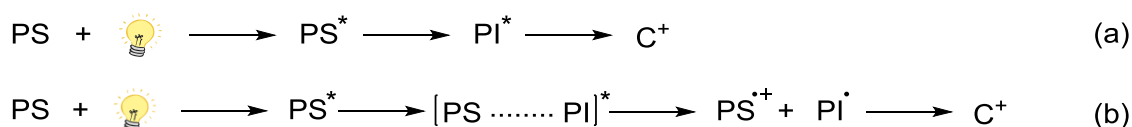


Fig. 35. Simplified mechanisms of: (a) energy-transfer photosensitization, (b) electron-transfer photosensitization in cationic photopolymerization.

In electron-transfer sensitization, the PS in its excited state forms an excited state complex (usually named exciplex) with the target molecule. The exciplex decay is followed by the transfer of an electron from the PS to the onium species. Consequently, the oxidation of the PS, giving rise to a radical cation $\text{PS}^{\bullet+}$, and the reduction of the onium salt, producing an unstable radical species PI^{\bullet} , takes places simultaneously (Fig. 35b) [5,48,49].

The radical cation PS^+ so generated is the initiating entity of the cationic photoprocess and may directly initiate it, but it most often interacts with a hydrogen donor to generate a Brønsted acid capable of initiating the CP process [48]. Regarding the radical PI, it irreversibly decomposes itself, thus avoiding back electron transfer [49,175]. Electron-transfer photosensitization is also referred to as a photoredox reaction and is notably the mechanism involved in free radical-promoted cationic polymerization [49]. During such a process, the PS is not recovered.

Photosensitizers featuring high molar extinction coefficients, low oxygen inhibition, high reactivity regarding the photolysis of onium salts, long-lived excited states, and suitable absorption properties specifically matching the emission spectra of the considered irradiation devices (in the visible light to near IR regions) are key parameters one should consider for the design of highly efficient photoinitiating systems [175,183]. Long excited state lifetimes of the PSs are indeed attractive features as their lengthening allows for more time for it to interact with the various constituents of the formulation. Highly reactive species are consequently formed more efficiently, thereby significantly improving the polymerization kinetics and final monomer conversions. Also, the higher the photosensitizers molar extinction coefficients, the lower the concentration of the said PSs is required [183].

Nevertheless, the limitations encountered with photosensitization are the limited solubility profiles of photosensitizers in conventional monomers and solvents as well as the toxicity of unmodified polynuclear aromatic hydrocarbons [49,175]. In this regard, the use of synthetic or natural dyes (i.e. organic molecules absorbing light within the 400-800 nm visible range) as effective PSs is a promising alternative as it presents several advantages such as commercial availability, good solubility and stability, lower costs and toxicity [51,183]. Natural dyes are particularly interesting starting materials for the design of innovative photoinitiating systems as they are abundant and address environmental and health concerns. Additionally, while synthetic dyes are obtained using expensive materials and sometimes long and tedious synthetic routes, natural dyes are obtained through economically competitive and relatively simple extraction steps [183].

3.1.4. Introduction to silyl radical chemistry

The search for PISs with enhanced photochemical reactivity (lower oxygen inhibition and visible light sensitivity even at lower light intensities) led to the introduction of silyl radical chemistry [186]. Silyl radical chemistry allows for the development of cationic photoprocesses using versatile photoinitiating combinations. It functions in aerated conditions and upon exposure to various low intensity visible light irradiation devices (light-emitting diodes (LEDs), lamps, laser diodes and sun) through a FRPCP mechanism [175,184].

The photolysis of polysilanes when combined with onium salts in the scope of cationic photopolymerization has been first explored by Yagci, Kminek and Schnabel in the 1990s [188]. The originality of this technique consists in the incorporation of a silane-based compound (R_3SiH) characterized by a low Si-H bond dissociation energy in a three-component PIS [189]. Such PISs are versatile, can easily work in very different experimental conditions and benefit from high extinction coefficients in the visible region as well as strong oxidation power of silyl-based FRPCP [175].

The general mechanism of PISs based on the photogeneration of silyl radicals for silane-based FRPCP reactions is presented in Fig. 36. Upon light exposure, the electron-transfer interaction between a given PS and a diaryliodonium salt generates an aryl radical which in turn reacts with the

considered silane-based compound R_3SiH through a proton abstraction step. The silyl radical $R_3Si\cdot$ so generated is then oxidized into a highly effective initiating silylium cation R_3Si^+ . Simultaneously, silyl radicals regenerate themselves along the process as they consume oxygen and scavenge peroxy radicals [175,186,190]. As a consequence, the total amount of initiating radicals $R_3Si\cdot$ increases continuously, oxygen being a mediator in the overall process.

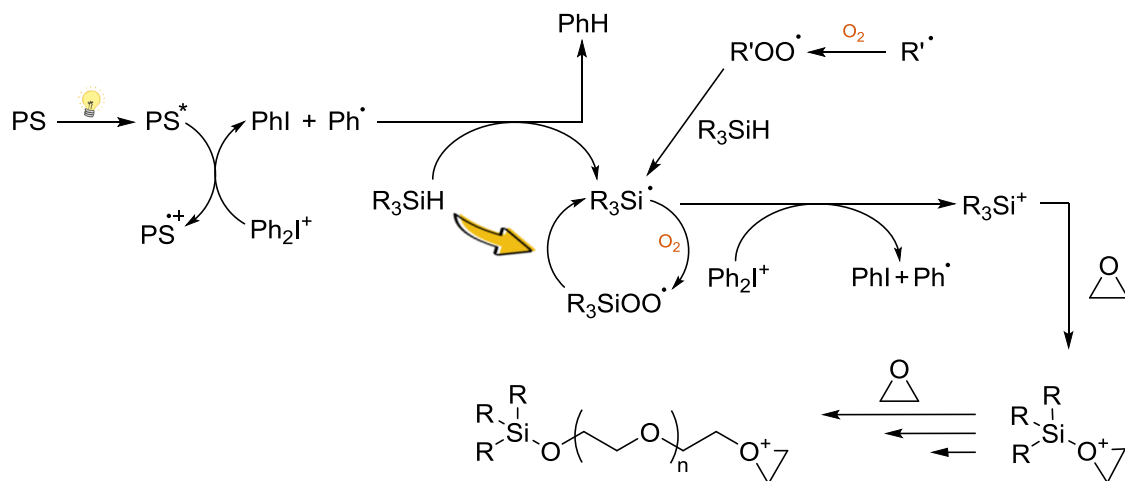


Fig. 36. General mechanism of the photogeneration of highly reactive silyl-based entities in PISs based on silyl radical chemistry for FRPCP.

PISs based on a general PI (or PS)/silane/iodonium salt system offers several very attractive advantages, among which are the following: (i) the PIS absorption properties can be easily tuned from the UV region to the near IR spectral area by carefully selecting an adequate PI/PS, (ii) the highly reactive silyl radical $R_3Si\cdot$ is regenerated along the process, (iii) the radical species overcome the oxygen inhibition by consuming it and act as oxygen scavengers, (iv) hence, oxygen becomes a mediator in the radical species production instead of preventing it, (v) such a photoinitiating system forms a highly reactive cation R_3Si^+ which can initiate the cationic polymerization process [48,51,184,186,190].

It has been demonstrated that two-component PISs based on PI (or PS)/iodonium salts show poor cationic polymerization, mostly due to the low absorption of various systems upon visible light exposure, a strong oxygen inhibition, the low oxidation ability of the considered photoinduced radicals and the poor reactivity of the so formed cation species [184]. The addition of silanes significantly improves polymerization profiles under visible light irradiation conditions in the various studies carried out on this matter [51,191–193].

Silyl-based FRPCP reactions exhibit excellent performances as this strategy combines the advantages of both photosensitization and FRPCP techniques without their distinct inconveniences [190]. This new approach allows for the use of low intensity visible light sources such as LEDs, laser diodes or sunlight to get tack-free coatings using relatively low viscosity matrices while working in aerated conditions [51,185,186,192]. However, this strategy suffers from at least two disadvantages: low cleavage quantum yield and side reactions which are competitive to the silyl radical formation [175].

3.2. An Outline on Cationically Photopolymerizable Monomers

At present, photoinduced CP enables the carbocationic addition polymerization of unsaturated monomers such as vinyl ethers and alkenes as well as the ring-opening polymerization of cyclic ethers and acetals, epoxy monomers and lactones (Fig. 37) [25,174].

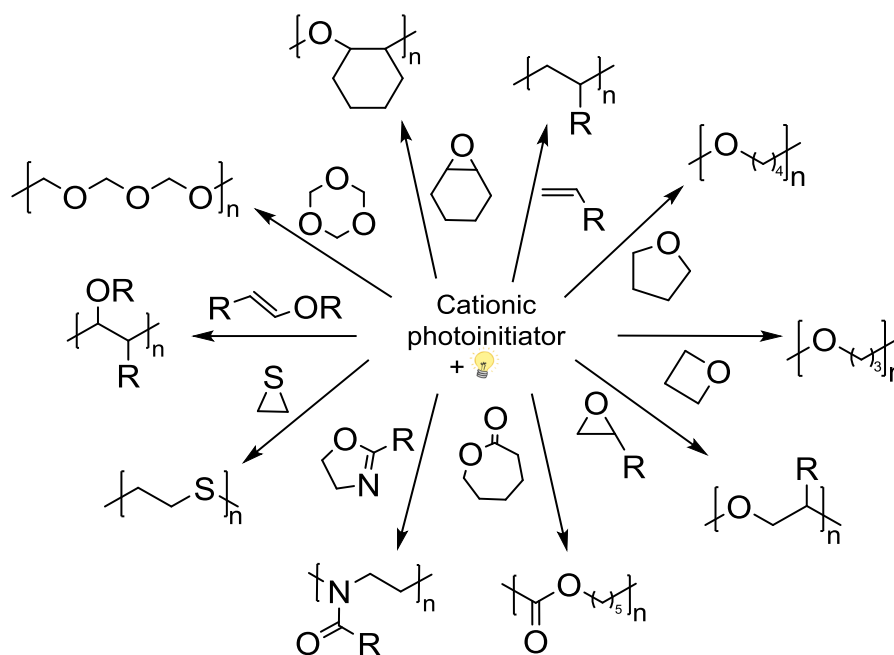


Fig. 37. Cationic polymerization of known monomers.

Epoxides and vinyl ethers are among the most commonly used cationically polymerizable monomers and generally allow for the synthesis of coatings that feature high thermal capability, excellent adhesion properties, good chemical resistance as well as an environmentally friendly nature [5]. Thanks to a rich collection of light-sensitive polymerization initiating species, a large range of different structures have already been polymerized using light as the source of energy.

3.2.1. Cationic ring-opening Photopolymerization of Epoxy monomers

Photoinduced polymerizations consist in a chain reaction mechanism in which an active centre propagates by interacting with a monomer [25]. The active centre can be a radical, more rarely an anion, or in the case of cationic photopolymerization, a cation.

Epoxy monomers are extensively used as thermoset precursors for numerous industrial applications such as surface coatings, electronics and electrical applications, adhesives, reinforced resins, inks or structural materials [27,61,194]. Their large scope of applications is mainly due to their high mechanical properties, relatively low shrinkage as well as their chemical and thermal resistance [24]. However, in the scope of epoxy UV-curing, some challenges still remain and need to be tackled, such as material toughness enhancement and shrinkage lowering upon curing.

Cationic ring-opening polymerization (ROP) photoprocesses implying epoxy monomers have already been brilliantly and exhaustively reviewed in the literature [25,27]. Briefly, it proceeds through an oxiranium intermediate in the presence of a photogenerated protonic acid and occurs following two chain formation mechanisms. In both mechanisms, commonly known as activated chain end mechanisms, the nucleophilic lone electron pair of the epoxy oxygen atom retrieves the photoacid generated by the onium salt photolysis, thus starting the initiation step. An electrophilic centre is hence formed, and the propagating step occurs through cationic chain growth following either a S_N1 or S_N2 mechanism. In the first case, the ROP of the epoxy monomer happens spontaneously, the positive charge being delocalized from the oxygen atom to the carbon chain, consequently forming a carbocation. The latter successively undergoes an attack from the electron pair of another epoxy monomer, and so on. In a S_N2 reaction, the ring-opening of the oxiranium cation is simultaneous to the nucleophilic attack of the neighbouring epoxide. Whether the process follows either one mechanism depends mostly on the cationic centre stability, and consequently on structural parameters such as functional groups or other electron donors in the surroundings. The simplified photoinduced ROP mechanism of a typical epoxy monomer is depicted in Fig. 38.

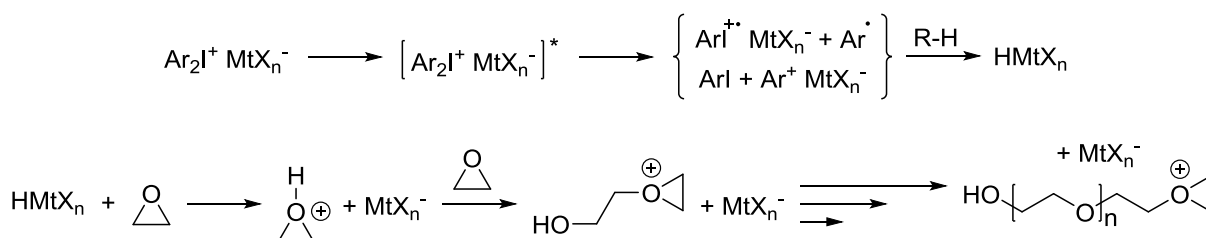


Fig. 38. Photoinduced cationic ring-opening polymerization of a typical epoxy monomer using an iodonium salt as photoinitiator.

Contrary to FRP reactions, the positively charged growing chain carrying the reactive species do not interact with each other, generating termination reactions. This feature allows for beneficial dark cure effect, meaning a continuous living polymerization takes place even after the light source has been switched off, which ensures high final conversions with low energy requirements [25,27].

During the photoinduced ring-opening polymerization of multifunctional epoxides, the curing speed generally reaches a maximum before quickly dropping [25]. This change in curing rate usually occurs upon gelation of the formulation. As the polymer network forms, polymerization progressively slows down as it depends on the diffusion of the unreacted monomers to the fixed propagating sites within the swollen gel. Polymerization ceases completely when vitrification sets in, meaning that the T_g of the polymeric network has reached the temperature at which the photocuring is taking place. At this point, significant amounts of unreacted photopolymerizable functional groups can remain trapped within the final coating.

This can be prevented by using chain-transfer agents, such as alcohols [25,27]. In the presence of an alcohol, the growing ionic chain of a polymerizing epoxy monomer undergoes a nucleophilic attack by the alcohol, yielding a protonated ether (Fig. 39). This extra proton is spontaneously retrieved by another epoxy monomer, which consequently terminates the previously growing chain and simultaneously starts another. Final resulting coatings contain thus alkoxy end groups, however the overall apparent cure of the photocationic polymerization process will have remained high [25].

This mechanism has been introduced in the 1980s and is commonly called activated monomer mechanism [195].

The addition of alcohols can also help in reducing or completely avoiding backbiting side reactions generating undesirable side products during the cationic polymerization of epoxides [27]. Indeed, intramolecular chain transfers can occur if oxygen atoms of the growing polymer chain feature a higher nucleophilicity than the propagating site. These chain transfers called backbiting consist in the nucleophilic attack of one of these oxygen atoms on the cationic active centre, resulting in the formation of unwanted macrocycles.

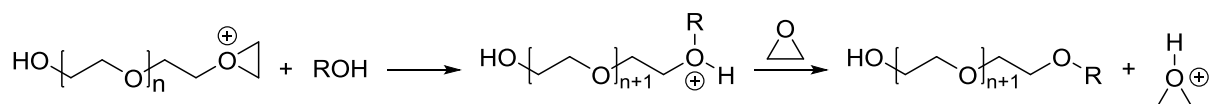


Fig. 39. Activated monomer mechanism in cationic ring-opening polymerization of epoxides.

Common epoxy monomers classically used in cationic ROP are gathered in three categories: cycloaliphatic epoxy monomers (based on cyclohexene oxide moieties), alkyl glycidyl ethers and aryl glycidyl ethers (such as DGEBA and DGEBA-based resins) [27]. Their reactivity depends on the stability of the oxonium intermediates generated: the more unstable the intermediate, the higher the reactivity of the corresponding epoxy entity. It also strongly depends on the basicity, the ring strain and on the steric hindrance of the considered monomer. They usually polymerize slower than vinyl ethers, therefore cyclic ethers such as oxetanes represent suitable alternatives to epoxides in order to get faster curing speeds in industrial contexts [5,27].

Nonetheless, there is a strong influence of structural characteristics on the different monomers reactivity, as some monomers containing epoxycyclohexane moieties exhibit higher rates of polymerization than those containing alkyl glycidyl ethers [25]. Usually, the presence of nucleophilic ester and ether functionalities in epoxides significantly reduces their reactivity, due to potential intramolecular interactions between these functional groups, thereby forming comparatively less reactive dialkoxycarbenium ions or macrocyclic by-products [25,27]. The generation of side products is hardly inevitable and often results in polymers of low molecular weights as well as cyclic polyether by-products. Therefore, epoxy monomers which do not contain any other competing nucleophilic functional group generally possess particularly high reactivity towards ring-opening polymerization.

It is worth mentioning that epoxy polymerization rates are influenced by water and moisture conditions. While high humidity conditions usually inhibit cationic polymerization rates, the presence of water can contrarily accelerate them, as water can act as a chain transfer agent [25]. However, high humidity conditions can result in a high-localized concentration of water, leading to excessive chain transfer and ultimately to low molecular weight polymers. In general, chain transfers can occur involving various nucleophilic entities, such as solvents, impurities present in the system or counter ions [27].

3.2.2. Ether derivatives: New Approach of the Cationic Photopolymerization and Reactivity

The use of ethers and ether derivatives such as vinyl ether monomers in cationic photopolymerization became popular as curing rates turned out to be faster than both epoxides and the alternative free-radical acrylic monomers [5,24]. In addition, vinyl ether monomers also feature low toxicity, low odour and high reactivity thanks to their carbon-carbon double bond rich in electrons, thus making them attractive substitutes to acrylates [25].

On the other hand, vinyl ethers are less available as their synthesis is inconvenient and expensive [24]. Nevertheless, one strategy consists in isomerizing allyl ethers in order to form propenyl ethers. Their structure slightly differs from vinyl ethers by the presence of an additional methyl group located after the double bond. This directly increases the double bond electron density and consequently further activates it while at the same time slightly inhibiting its reactivity via steric hindrance. The simplified photoinduced cationic polymerization mechanism of a typical vinyl ether monomer is depicted in Fig. 40.

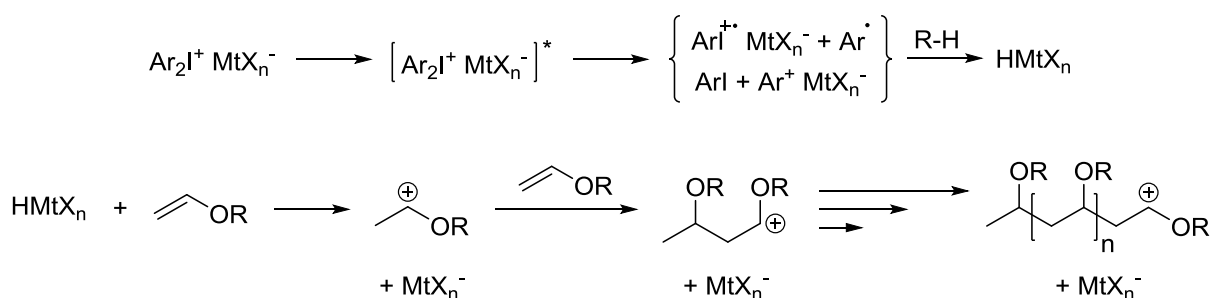


Fig. 40. Photoinduced cationic polymerization of a typical vinyl ether monomer using an iodonium salt as photoinitiator.

Vinyl ether polymerization rates are usually hindered by the gelation and vitrification phenomena, as observed for the cationic ROP of epoxides. During the propagation step, polymerization proceeds, thereby consuming ether derivatives, until the density of the crosslinked network prevents the diffusion of unreacted monomer towards fixed reactive propagating centres. Gelation and subsequent vitrification drastically lower polymerization rates and significant amounts of vinyl ether monomers can remain trapped within the glassy polymer matrix [196].

The use of additives such as alcohols has been reported to have the same effect on the curing kinetics of vinyl ethers than for epoxides [24]. In the presence of alcohols, the double bond final conversion increases and even reaches 100% in some cases, indicating an activated monomer mechanism such as depicted in Fig. 41. As a consequence, polyvinyl ether chain length is reduced, and the final structures feature a more flexible character.

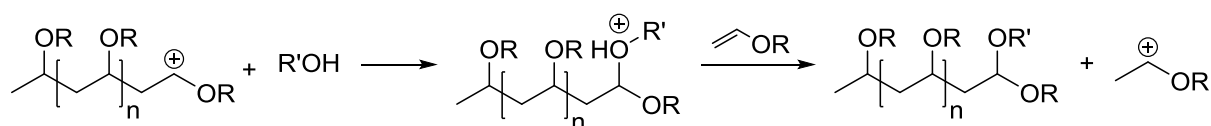


Fig. 41. Activated monomer mechanism in cationic polymerization of vinyl ethers.

Vinyl ether cationic polymerization is inhibited by hydrolysis, since the latter is catalysed by the same acid species, resulting in the formation of acetaldehyde and an alcohol [25]. Other drawbacks are high costs of multifunctional vinyl ether monomers and relatively low T_g of the resulting polymers, consequently their use in industrial UV-curing is still scarce.

3.3. Design of visible light sensitive Photoinitiating Systems for Cationic Photoprocesses

Onium salts initiate efficiently cationic photoprocesses when irradiation is carried out in the short- to mid-UV wavelength regions (200-300 nm) [21,26,48,49]. However, this feature raises safety concerns and increases energy costs [174], making these PIs inadequate for applications requiring the use of visible light or for specific cationic photopolymerization applications, such as medical and dental applications as well as stereolithography [49].

Consequently, recent strategies to develop photoresponsive cationic systems in the visible and near-IR regions of the light spectrum have been investigated. The synthesis of coloured onium salts containing chromophores and light-absorbing groups to get a red-shifted absorption [197], the use of organometallic complexes and metal based photoinitiating systems [198,199], the study of photosensitization [49,50], the investigations on free radical-promoted cationic polymerization [175] and the use of charge transfer complexes [200] represent various approaches to extend the range of spectral sensitivity of onium cationic photopolymerization initiators to the visible region [5,23,25,51].

3.3.1. Innovative visible light-absorbing onium salts

As previously stated, onium salts suffer from spectral limitations confined to the UV-range of the light spectrum, thereby strongly inhibiting their scope of application under visible light. As a consequence, they usually react in presence of additives through multimolecular reactions, which might raise issues concerning the onium salt solubility and diffusion in the polymerizable formulation [197].

Among the different strategies investigated for the extension of their photochemical properties into the visible light range, the design of versatile visible light-sensitive onium salts allowed to avoid the use of two- and three-component PISs. One-component PIs have been thus synthesized following various approaches [197]:

- strategic structural modifications of the aromatic rings of typical diaryliodonium and triarylsulphonium salts, such as the addition of electron-donating groups, chromophores and conjugated groups on their aromatic rings.
- The substitution of one or all benzene rings of iodonium and sulfonium salts.
- Onium salts centred on a nitrogen, oxygen, phosphorus, or sulphur atom.
- The introduction of iron complexes such as ferrocenium salts.

In this regard, the synthesis of a multitude of new compounds have been reported, including phenacyl onium salts (such as 2-isopropylthioxanthonium phenacyl salt [47], phenacyl benzoylpyridinium salts [201,202], α -aminoalkylphenone type phenacyl ammonium salt [203,204], diethoxy-azobis(pyridinium) salt [205], iodonium salts bearing chromophoric entities (such as

fluorenone [206] or coumarin [207,208], arylthianthrenium salts [209], π -conjugated sulfonium-based PAGs [210], and new ferrocenium salts [197,211–215]. Ferrocenium salts have demonstrated the broadest visible light absorptions and probably constitute the most versatile near UV and visible light one-component cationic photoinitiators [197].

An alternative to these different approaches was recently proposed, in which a carefully selected counter anion is capable of boosting the molar extinction coefficient of its cationic half and acts as a PS. This method involves polyoxometalates (POMs) as new counter anions [187,216].

In an industrial curing context, the use of one-component, visible light-sensitive PIS is particularly interesting since it prevents issues associated with the solubility, compatibility, migration and costs of other co-initiators.

3.3.2. Organometallic complexes and metal-based photoinitiating systems

Although onium salts have been widely investigated for the cationic photopolymerization of cycloaliphatic epoxides, organometallic and metal-derived complexes have proven to be efficient for the photoinitiation of cationic polymerization processes [51]. Metal-based complexes are sensitive in the visible light range of the electromagnetic spectrum and are characterized by intense visible light absorptions [50]. Therefore, they are of great interest for the photoredox catalysis of polymerization processes [198].

The development of organic photoredox compounds (OPCs) for the photoredox catalysis of polymerization reactions presents several advantages, including lower costs, commercial availability and lower toxicity in some cases, good stability and solubility as well as the fact that only low quantities are required [175]. These compounds act either as photoinitiators or as photosensitizers with the distinct benefit to be recovered during the initiation step [175,217].

Amongst such compounds are transition metal complexes like ruthenium and iridium-based complexes [198,199]. Under irradiation, their excited states react with a sacrificial quencher via an electron transfer mechanism and give rise to strong reductant or oxidant metal complexes. These latter intermediate species are able to react with other components of the PIS and thus efficiently initiate radical processes as well as free radical-promoted cationic polymerization reactions using low intensity visible light irradiation devices (fluorescent bulbs, LEDs, sunlight).

Other metal-based PIS have been studied in the scope of cationic photopolymerization reactions, including but not limited to organotellurium compounds [218], metal carbonyls derivatives [217,219], POMs [191], iron and copper salts [220], metal-organic frameworks [221], titanium complexes [222] or ferrocene [211,212,215], titanocene [185] and zirconocene derivatives [223]. Some of these works investigated the combination of silyl chemistry with photoredox cycles, thereby evidencing exciting prospects for FRP and FRPCP reactions carried out under soft conditions in aerated media.

Recent developments in the field of organometallic PISs for FRPCP include germane-based photoinitiators in combination with onium salts [224–226]. Acylgermane-based PIs are particularly interesting since the interaction of the lone electron pair of the carbonyl oxygen with the free d-orbitals of germanium results in a strong red-shift in their absorption properties. Upon light irradiation, these photoinitiators can photogenerate germyl radicals via α -cleavage, which are

subsequently oxidized by onium salts in germanium cations [51]. The latter species are highly reactive cations capable of efficiently initiating the CP of epoxides and vinyl ether monomers.

Despite a lot of dedicated work, the design of innovative PIs with red-shifted absorption spectra requires much time-consuming, complicated, indirect and expensive work [49,50]. Additionally, onium salts and metal based PIS usually involved in photoinduced CP reactions are synthetic compounds which can be rather toxic in some cases and not environmentally friendly. There is hence a growing interest for the design of renewable photosensitizers and the use of naturally derived PIS.

4. Environmental, Safety and Health Considerations: towards Greener Materials

The following part of this review provides a state of the art of all the parameters currently involved in the obtention of more environmentally-friendly cationically photoinduced materials. The different light sources covering the UV, visible light and near IR light range currently used in photopolymerization studies are first presented. The focus is then put on the description of renewable and naturally occurring photosensitizers and monomers that have been reported so far in the literature on the matter. The toxicities of different resins and photoinitiating systems are discussed. Finally, alternative cyclo-addition photoprocesses are introduced.

4.1. Usual Light sources and Newly Developed Laser Diodes and LEDs irradiation systems in the visible/IR range

In photopolymerization reactions, the light spectrum usually used goes from the ultraviolet area (200-400 nm range), through the visible light part of the electromagnetic spectrum (400-800 nm) to near-infrared light (800-1000 nm) and a large variety of light sources, systems and parameters can be operated [5]. As a consequence, a broad set of situations can be investigated depending on the lamp spectral nature, on whether it is monochromatic or polychromatic, on its intensity and on the way light is delivered (continuously, as a pulse or as a series of pulses).

Typical light sources and devices used in the scope of photopolymerization are xenon lamps, mercury lamps, doped lamps, excimer lamps, household lamps, light-emitting diodes, laser beams, pulsed light sources, UV plasma sources, microwave powered lamps and naturel sunlight [5,227,228]. Delivered fluxes of photons can be very high for all types of Hg lamps, highly packed arrangements of LEDs centred around small wavelengths (< 400 nm), Hg-Xe and Xe lamps whereas household irradiation devices, diode lasers and sun deliver lower light intensities [186].

Mercury lamps along with doped mercury lamps and microwave powered lamps were the most commonly used type of light devices in the scope of light induced polymerization [186,227,228]. Their typical emission spectra are shown in Fig. 42.

Under the operation of an electric field, commercial medium pressure Hg lamps provide a high flux of photons in the UV/near visible range of the light spectrum (280-445 nm range, Fig. 42c), thereby matching the absorptions of most PIS. Along with xenon lamps, they require high electrical power and generate heat. However, they can provide high light intensity on a wide spectral range. A

set of particular wavelengths is emitted because of characteristic narrow transitions between the ground state and some excited energy levels generated by electrical discharges in a Hg vapor: 254, 313, 366, 405, 435, 546 and 579 nm [5]. These intense emission lines can slightly differ from one Hg lamp system to another, but they are mostly centred around the same energies [229]. As for low pressure Hg lamps, they mostly deliver photons in the 254 nm region [5]. Concerning microwave powered lamps, the excitation provided by microwaves enables an emission spectrum centred around the 380-420 nm area as depicted by Fig. 42a,b.

Xenon, doped mercury lamps and household halogen lamps on the other hand enabled the extension of the irradiation range to the visible area of the light spectrum (polychromatic light: [400-800] nm) [51,227], since newly developed photosensitizers allow to extend the photosensitivity of the photopolymerization systems towards longer wavelengths (Fig. 43) [183,186,230,231].

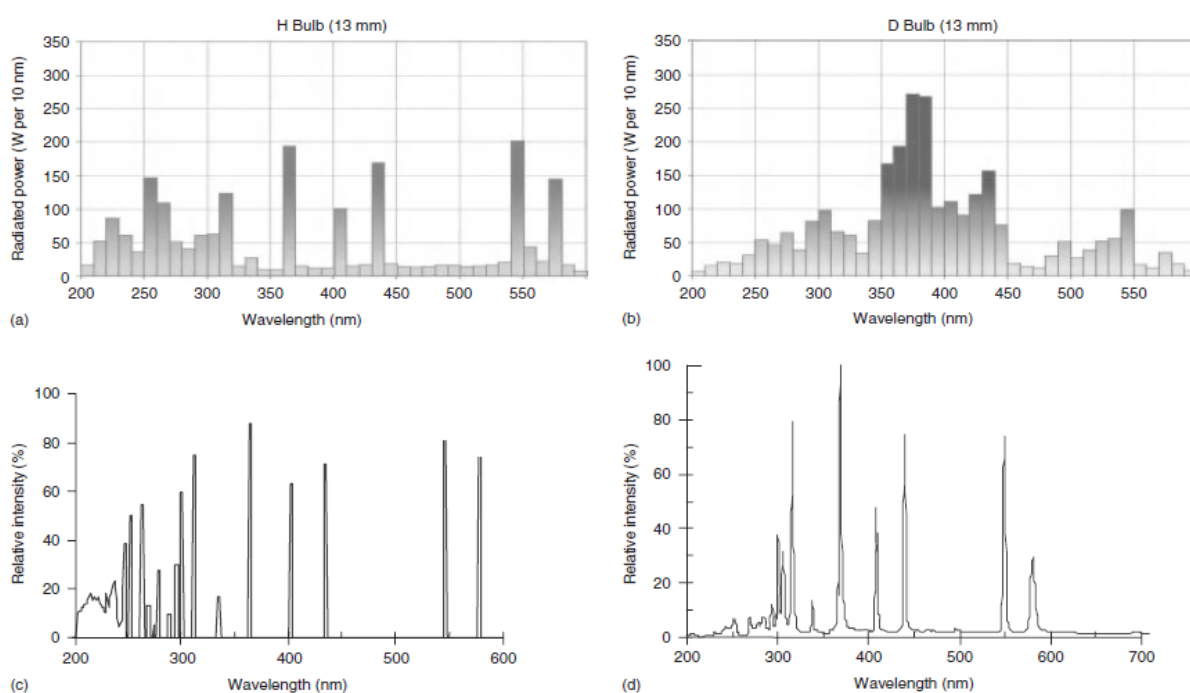


Fig. 42. Emission spectra of: (a, b) different microwave lamps, (c) a mercury lamp, (d) a doped mercury lamp (Xe-Hg lamp) equipped with a 366 nm reflector. Reprinted with permission from Fouassier et Lalevée [5]. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

Mercury lamps can be doped by xenon, gallium, indium and iron halides in order to increase the light emission spectrum in the near-UV and visible regions towards 420 nm, as shown in Fig. 42d [5]. Xenon lamps cover a wide range of the near-UV-visible light spectrum since they emit light in the 300-800 nm area, as depicted in Fig. 44.

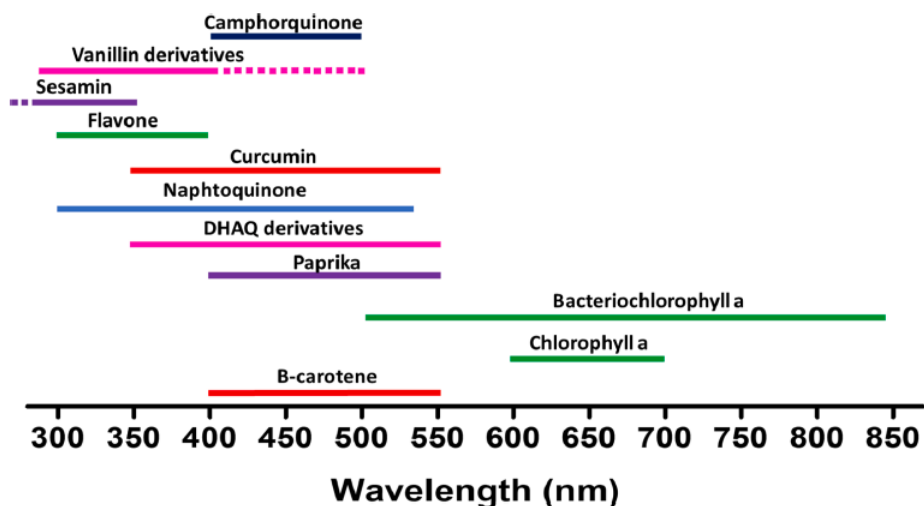


Fig. 43. Representative absorption properties of natural and biosourced photoinitiators and dyes. Dotted lines mean that dyes only weakly absorb at these wavelengths. Reprinted with permission from Noirbent et Dumur [183]. Copyright 2021 Elsevier.

Finally, household bulbs also attract interests in the framework of photochemical processes as they offer soft irradiations conditions for photopolymerization reactions [5,186]. The emission spectra of a household halogen lamp, household fluorescent, blue and white bulbs are respectively presented in Fig. 46a and in Fig. 45.

Household bulbs feature several interesting advantages: high luminous power available in the visible range (three times that of solar irradiation), cheap, safe, environmentally friendly and commercially available light devices, and are not affected by weather or location [5,198]. Household LED bulbs also avoid IR and UV radiations, need lower energy requirements, are available in a large array of colour, usually suffer no frequency interference and present a relatively low divergence of their light beam, which can be exploited by using light strips or concentrated arrays [5].

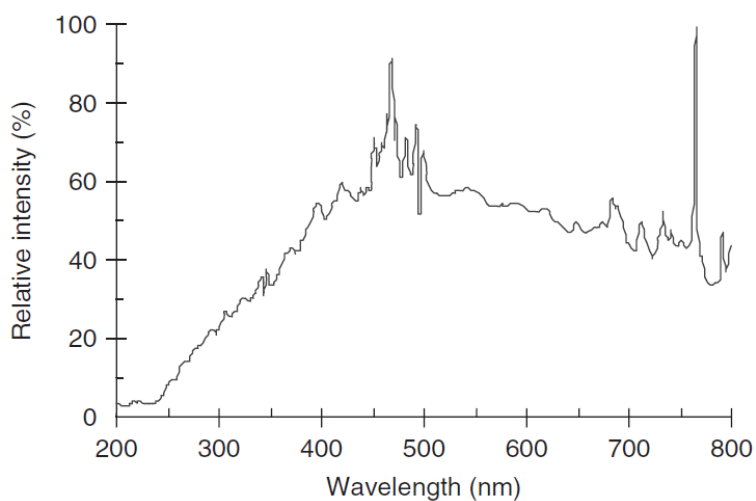


Fig. 44. Emission spectrum of a xenon lamp. Reprinted with permission from Fouassier et Lalevée [5]. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

Nevertheless, most of the energy delivered by these previously described systems is lost, as the light bulbs often generate a lot of heat. This leads to detrimental photoproducts and/or to overheating samples, which prevents a good control over the polymerization process [49,229]. Various types of filter can then be used to narrow the output of such lamps, as illustrated in Fig. 47, but this also leads to a loss of energy as well as additional devices required in the experimental setup [229]. Finally, these light sources can be ill-suited for the direct photolysis of onium salts in the framework of cationic photopolymerization as the latter species strongly absorb at relatively short wavelengths (200-300 nm). Even though these irradiation devices do emit light in the short UV range, their emission cover mostly the long wavelength UV region and the visible range. As a consequence, the emitted long wavelength photons are lost since they are not involved in the photopolymerization reaction [49].

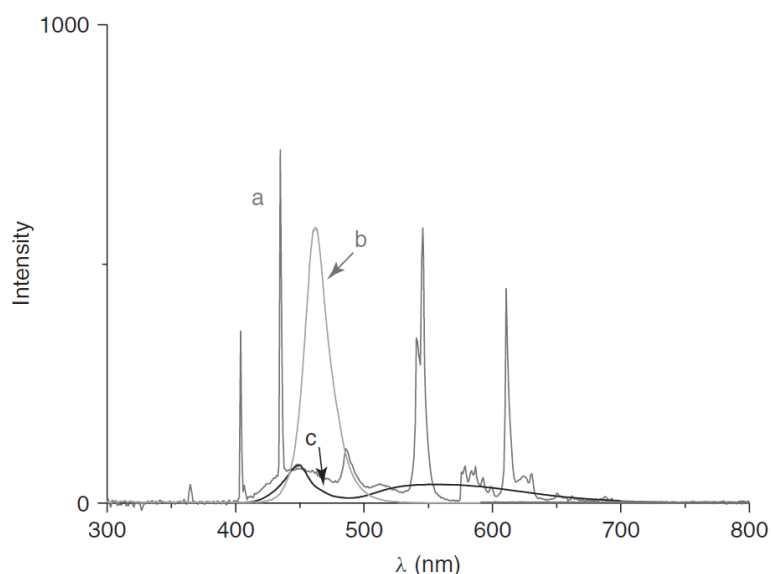


Fig. 45. Emission spectra of (a) a household fluorescent bulb, (b) a household blue LED bulb, and (c) a household white LED bulb (intensity in $\mu\text{W}\cdot\text{cm}^{-2}$). Reprinted with permission from Fouassier et Lalevée [5]. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

The recent development of new LED technology (quasi monochromatic light) and the design of several laser sources operating at specific wavelengths (monochromatic light: 405, 455, 470, 505, 530, 590, 660 nm...) further extended the excitation range of photoinitiating systems from UV to near infra-red regions without the loss in energy [227,232]. Emission spectra of several laser diodes and some LEDs are presented in Fig. 46b,c.

Laser sources offer many attractive characteristics: monochromatic light, narrow emission bandwidth, a large wavelength selection, high power output, high energy concentration onto a small surface, thus ensuring immediate curing and reduced oxygen inhibition, simple design, easy stacking and arrangement, high focalization along with short irradiation time, allowing for the handling of the laser spot as a pencil of light, high spectral selectivity as well as spatial resolution [5,233]. Continuous-wave lasers, pulsed lasers, femtosecond lasers and diode lasers are amongst the different types of laser sources currently available.

Last but not least, the LED system (as well as the laser diode technology) is based on a semiconductor material device and enables the emission of light following a quasi-Gaussian distribution centred around a narrow and specific wavelength region with a larger bandwidth than for laser sources ($\sim 20\text{-}30\text{ nm}$, Fig. 46c) [5]. Commercial LED systems allow curing speeds as high as those attained with Hg lamps while being safe as they avoid the use of UV rays [51,186]. However, their total intensity over the whole emission spectrum is significantly lower for LEDs than for mercury lamps, even when packed in an arrangement of multiple LEDs [5,229]. The lower power of LED systems can nevertheless be compensated by perfectly overlapping the absorption spectrum of a given photoinitiator and the emission spectrum of the considered LED.

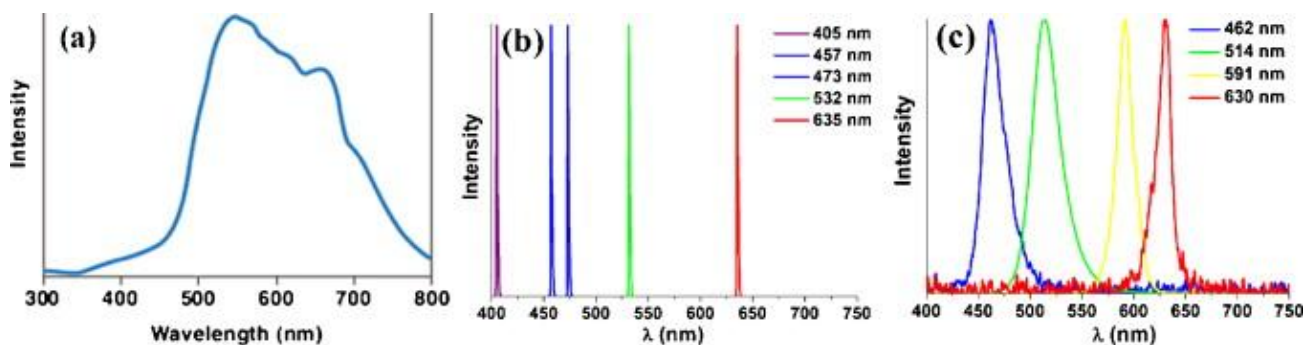


Fig. 46. Emission spectra of: (a) halogen lamp, (b) laser diodes at 405 nm (purple), 457 nm (blue), 473 nm (blue), 532 nm (green) and 635 nm (red), and (c) household LEDs centred at 462 nm (blue), 514 nm (green), 591 nm (yellow) and 630 nm (red). Reprinted with permission from Xiao et al. [51]. Copyright 2015 Elsevier.

The development of light-emitting diodes offers several advantages over other traditional systems that are similar to laser sources. Not only do they avoid the generation of heat and have low energy requirements, but they also need less maintenance and lower operating costs, offer longer lifespans, high portability and can be easily incorporated in remote-controlled, programmed devices and robots permitting the curing of shadowed areas. Other attractive features include no ozone release, easy handling and safer operating conditions by avoiding harmful UV-rays, the recording of excellent conversion vs. time curves, close distance to photopolymerizable systems, full intensity immediately obtained after turn-on, easily controlled characteristics such as delivered intensity, potential pulsing and clocking [5,186,228,229].

The LED technology appears to be an excellent alternative to many irradiation devices thanks to its many advantageous characteristics and allows for a large array of potential applications [5,228]: digital inkjet printing [234], 3D printing [220,235], adhesives [236], coatings, heat-sensitive materials curing, spot curing (topcoat repair), all types of photopolymerization (FRPCP, cationic, free radical, thiol-ene, living radical polymerization...) [237–239] and biomedical applications such as dentistry [240] or antibacterial materials [6,241].

Most light devices described above deliver light continuously as a function of time. But some laser sources, flash lamps and UV light devices are designed to emit photons in a single flash or in pulses of light [5]. This technique, called pulsed laser polymerization (PLP), is used to trigger the initiation during irradiation while the propagation and terminations steps occur in the dark period, as described for CP. Very high amounts of power density can be obtained, and molecular weights and molecular weight distributions can therefore be tuned according to the frequency and to the pulse width.

Many studies are currently undergoing to design photoinitiators and photoinitiating systems with specific intrinsic absorption characteristics in order to optimally match emission spectra of the considered irradiations devices and light sources [49]. This would result in a significant improvement of the overall photopolymerization reaction efficiency.

4.2. Use of Sunlight irradiation Conditions

Natural sunlight is a cheap, very convenient, and promising source of low intensity visible light. It affords practical, low cost and environmentally friendly photocuring processes which function without any device and do not release any volatile organic compounds [5,227]. This inexhaustible source of visible light is particularly interesting for outdoors applications and might allow for the curing of large pieces and surfaces without the need of any irradiation device [186]. However, it remains strongly affected by the weather, geographical location as well as year period. The emission spectrum of the sun is shown in Fig. 47.

Sunlight curing is far from being a recent development in the field of photochemistry as it dates back 4000 years ago. As a matter of fact, ancient Egyptians and Babylonians already used solar irradiation for the photocrosslinking of linen in mummification rites. The sun was also involved in the waterproofing of papyrus boats thanks to the polymerization of an asphalt oil upon sunlight exposure [242,243]. To date, there are only a few studies dealing with the use of natural sunlight as the visible light source for cationic photopolymerization purposes. Even fewer tackles the use of biosourced photoinitiators/photosensitizers for sunlight-induced cationic photoprocesses.

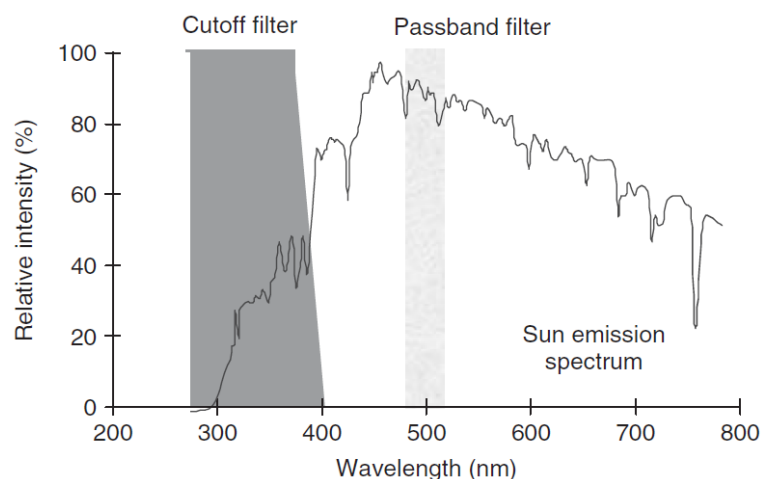


Fig. 47. Emission spectrum of the sun. Schematic transmission curves of typical filters (cut-off filter: $T = 0\%$ for $\lambda < 390$ nm and passband filter: $T = 100\%$ for 500 nm). Reprinted with permission from Fouassier et Lalevée [5]. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

The earliest studies using sunlight as visible light source in this respect dealt with the curing of cycloaliphatic epoxy monomers as well as aromatic glycidyl ether resins in presence of a diaryliodonium salt [244]. Other early investigations evaluated the use of renewable and naturally derived epoxidized monomers in presence of cationic photoinitiators upon sunlight irradiation. ESO, ELO or LDO have thus been reported for the fabrication of glass fibre-reinforced composites by a

direct 25-minute exposure to sunlight [245] and interpenetrated polymer networks have been synthesized within minutes using epoxidized natural rubber with a sulphonium salt and an acrylate monomer under solar radiation [246]. More recently, uncoloured tack-free coatings have been obtained using three-component, visible light sensitive, silane-based photoinitiating systems using renewable natural oils such as ESO and LDO upon sunlight irradiation [186,192,227].

In the scope of CP and FRPCP, three-component PISs composed of a photoinitiator, an onium salt and a silane derivative have indeed been reported to successfully cure cationically polymerizable monomers under air and upon sunlight irradiation. Recently, ruthenium and iridium complexes, polyoxometalates, phosphine oxide derivatives as well as several other compounds have shown successful cationic polymerization initiations under sunlight exposition [51,184,227]. When mixed with iodonium salts and silane derivatives, excited states of transition metal complexes based on ruthenium and iridium react and generate highly reactive species able to initiate ring-opening polymerization of epoxy monomers under air and under sunlight irradiation via FRPCP [198,199,247,248]. The same can be observed when using dimanganese (0) decacarbonyl in a type II photoinitiating system based on transition metal carbonyls, silane derivatives and diaryliodonium salts [219]. Likewise, POMs [191], titanocene compounds [185], acridinedione derivatives [249], violanthrone dyes [247], various phosphine derivatives as well as 2-isopropylthioxanthone, benzil, camphorquinone, eosin-Y and difunctional ketosulphones (Esacure 1001 M) [184,227] combined with silanes and a iodonium salt have been described to promote CP reactions through a FRPCP mechanism using sunlight as the visible light source. From minutes up to a few hours of direct solar exposure, these studies demonstrate the obtention of tack-free coatings using silyl radical chemistry-based photopolymerization initiating systems.

Kaya & al. recently worked on organotellurium-mediated cationic polymerizations of cyclohexene oxide (CHO, see Fig. 56), isobutyl vinyl ether (IBVE) and N-vinylcarbazole (NVK) under solar exposure [218]. Together with diphenyliodonium salts, organotellurium compounds constitute an efficient visible light photoinitiating system for the photoinduced polymerization of various cationically polymerizable monomers, since organotellurium derivatives are visible light sensitive. They reported polymerization conversions up to 49% under direct solar irradiation. The same group of researchers described later the synthesis of a chromophore-bearing sulfonium salt possessing light-absorbing thioxanthone and phenacyl groups and demonstrated its ability to initiate the cationic photopolymerization of IBVE under natural sunlight [47].

Other studies focused on the use of photosensitizers as a way to extend the spectral region over which onium salts effectively absorb. For instance, curcumin and its derivatives have been investigated as abundant, highly efficient and naturally-derived photosensitizers [250,251]. In these studies, fully hardened, orange-coloured, flexible cross-linked composites have been reported after direct sunlight irradiation for 10 minutes. In the framework of cationic ring-opening polymerization of oxiranes and oxetanes, quinoxaline derivatives have been described as efficient photosensitizers initiating the synthesis of film coatings under 5 minutes of sunlight irradiation [252]. Other work evidenced versatile multicomponent systems based on camphorquinone [253], and chalcone derivatives [254], which were found to be efficient photosensitizers for sunlight-induced cationic polymerization.

If the use of sunlight irradiation still remains one of the biggest challenges in the scope of photopolymerization reactions carried out under air, it is mostly due to a very strong oxygen inhibition preventing the photopolymerization process to occur [227]. Several studies such as some described here have investigated the use of silyl radical chemistry as a way to counterbalance this phenomenon.

4.3. Update on the current Bio-sourced cationic Photoinitiating Systems and Evaluation of their Toxicity

Photopolymerization faces several short- to long-term issues from environmental, health and safety points of view. As a response, the search for greener technologies in the scope of photopolymerization has lastly led to various pathways, among which is the design of new PISs based on natural products: biosourced PIs/PSs and renewable monomers [183,186].

4.3.1. Biosourced Photoinitiators/Photosensitizers derived from natural dyes

Recently, natural products have attracted the spotlight for the design of photoinitiators addressing environmental and safety concerns. Natural dyes promise indeed the supply of cheap, available, abundant and renewable photoinitiators while being visible light-sensitive and responsive even under low light intensities [183]. Extracted from various parts of plants (roots, bark, stems, leaves, petals, fruits, seeds, wood, etc.) [255], these compounds are parts of their specialized metabolites and require appropriate extraction procedures. As this extraction process can be carried out without environmental threats and with a very limited number of steps and chemicals involved compared to the obtention and isolation of synthetic dyes in their pure form, natural dyes are highly competitive, environmentally friendly, and promising materials for their incorporation in visible light PISs [183]. Additionally, natural dyes offer several health-related advantages as they are often non-toxic, less polluting and do not raise carcinogenic nor poisonous concerns [255].

Over the years, several natural compounds have been identified as interesting and efficient scaffolds for radical, cationic and thiol-ene photopolymerization reactions, such as anthraquinones [235,256–259], carotenoids [230,231], various derivatives of chlorophyll [260,261], curcuminoids [18,250,251,262–266], flavonoids [267–273], naphthoquinones [274,275], riboflavin [276–281] and lignin derivatives [282].

However, to date, only a few studies investigated the use of biosourced compounds and natural dyes as effective photoinitiators/photosensitizers for cationic photopolymerization reactions [22,183]. In the following sections, an overview of these recent investigations carried out in the framework of visible light-induced CP is provided.

4.3.1.1. Anthraquinone derivatives

Anthraquinones are among the most common and important red natural dyes which have been mostly and extensively used for textile dyeing purposes, dating back to the Bronze Age more than 3000 years ago until the late 19th century [283]. They consist of a large number of derivatives which differ by the positions and nature of the different substituent groups and allow for a wide array of applications ranging from food colouring, textile dyeing, paints to medical applications [284]. They can be extracted from various species of plants but they can also be found in insects [255].

In the framework of photoinduced polymerization processes, anthraquinones have mostly been investigated as free radical PIs [285–290]. Thanks to excellent absorption properties in the visible light range, naturally derived multihydroxy-anthraquinones have recently enabled to extend their scope of applications to cationic photoinduced polymerization reactions.

Notably, naturally occurring quinizarin (QUIN) as well as red-shifted synthetic derivatives disperse blue 1 (DB1), disperse blue 3 (DB3) and oil blue N (OBN) (Fig. 49) have been studied in combination with an iodonium salt (Iod) for the development of cationic PISs functioning upon exposure to monochromatic red lights [256]. Due to their wide absorption range reaching as far as 700 nm in the visible light area, photopolymerization experiments have been carried out using a 635 nm red laser diode, a household LED bulb centred at 630 nm and a polychromatic halogen lamp, thus ensuring a good overlapping with the irradiation devices emission spectra.

Classic reference monomers have been used for the photopolymerization kinetics studies, that are tri(ethylene glycol) divinyl ether (DVE-3) and (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) (Fig. 48). Good final monomer conversions regarding the vinyl ether double bond of DVE-3 are obtained in laminate conditions using an OBN/Iod PIS in presence of a trifunctional thiol crosslinker, upon exposure to monochromatic red light irradiation devices. Indeed, final conversions of 68% using a household LED red bulb going up to 98% under a 10-fold more powerful red laser diode in terms of incident light intensity have been obtained. Results tended to evidence the predominance of a cationic photopolymerization mechanism over a thiol-ene process when using a trifunctional thiol crosslinker additive.

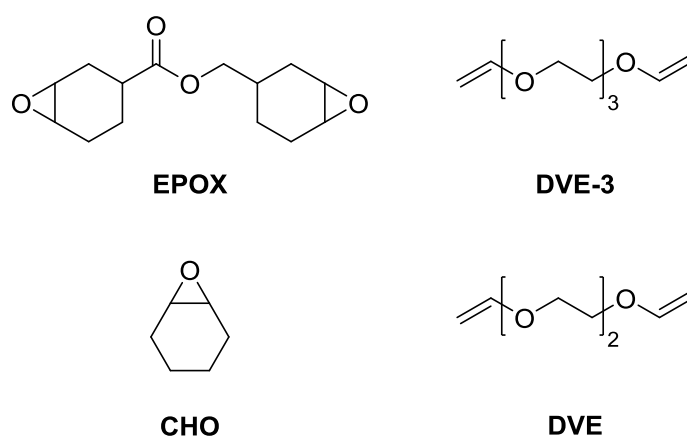


Fig. 48. Chemical structures of typical cationically polymerizable monomers used in photopolymerization studies.

However, despite results supporting overall favourable photoprocesses as well as fast systems photobleaching, almost no polymerization reaction was observed for the other PISs considered, that were QUIN-, DB1- and DB3-based PISs, under the given irradiation conditions. Tack-free coatings have only been obtained when using various OBN-based formulations. On that note, it is important to mention that aminoanthraquinone derivatives are synthetic entities and do not occur naturally.

Further investigations carried out by the same research group evidenced the impact of the positions of the different hydroxyl substituents in the anthraquinone chemical structures on their photoinitiating ability [257]. In this study, they focused their work on four dihydroxyanthraquinone derivatives, namely 12-DHAQ, 14-DHAQ (also known as quinizarin, natural dye), 15-DHAQ and 18-

DHAQ (Fig. 49) and studied the relation between their chemical structures and their photoinitiating efficiency.

Despite the fact that the four investigated molecules are isomers, the position of their hydroxyl substituent groups significantly alters their optical properties, starting with their absorption spectra. If absorption maxima are observed at 417 and 426 nm for 15-DHAQ and 18-DHAQ respectively, 14-DHAQ undergoes a significant red-shift evidenced by its absorption maximum centred around 477 nm. Due to solubility issues encountered for 12-DHAQ in the selected solvents and monomers, its absorption spectrum could not be compared to its isomers. Regarding these optical properties, photopolymerization studies have this time been carried out under a blue LED bulb centred at 455 nm, in order to maximize the overlap between the anthraquinone derivatives absorption maxima and the irradiation device emission spectrum.

Two-component systems based on DHAQ and Iod alone did not initiate the cationic polymerization of epoxides due to a back electron-transfer reaction between the two considered species, as demonstrated by steady state photolysis and fluorescence quenching experiments. However, the addition of NVK greatly enhanced the photoinitiating ability of the overall system and prevented the back electron-transfer.

CP experiments evidenced that the most efficient PI upon exposure to a 455 nm LED bulb was 18-DHAQ when used in a three-component system composed of DHAQ, an iodonium salt and NVK. This combination allowed for a high polymerization rate and a final conversion of 79% of EPOX monomer after 800 seconds of blue LED light irradiation. In terms of photoinitiating properties, 14-DHAQ and 15-DHAQ-based PISs showed less efficiency. 12-DHAQ turned out to be an ineffective PI probably due to its solubility issues.

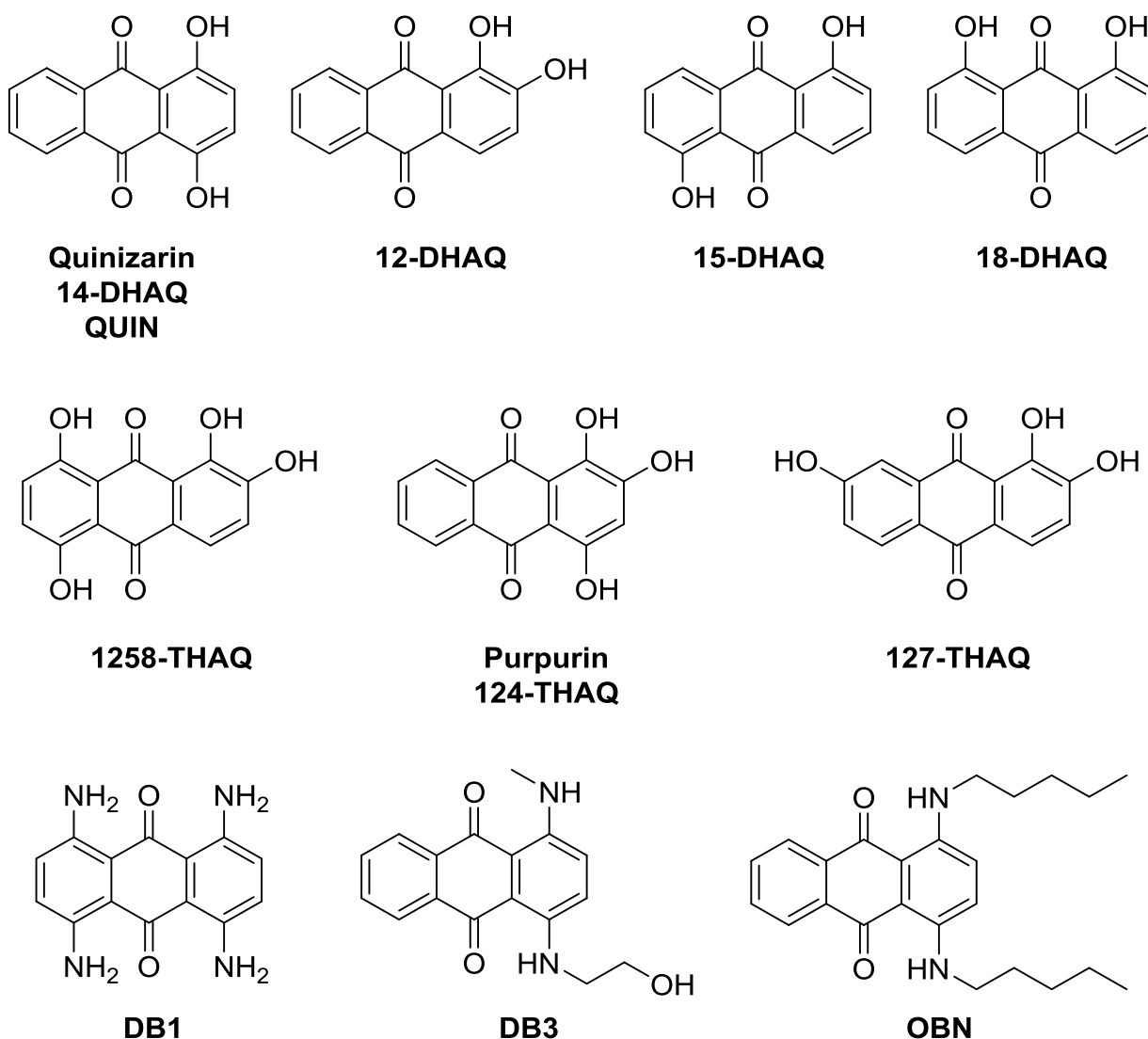


Fig. 49. Chemical structures of the different anthraquinone derivatives studied for the design of biosourced photoinitiating systems for cationic photopolymerization reactions [235,256–259].

Following this work, the same authors recently investigated three naturally occurring multihydroxy-anthraquinone dyes differing by the number and the positions of the different hydroxy groups [258]. In particular, the photochemical reactivities of purpurin (124-THAQ), anthrapurpurin (127-THAQ) and quinalizarin (1258-THAQ) upon exposure to a household green LED bulb in presence or absence of various additives are studied (Fig. 49). Regarding their absorption properties, these three natural dyes make for suitable visible light-sensitive PI candidates for photopolymerization reactions carried out at 518 nm. They notably exhibited broad absorption bands in the visible light range, extending from 350 to 500 nm for 127-THAQ (maximum reached at 411 nm) and from 350 to 550 nm for 124-THAQ and 1258-THAQ (maximum reached at 477 and 480 nm respectively), thereby overlapping the emission spectrum of the green LED bulb.

Fluorescence experiments evidenced that both 127-THAQ and 1258-THAQ were inefficient in presence of additives whereas the addition of Iod led to a fluorescence quenching of 124-THAQ in acetonitrile, indicating the occurrence of an electron-transfer reaction between the excited state of

124-THAQ and ground state Iod. Cyclic voltammetry showed an overall negative free energy change, highlighting thus a favourable interaction between 124-THAQ and Iod towards the generation of cationic polymerization initiating species.

Upon green light irradiation, light absorptions of both 124-THAQ and 1258-THAQ slightly decreased in the presence of Iod or a chlorotriazine additive, showing a rather low reactivity of these systems. Nonetheless, the addition of NVK to the 124-THAQ/Iod system resulted in the same observation as the one evidenced for 18-DHAQ, that is a drastic increase of the baseline of the light absorption of the considered system upon green light exposure. This phenomenon is attributed to the in-situ precipitation of poly(vinylcarbazole), leading to a cloudy suspension. It also means that the so generated Ph-NVK⁺ cation is a strong cation for the initiation of cationic photoprocesses. On the other hand, the absence of any photobleaching during steady state photolysis of a 127-THAQ/Iod solution indicated a complete lack of reactivity of this system.

Cationic photopolymerization experiments carried out on both THAQs/Iod and THAQs/Iod/NVK systems using EPOX as monomer demonstrated once again that in the absence of NVK, THAQs/Iod systems were inefficient to initiate cationic polymerization processes. This result supported the low electron transfer quantum yield of 124-THAQ/Iod, the non-existent fluorescence quantum yield of 127-THAQ and the absence of fluorescence quenching of the 1258-THAQ/Iod system previously observed. However, the addition of NVK to the 124-THAQ/Iod system enabled the initiation of the overall system as well as the achievement of a 50% epoxide conversion after 2000 seconds of green light irradiation. The 127-THAQ and 1258-THAQ-based systems remained inefficient upon addition of NVK towards the photopolymerization of EPOX.

Interestingly, a 90% monomer conversion of the vinyl ether double bond of DVE-3 in laminate conditions was reached using the 124-THAQ/Iod system after 2000 seconds of green LED bulb irradiation. The addition of NVK to such a system enabled to drastically enhance the DVE-3 polymerization rate, attaining 90% of conversion within 500 seconds of irradiation.

Going a step further on the subject of natural anthraquinone derivatives, Sautrot-Ba et al. lastly described the synthesis of quinizarin (QZ) and purpurin (P) derived monomers in a three-way strategy: the natural dyes derivatives not only act as visible light PSs for various types of photoprocesses, but they also play both the role of photopolymerizable monomers thanks to photoreactive functional groups and the role of photoactive antibacterial agents [235,259]. They described the successful synthesis of both allylated and epoxidized quinizarin as well as a mono-allylated purpurin (PmA) and a tri-allylated purpurin compound (PA) (see chemical structures in Fig. 57 and in Fig. 58).

The functionalization of quinizarin induced a hypsochromic effect as the maxima of absorption of allylated quinizarin (QA) and epoxidized quinizarin (QE) are shifted towards the shorter near-UV wavelengths (415 nm and 407 nm respectively) [259]. However, they feature relatively high molar extinction coefficients and seem to be suitable photoinitiators upon exposure to household 405, 455 and 470 nm blue LEDs. The same hypsochromic effect is observable for the allylated purpurin derivatives, as the maximum of absorption located at 480 nm for P and PmA is shifted at 401 nm for PA [235]. Interestingly, PA and PmA feature higher molar extinction coefficients than purpurin.

Steady state photolysis experiments indicated that QA, QE, P and PmA alone exhibited a low photochemical reactivity, whereas significant decreases of the absorbances of all the studied derivatives along with the concomitantly successful generation of a photoacid were observed when combined with Iod [235,259]. Fluorescence as well as electronic paramagnetic resonance (EPR) spin-trapping experiments evidenced the excited state of the quinizarin derivatives to be an excited triplet

state, from which the photosensitizers convey their energy to Iod via a favourable electron-transfer reaction. On the other hand, results highlighted an electron-transfer reaction between both singlet and triplet excited states of purpurin derivatives and Iod.

As expected, quinizarin alone did not initiate cationic polymerization reactions, nonetheless QA and QE derivatives successfully promoted the cationic polymerization of EPOX under multiple visible light wavelengths, with final monomer conversions reaching more than 50% whatever the light source considered [259]. Even better kinetic profiles are obtained when using a combined thiol-ene and cationic polymerizable blend of DVE and a trifunctional thiol additive. Indeed, 89% and 83% of vinyl double bond conversions in laminate conditions are obtained upon exposure at 455 nm and at 470 nm respectively, going up to 100% in presence of Iod.

Regarding purpurin derivatives, purpurin alone along with mono-allylated purpurin exhibited a lower photoreactivity than tri-allylated purpurin [235]. 62% of EPOX monomer conversion has been reached for the reactive PA/Iod/EPOX system upon exposure to visible light irradiation sources (xenon lamp and 405 nm LED).

When exposed to visible light, natural dyes can act as antibacterial agents via the generation of singlet oxygen. As a matter of fact, under irradiation, photoexcited dye-based photosensitizers can transfer their energy to ambient molecular oxygen, whose excited singlet state is highly toxic to bacteria. In this respect, quinizarin and purpurin derivatives have been investigated for bactericidal purposes and antibacterial assays against *Staphylococcus aureus* (S. aureus) of associated anthraquinone-derived films have been carried out. Interestingly, these coatings showed excellent bacterial anti-adherence properties under visible light irradiation as well as a potential reusable and recyclable character [235,259].

It seems interesting to mention that some other studies investigated the use of anthraquinone derivatives as efficient photosensitizers to initiate cationic photopolymerization reactions upon exposure to visible light sources, however the amino- and hydroxy-substituted anthraquinones that are described in these works are not naturally occurring dyes [291–293].

4.3.1.2. Carotenoids

Carotenoids are mostly C₄₀ tetraterpene dyes exhibiting bright colours ranging from yellow to purple. They are among the most abundant and most widely distributed naturally occurring dyes on Earth and include about 850 different structures to date [294,295]. Carotenoids are composed of two main categories:

- carotenes, whose chemical skeletons are exclusively composed of carbon atoms (such as β -carotene represented in Fig. 50).
- Xanthophylls, carotenoids comprising oxygen atoms along their carbon backbones (such as capsanthin, capsorubin and cryptocapsin shown in Fig. 51).

Along with chlorophylls, carotenoids are essential molecules for various biological processes in photosynthetic organisms such as bacteria, algae, and plants. They are notably involved in various photoprocesses such as photosynthesis or photoprotection in living organisms and play a significant role as precursors for the synthesis of various impactful molecules such as Vitamin A. Finally, they are also involved in different human health-related areas such as the prevention of cancer and vision processes, as well as in the beauty industry.

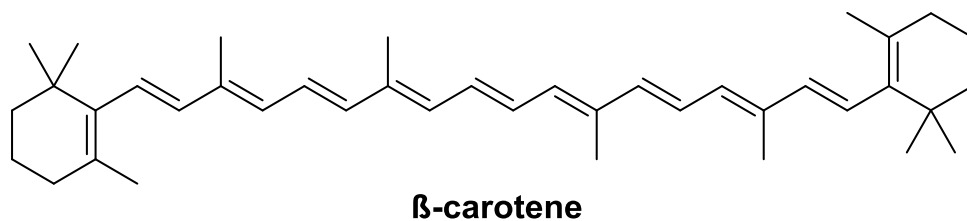


Fig. 50. Chemical structure of β-carotene.

One of the most widespread and popular carotenoids is β-carotene. For antibacterial purposes, Breloy et al. recently reported for the first time the use of β-carotene as an efficient photosensitizer for visible light-induced polymerization reactions. They described the successful synthesis of tack-free coatings using an all-green approach and a dye-based system composed of β-carotene (Fig. 50), limonene derivatives (Fig. 28) and eugenol (Fig. 18) [230]. As previously stated, limonene and eugenol are also naturally occurring compounds which respectively originate from citrus and a large variety of plants such as cloves, pepper or cinnamon among many other aromatic herbs and spices.

β-carotene absorbs intensely between 400 and 500 nm and its higher molar extinction coefficient than some reference PIs makes it a perfectly suitable candidate for the photosensitization of polymerization processes in the visible light range [230]. Additionally, β-carotene also acts as a bactericidal agent upon irradiation. Indeed, upon exposure to visible light, β-carotene interacts with ambient molecular oxygen while in its excited state via energy transfer to generate singlet oxygen, a highly toxic compound for bacteria. Interestingly, eugenol also plays a dual role as it is both a monomer and an antibacterial agent. It has in fact been reported to have an excellent bactericidal activity against a wide range of microorganisms [296].

In their work, Breloy et al. investigated various formulations for cationic photopolymerization reactions using β-carotene as a PS, bis(4-methylphenyl)iodonium hexafluorophosphate (Iod) as a cationic PI, and limonene-1,2-epoxide (Lim), limonene dioxide (LDO) and eugenol as biosourced monomers [230]. Steady-state photolysis studies have demonstrated a strong and efficient interaction between β-carotene and Iod, as they observed a fast photobleaching of a β-carotene/Iod solution under irradiation at 405 nm. This result was also confirmed by fluorescence and laser-flash photolysis experiments. The excited state has been found to be a triplet state and cyclic voltammetry analyses have evidenced that the overall cationic photopolymerization process is highly favoured. Finally, experiments showed the successful generation of photoacids by the two-component β-carotene/Iod system, which is favourable for the ring-opening cationic polymerization of epoxy monomers.

Since the absorption of β-carotene is strong between 400 and 500 nm with a maximum observed at 450 nm, cationic and thiol-ene photopolymerization studies of limonene-1,2-epoxide, limonene dioxide and eugenol have been carried out upon exposure to LEDs centred at 405, 455, and 470 nm and under a xenon lamp. Several formulations containing the different monomers in various proportions have been tested according to the monomers' viscosities and the target application of the final coating. Ultimately, regarding the copolymerization of LDO (50 wt%) with Lim (25 wt%) and eugenol (25 wt%) using an optimized β-carotene/Iod/trifunctional thiol crosslinker (1/3/6% w/w/w)

system, high final conversions (> 59%) are obtained considering the epoxy group of Lim, whatever the light source considered, with a maximum of 80% after 800 seconds of irradiation at 405 nm.

Comparisons using reference PIs (camphorquinone and isopropylthioxanthone) as well as other natural dyes (quercetin as a typical flavone and purpurin from the family of anthraquinones) using the three-component dye/Iod/trithiol system demonstrated the greater performance of the β -carotene-based system, irrespective of the irradiation device. Interestingly, the other natural dyes did not promote any polymerization process for wavelengths higher than 405 nm. Finally, antibacterial assays showed a significant bacteria growth inhibition for coatings containing eugenol compared to limonene derivatives-based coatings, thus confirming the bactericidal action of eugenol.

Prior to the investigation of β -carotene as an effective PS, the same research group designed a performing PIS based on paprika, a well-known food dye containing numerous carotenoids, for the FRPCP of a biosourced epoxy monomer based on gallic acid [231]. Up until then, neither paprika nor epoxidized gallic acid had ever been studied in the framework of photoinduced polymerization processes.

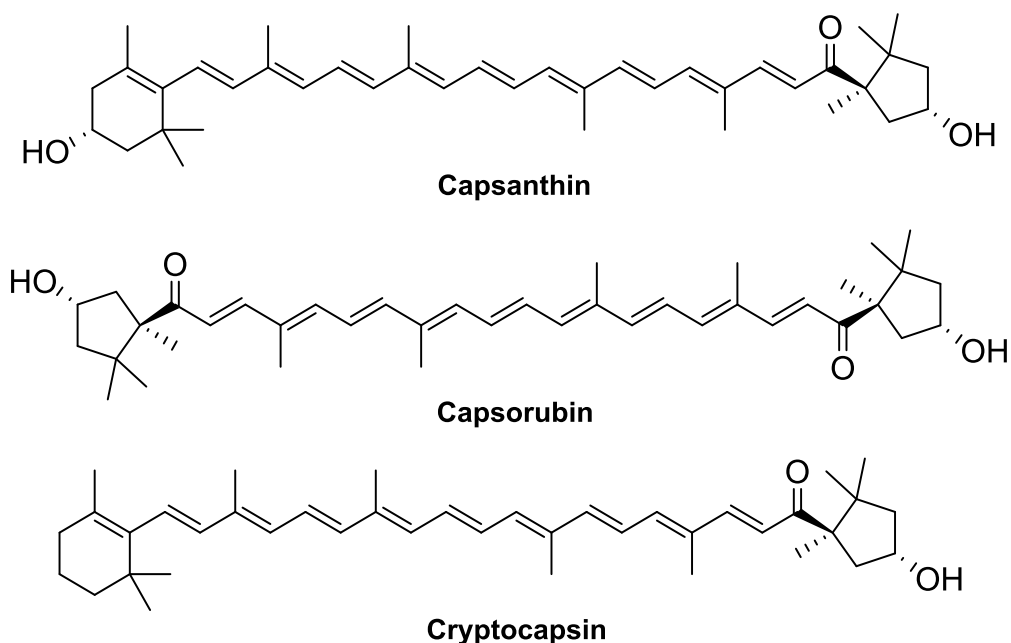


Fig. 51. Chemical structures of some of the principal carotenoid dyes recovered in paprika.

Paprika is one of the oldest, most widely spread and used carotenoid food dye [297]. Although paprika is rich in yellow xanthophylls and contains β -carotene in large proportions, it is mainly composed of the following red xanthophylls: capsanthin, capsorubin and cryptocapsin (chemical structures are depicted in Fig. 51) [183,297]. Since paprika features a broad absorption band between 400 and 550 nm, it appears to be a particularly interesting PS for visible light-induced photopolymerization reactions [231].

Gallic acid is a polyphenol mostly found in astringent plants from which it can be easily extracted using various techniques [231]. Thanks to its multiple phenolic hydroxyl groups and a carboxylic acid moiety, it can be easily functionalized and turned into a cationically polymerizable monomer, such as depicted in Fig. 64.

In the framework of antibacterial polymer coatings for stainless steel substrates, Sautrot-Ba et al. have thus reported the design of a simple and versatile photoinitiating system based on paprika acting as a photosensitizer, for the cationic photopolymerization of biosourced renewable monomers based on gallic acid [231].

Steady-state photolysis studies showed a substantial decrease in the UV-visible absorption band of paprika when mixed with an iodonium salt after only 50 seconds of light irradiation, whereas paprika on its own did not suffer from any photobleaching after the same period of irradiation. Fluorescence investigations confirmed a strong interaction between paprika and the considered iodonium salt and indicated a singlet excited state. Photoacids generation experiments as well as the study of the polymerization of epoxidized gallic acid demonstrated the very high efficiency of the paprika/Iod system for the cationic photopolymerization of epoxides.

According to their results and considering photochemical mechanisms previously described in the literature, they have proposed the electron-transfer based photosensitization mechanism depicted in Fig. 52 for the description of their paprika-photosensitized PIS.

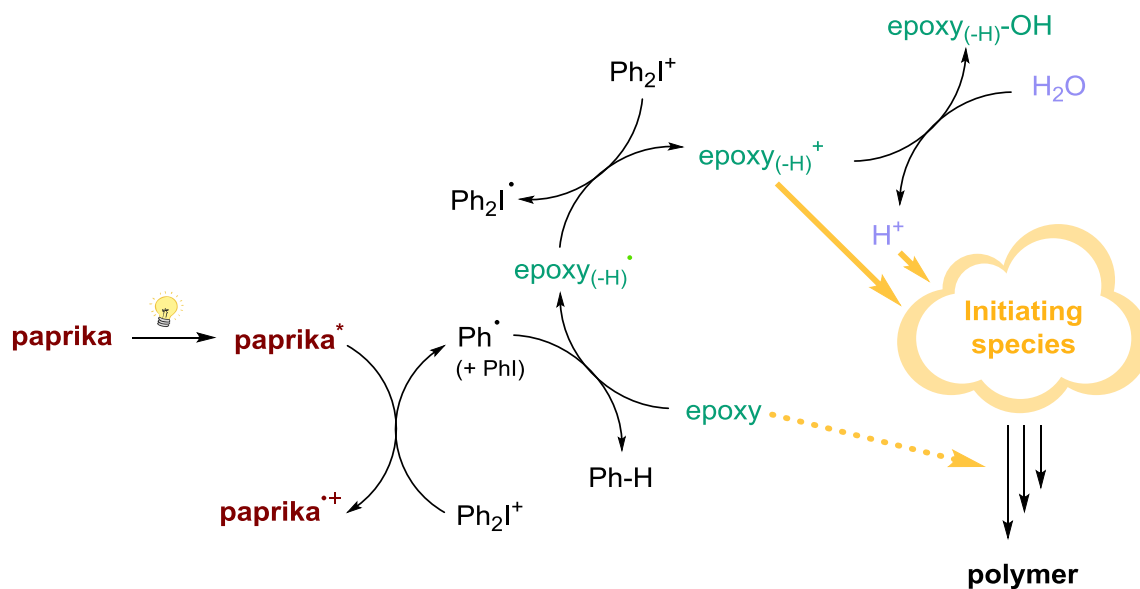


Fig. 52. Paprika-photosensitized cationic polymerization mechanism of epoxides.

A final monomer conversion of 90% has been reached after 1200 seconds of visible light irradiation, allowing for the synthesis of a coating showing no evidence of diffusing the PS outside of its matrix after 6 hours of incubation in water. This feature is particularly interesting as released compounds from polymer matrices can be an issue and raise high concerns from environmental and health points of view depending on their application field. Electronic paramagnetic resonance and in-situ photolysis experiments using DPBF as a typical singlet oxygen trap evidenced the photogeneration of singlet oxygen from the illuminated paprika solution and paprika-derived coatings respectively, with a linearly increasing singlet oxygen concentration under irradiation. These results supported the potential bacterial growth inhibition capacity of the paprika-derived coatings. Finally, antibacterial assays demonstrated an excellent bactericidal action of the paprika-derived coatings under illumination on both bacteria strains tested, whereas paprika-based films kept in the dark showed no sign of inhibiting bacteria proliferation. These observations confirmed the paprika-

derived film ability of completely inhibiting Gram-positive and Gram-negative bacteria proliferation via $^1\text{O}_2$ photogeneration.

These studies using carotenoids as both efficient visible light PSs and antibacterial agents open the road for the synthesis of natural dye-based and environmentally friendly bactericidal coatings with potential applications in medical and healthcare environments.

4.3.1.3. Curcuminoids

Curcumin, as well as demethoxycurcumin and bis-demethoxycurcumin, are biologically active polyphenolic compounds and are primarily found in the roots and rhizomes of *Curcuma longa*, the turmeric plant [298]. Turmeric plants are part of the ginger plant family and are widely grown in India and Southeast Asia [250]. Their rhizomes are mainly used to produce the well-known spice curry powder, and curcuminoids make up for 2 to 4% of dry turmeric root powder [298].

Curcumin is constantly being investigated in a broad range of application fields such as medicinal chemistry, food chemistry, pharmacology, toxicology, biology, biochemistry, and analytical chemistry [299]. Curcumin has attracted interest from numerous scientists across space and time thanks to its wide array of beneficial effects, including anti-inflammatory, antioxidant, chemoprotective, tissue protective, antibacterial, anticancer, antifungal, antiviral, metabolism regulating, immune-modulating, antineoplastic, and anti-depressant properties as well as a potential activity against chronic diseases such as Alzheimer's, diabetes, allergies or arthritis [250,262,298,299].

Curcumin was among the first natural compounds to attract interest for the design of biobased PISs as the first studies mentioning its efficiency as a visible light-sensitive PS for the photolysis of onium salts were published in 2005 and 2006 by Crivello & Bulut [250,251]. This naturally occurring intense yellow dye, whose chemical structure is depicted in Fig. 53, features an extended conjugation throughout its chemical structure thanks to the presence of aromatic rings and enol tautomerism. These characteristics result in a strong absorption of wavelengths in the visible light region. Additional methoxy and hydroxy functional groups in the 3- and 4- positions of the terminal phenyl groups allow for a further bathochromic shift of the absorption range, stretching from 340 nm to 535 nm. Finally, curcumin is all the more interesting that it is abundant, inexpensive, biocompatible, and soluble in a wide range of monomers and solvents.

In their studies, Crivello & Bulut investigated curcumin as an electron-transfer photosensitizer for the cationic polymerization of various monomers in the presence of different onium salts: CHO, EPOX, oxetane monomers, 2-chloroethyl vinyl ether as well as epoxidized natural compounds such as epoxidized linseed oil (ELO), epoxidized soybean oil (ESO), LDO, vernonia oil (see all four chemical structures in Fig. 62) and Lim [250,251].

Fluorescence and steady-state photolysis studies confirmed a strong electron-transfer photosensitization mechanism between curcumin and diaryliodonium salts, evidenced by a strong photobleaching of the analysed solution. In presence of the natural dye, the photoinduced cationic polymerization of CHO under a broad-band UV light emitting wavelengths greater than 300 nm happens rapidly and exothermically as soon as the irradiation device is switched on. The same results are observed when investigating the cationic polymerization of the other aforementioned

monomers. Experiments carried out using a LED light source centred at 470 nm proved to satisfactorily enable the polymerization process to occur, even with a much lower light intensity.

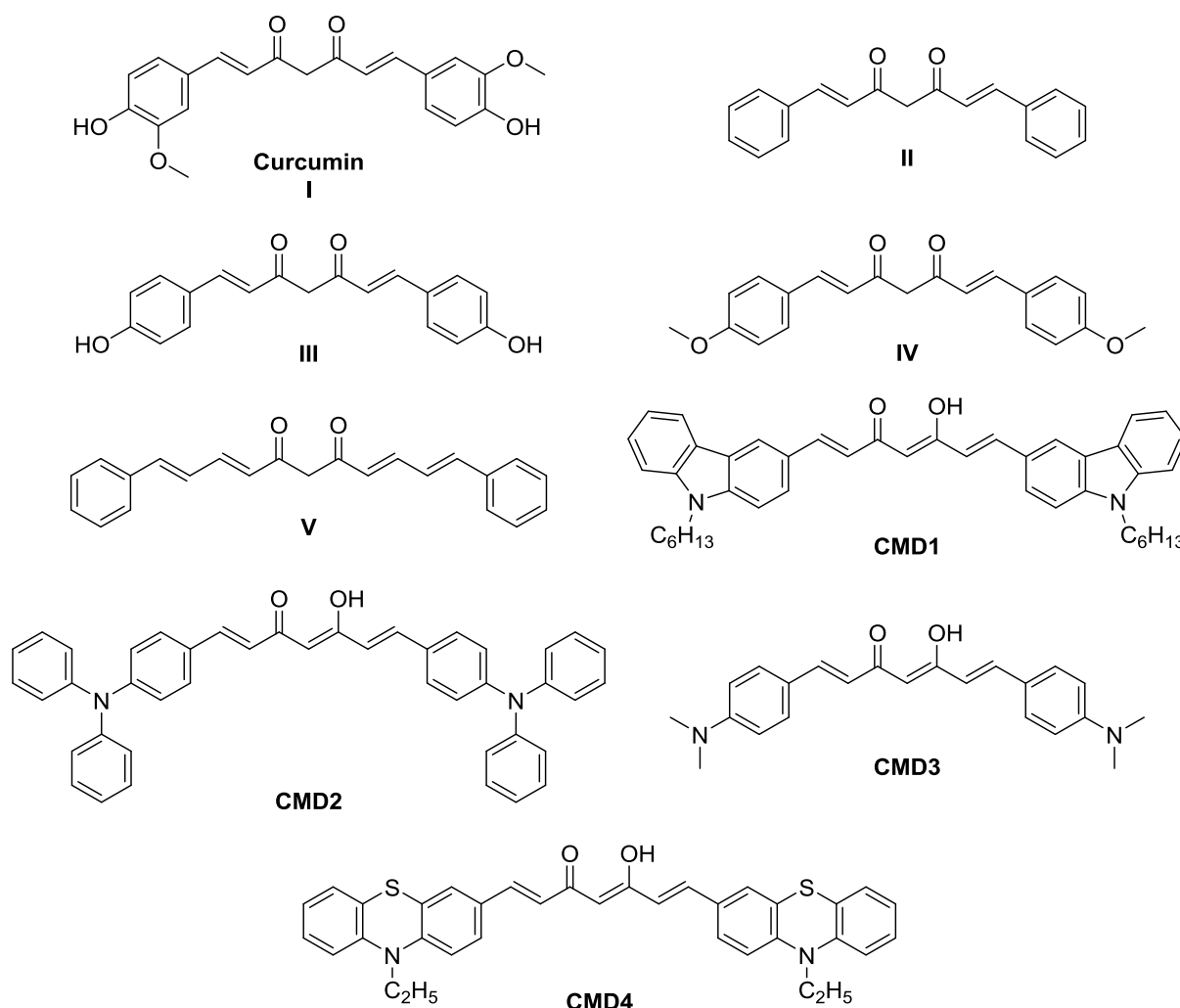


Fig. 53. Chemical structures of the different curcuminoids investigated for the design of biosourced photoinitiating systems for cationic photopolymerization reactions [250,251,262,263].

It is interesting to mention that the efficiency of the cationic polymerization reactions photosensitized by curcumin has been observed to be considerably higher when using a diaryliodonium salt instead of triarylsulphonium salts, which is due to the difficulties of reducing the latter.

Investigations of solar-induced CP of monomers derived from natural resources such as epoxidized vegetable oils (ESO, ELO) and epoxidized natural rubbers has also been carried out using curcumin as the photosensitizer [250]. It is particularly interesting since curcumin is notably soluble in oily compounds [298]. Within ten minutes of direct sunlight exposure, an intense-yellow formulation based on ELO, a diaryliodonium salt and curcumin turned into a pronounced-orange, tack-free, rigidified composite [250].

Analogues of curcumin have also been studied by Crivello & Bulut in order to possibly further extend the absorption sensitivity of onium salts into the visible light area as well as to investigate the effects of the curcumin structure on its oxidation potential [250]. These curcuminoids are respectively numbered I through V in Fig. 53.

Experiments using compounds I-IV for the photosensitized polymerization of CHO highlighted the importance of the phenolic moiety on the optical properties of the curcuminoid derivatives, as compound II was inefficient when used as a PS and compound III showed better performance than derivative IV [250]. Overall, curcumin demonstrated the best photosensitizing capacity, which can be explained by the proposed mechanism depicted in Fig. 54.

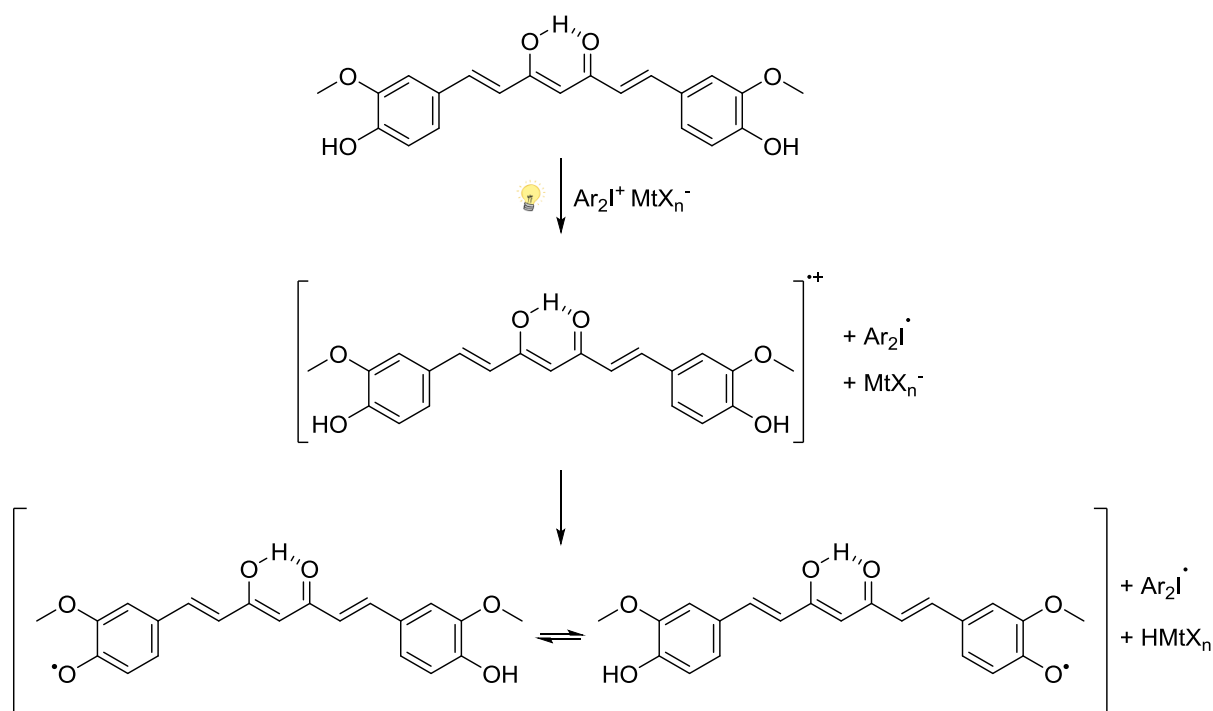


Fig. 54. Proposed mechanism for the photosensitization of a diaryliodonium salt by curcumin.

The photoexcitation of curcumin in presence of a diaryliodonium salt ultimately results in the formation of a highly resonance stabilized symmetrical phenolate radical. From these considerations, it is expected that 4-hydroxy-bearing curcumin and compound III feature better performance as PSs than compounds I and IV. The presence of methoxy functional groups on curcumin would enhance the stabilization of the generated radicals, explaining why curcumin demonstrated better photoinitiating results than compounds III.

The grafting of two additional double bonds onto the curcumin chemical structure as featured by compound V enabled to extend its conjugation, thereby its visible light absorption. Compound V appeared to be an active PS for the cationic ROP of CHO, nonetheless the introduction of additional hydroxy and methoxy groups onto its structure would allow for a further enhanced activity.

With the aim of investigated the antibacterial property of curcumin via photodynamic inactivation, Condat et al. recently reported the successful synthesis of biobased antibacterial coatings using curcumin as both a PS and an antibacterial agent combined with ESO and a

diaryliodonium salt [262]. Characterization analyses of the PIS composed of curcumin and the iodonium salt confirmed the strong electron-transfer mechanism previously described and photopolymerization experiments evidenced a final monomer conversion of 80% using a xenon lamp. Antibacterial assays highlighted the antibacterial action of curcumin against two strains of bacteria (*S. aureus* and *Escherichia coli*) in both solutions and embedded in the biobased coatings. The capacity of curcumin to generate singlet oxygen upon exposure to visible light even when incorporated in a polymeric matrix was demonstrated by EPR analysis and final coatings inhibited 99% and 95% of bacteria growth after 48H of incubation under illumination for *S. aureus* and *E. coli* respectively.

Lastly, a novel series of red-shifted curcuminoid derivatives has been investigated, namely CMD1 through CMD4 in Fig. 53, containing carbazole, triphenylamine, dimethylaniline and phenothiazine substituents as electron donor groups [263]. These substituents were carefully selected for their electron-donating ability, and final structures demonstrated a bathochromic effect as well as higher molar extinction coefficients compared to curcumin. Cationic photopolymerization experiments of DGEBA using CMDs/Iod as PIS under blue and green LEDs showed enhanced performance as opposed to curcumin, since higher overall final monomer conversions were obtained for both light sources. The addition of NVK within the PIS had the effect of increasing the initiating efficiencies of the considered PISs since higher final monomer conversions were obtained. CMD2/Iod appeared to be the most efficient PIS whereas curcumin/Iod was noticeably the least efficient, regardless of the light source. Due to its strong basicity, CMD3 could not initiate the cationic polymerization of DGEBA as terminating dimethylamino functional groups can easily abstract protons, thereby terminating propagating cationic chains.

4.3.1.4. Flavonols

Flavones and flavonols are polyphenolic natural products included in a larger family of compounds called flavonoids. Flavonoids are specialized metabolites widely distributed in the plant kingdom which consist in more than 9000 structures known to date. They are subcategorized according to their chemical structures into flavones, flavonols, flavanones, catechins, anthocyanidins, dihydroflavonols, isoflavones and chalcones, among which flavones and flavonols compose the largest subgroups [300].

Flavones and flavonols feature a set of attractive properties and have been discovered to play a significant role in various aspects of plant biology. They have actually contributed to make plants better adapt to their terrestrial environment by providing UV radiation and oxidative stress protection, interspecies interaction, flower pigmentation as well as a defence line against potential external pathogens [300,301]. Other noteworthy properties are their nutritional values and medicinal benefits to animals and humans. They are reported as being powerful antioxidants and exhibit anti-inflammatory, antiallergic, cardioprotective, antibacterial, antifungal, antiviral, neuroprotective, hepatoprotective, antidiabetic, photoprotective as well as anti-cancer activities [300–303]. Their daily intake varies between 20 and 500 mg and originates from various dietary sources, such as tea, apples, coffee, onions, red wine, beer, tomatoes and other fruits and vegetables [302,303].

Within the flavonol class, quercetin (see Fig. 55) is one of the most investigated flavonoid [302]. With the aim of exploiting the antibacterial activity of flavonols, Condat et al. lately developed a photoactivable biobased antibacterial coating using quercetin and glycerol triglycidyl ether,

combined with a diaryliodonium salt as cationic PI [267]. This is the first time that a flavonol derivative has been described as both an efficient cationic polymerization photosensitizer and a bactericidal agent via photodynamic inactivation. Quercetin features an absorption range in the near-UV area, with a maximum located at 370 nm. The photochemical studies showed that the quercetin/Iod system successfully generated a photoacid upon exposure to a light source, mostly from quercetin's singlet excited state, exhibiting concomitantly a strong photobleaching effect. Within 1200 seconds of UV irradiation, they obtained a completely tack-free coating exhibiting a final monomer conversion of 75%. Quercetin advantageously featured a bactericidal activity against *S. aureus* via the formation of singlet oxygen under irradiation both in solution and incorporated in the polymeric network, inhibiting bacterial growth by 99% in each case. Final coatings evidenced excellent adherence properties as well as high thermal stability, thus promising successful applications of flavonols as efficient photosensitizers for the synthesis of antibacterial coatings for biomedical purposes.

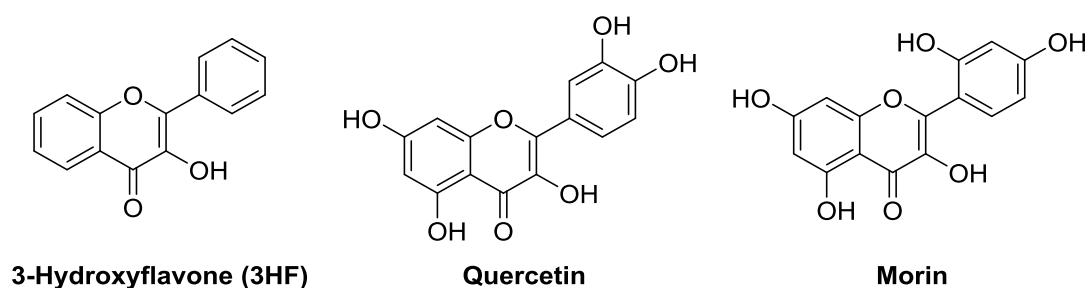


Fig. 55. Chemical structures of the different flavonoids tested for the design of biosourced photoinitiating systems for cationic photopolymerization reactions [267,270,273].

Several examples of photopolymerization reactions using flavones as PSs have been reported ever since this work, notably with the study of the photochemical properties of 3-hydroxyflavone (3HF) in a three-component PI/amine/Iod system [270]. The 3HF/Iod system has been reported to interact via a typical photoredox electron-transfer mechanism, although the overall initiating efficiency for the cationic photopolymerization of EPOX was much higher in presence of an amine co-initiator. EPR experiments indeed confirmed the formation of a charge transfer complex between N-phenylglycine and the iodonium initiator, enhancing visible light absorption of the PIS and accounting for the 55% of final EPOX conversion obtained under a LED centred at 385 nm.

More recently, quercetin along with morin, another naturally occurring penta-hydroxy flavone (PHF, chemical structures are shown in Fig. 55), was further investigated as visible light-sensitive PI for the cationic polymerization of DVE-3 [273]. Steady state photolysis analyses confirmed a strong interaction between the PHFs and Iod when irradiated with a LED centred at 394 nm while photopolymerization experiments of DVE-3 carried out upon exposure to a LED bulb centred at 410 nm reached 89% and 78% of conversions for the quercetin/Iod and the morin/Iod PISs respectively.

4.3.1.5. Naphthoquinones

Naphthoquinones are a class of natural dyes widely spread throughout all kingdoms of life. They are not only found in a large variety of plants, but they are also synthesized in numerous animal species, including human beings [304]. A broad array of different naphthoquinones is indeed biosynthesized by a great number of species of plants, fungi, bacteria, marine organisms (cyanobacteria, diatoms, sea urchins), insects (beetles, arachnids, millipedes, termites) as well as by the human body (such as vitamin K3 for instance) [304,305].

These naturally occurring compounds possess a multitude of biological and biochemical properties and are involved in vital metabolic processes and/or contribute to the adaptation of a considered species into its living environment [305]. Numerous species of plants containing naphthoquinones have actually been used in traditional medicine of different cultures across the world and in different eras to treat cardiovascular and cerebrovascular diseases as well as cancer or abdominal pain to cite but a few [304].

Naphthoquinones generally occur in either of two isomers: 1,4-naphthoquinone and 1,2-naphthoquinone. 5-hydroxy-1,4-naphthoquinone (5HNQ), which can be found in the heartwoods of *Caesalpinia sappan*, and 2-hydroxy-1,4-naphthoquinone (2HNQ, also typically known as lawsone), which is a yellow dye abundantly found in the leaves of *Lawsonia inermis* (henna plant) [304], have recently been examined for the design of natural dye-based PISs in the framework of cationic photopolymerization due to their excellent visible light absorbing properties [274,275]. Their respective chemical structures are shown in Fig. 56.

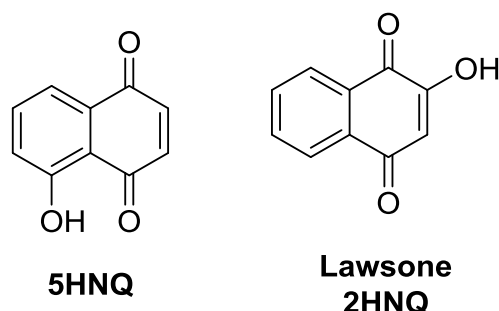


Fig. 56. Chemical structures of 5-hydroxy-1,4-naphthoquinone (left) and 2-hydroxy-1,4-naphthoquinone, also known as Lawsone (right).

Absorption spectra of both dyes demonstrated a broad absorption band encompassing parts of the visible light area for 5HNQ, with a maximum located at 420 nm, whereas 2HNQ mostly absorbs in the near-UV range of the spectrum. However, cationic photopolymerization experiments involving DVE-3 combined with 2HNQ/Iod as PIS demonstrated a higher efficiency than the 5HNQ/Iod PIS. Upon exposure to a blue LED at 445 nm, respective final double bond conversions of 86% and 59% are obtained, while reaching 92% and 85% respectively when irradiated with a 410 nm-centred LED [274]. The addition of NVK within the 5HNQ-based PIS did not significantly improved its efficiency, it even resulted in a slight decrease in monomer conversion in the case of 2HNQ, evidencing the excellent photoinitiating efficiencies of the HNQ-Iod combination.

Going deeper into the investigation of the photoinitiating ability of lawsone, Elian et al. have just now reported the successful synthesis of two new biobased photopolymerizable PIs derived from 2HNQ [275]. Their aim was manifold: the natural dye-based derivatives can act as visible light

photosensitizers as well as photopolymerizable monomers thanks to the grafting of both allyl and epoxy functional groups (see chemical structures in Fig. 59).

Although allylated (HNQA) and epoxidized (HNQE) lawsone derivatives demonstrated a decrease in molar extinction coefficients compared to 2HNQ (with no significant shift in their absorption spectra), the photochemical characteristics of the HNQ derivatives/Iod PISs showed favourable electron-transfer reactions from singlet excited states of the lawsone derivatives to the iodonium salt as well as the successful photogeneration of an initiating Brønsted acid. The study of the cationic photopolymerization kinetics of EPOX highlighted enhanced initiating properties of HNQA and HNQE with final epoxy conversions reaching 50% after 600 seconds of irradiation under air upon exposure to blue LEDs (385 and 405 nm). In comparison, benzophenone and camphorquinone as commonly used PSs as well as 2HNQ were tested under the same conditions but failed to initiate the photopolymerization of EPOX, thereby proving the improved efficiencies of the newly described PIs. The allylated lawsone derivative/Iod combination also exhibited excellent initiating properties for the concomitant thiol-ene and cationic photopolymerization of a limonene-1,2-dioxide/trifunctional thiol mixture, with final vinyl bond conversions of 100% under air, regardless of the irradiation source.

In short, the use of natural dyes as effective photoinitiators is a very recent source of interest from the scientific community deserving to be more widely investigated in the coming years. A lot of natural structures still await to be examined and exploited as only a few have been described to efficiently initiate photopolymerization reactions to date. Naturally occurring dyes raise nevertheless a few concerns regarding their isolation and purification from natural resources. From an economic point of view, key parameters include the dye content in natural raw materials, the number of purification steps required for their isolation and overall yields [183].

4.3.2. Design of new Photoinitiating Systems incorporating Epoxy/Ether derivative groups: recent advances

Applications of photopolymers in food packaging [306] or as biocompatible materials is severely limited by the migration ability of photoinitiators and photosensitizers within polymer matrices [183]. The potential and slow leaching of embedded PIs/PSs outside of polymer matrices raises environmental and health concerns as it can negatively impact the surrounding environments and ecosystems as well as adversely impact the potential use of the considered coatings upon application.

In this regard, several strategies have been investigated to covalently immobilize PSs within the polymer networks. Natural resources featuring unsaturated double bonds are promising building blocks for the development of sustainable photopolymerizable PIs, as these electron rich carbon chains can easily be transformed into reactive monomer functions (such as epoxy or acrylate groups) through simple and inexpensive modifications [183].

In this respect, Sautrot-Ba et al. very recently described the synthesis of allylated as well as epoxidized derivatives of both quinzarin and purpurin natural anthraquinones [235,259]. Various photopolymerizable functional groups have been grafted onto the dyes' chemical structures via easy and quick one-step procedures as described in Fig. 57 and Fig. 58.

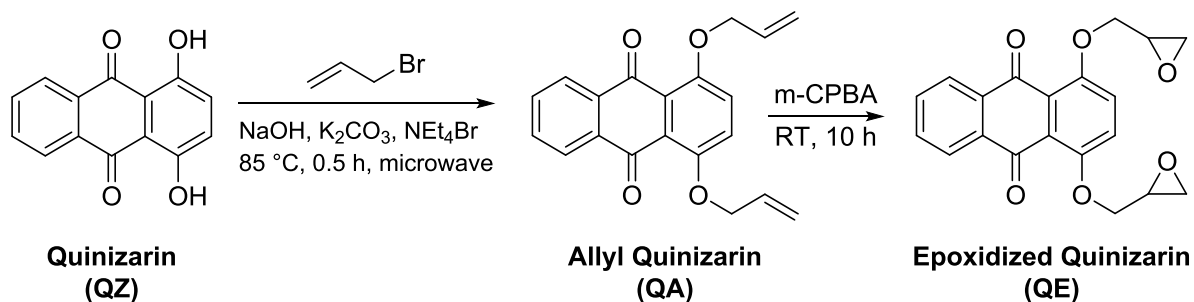


Fig. 57. General procedure for the synthesis of quinizarin derived photopolymerizable photosensitizers.

Thanks to chemical structures rich in reactive phenolic hydroxyl groups, the addition of photoreactive allyl functionalities onto quinizarin and purpurin can be easily carried out using allyl bromide under microwave irradiation. In the presence of a phase-transfer catalyst, using nucleophilic bases and allyl bromide as both the reactant and the reaction solvent, the procedures are completed within an hour at 85 °C. Purification of crude extracts by flash chromatography on silica gel yielded 85% of QA, 40% of PA and 10% of PmA in the respective studies. Regarding quinizarin, a second step has been carried out, that is the epoxidation of QA. The portion wise addition of m-CPBA at room temperature to a solution of QA enabled the conversion of the allyl functional groups into epoxides in an 80%-yield within 10 hours. Interestingly, the authors did not observe any diffusion of their functionalized hydroxyanthraquinone derivatives from their crosslinked samples when incubated in different solutions, thereby evidencing the successful covalent grafting of the PSs to the polymer networks.

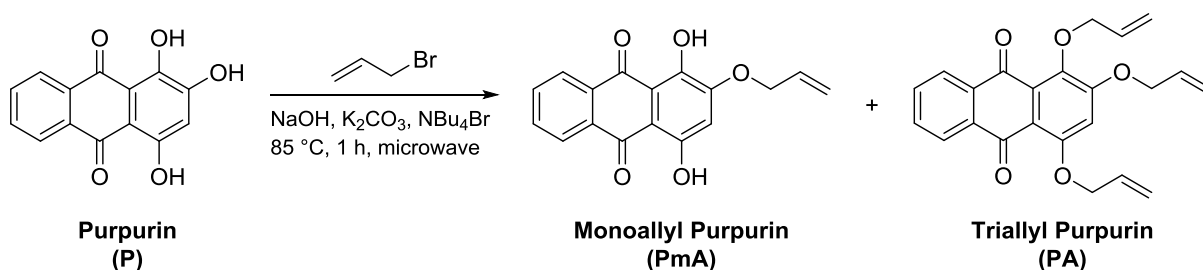


Fig. 58. General procedure for the synthesis of purpurin derived photopolymerizable photosensitizers.

The same strategy was also applied by the same authors to lawsone, the main dye contained in the leaves of *Lawsonia inermis*, also widely known as henna plant [275]. They designed two lawsone-derived photopolymerizable photoinitiators containing respectively an allylated and an epoxidized functional group by following a similar procedure (Fig. 59). Lawsone was mixed with NaOH, K₂CO₃ and tetraethylammonium bromide as a phase-transfer catalyst before adding allyl bromide. The reaction was performed under microwave irradiation for an hour at 75 °C. Post-reactional extraction treatments and purification by column chromatography allowed for the obtention of allylated lawsone (HNQA) with a yield of 48%. Next, m-CPBA was added to a cooled HNQA solution at 0 °C four times over a period of 10 hours. Meanwhile it was allowed to warm to room temperature. Epoxidized lawsone (HNQE) was obtained in a 10%-yield after another column chromatography purification step.

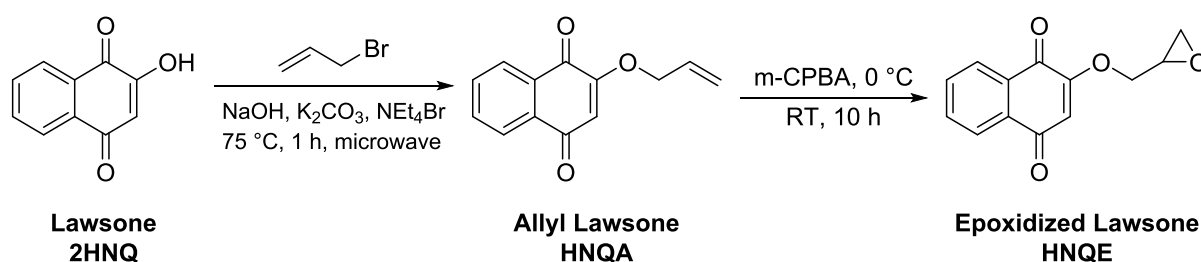


Fig. 59. General procedure for the synthesis of lawsone derived photopolymerizable photosensitizers.

Alternatively, a photopolymerizable type I free radical PI has been synthesized for the first time from a biosourced substrate. If vanillin has been mostly exploited as a reference building block for the development of biobased monomers and sustainable polymers so far, it was recently modified into a functional type I photoinitiator [282]. The synthetic procedure of (4-allyloxy-3-methoxybenzoyl)diphenyl phosphine oxide (PM, see chemical structure in Fig. 60) consists in a three-step process. First, vanillin is mixed with potassium carbonate and allyl bromide, and stirred at room temperature in dimethylformamide for two days. The resulting crude is then purified before being combined with diphenyl phosphine oxide in dry tetrahydrofuran. Triethylamine is added dropwise to the solution, which is left to stir for another day at room temperature. The precipitated product is then filtered, washed several times with THF, dried, and subsequently combined with activated MnO_2 in anhydrous dichloromethane. The system is purged with N_2 and allowed to react at 25 °C overnight. A final filtration step under celite followed by the removal of DCM using a rotary evaporator afforded the obtention of PM with a global yield of 50%. The vanillin derivative successfully initiated the FRP of both triacrylate and natural oil acrylate monomers when used alone as well as combined with a trifunctional thiol compound. This newly described type I PI proved to be as efficient as other well-known type I and type II FRP PIs, if not better.

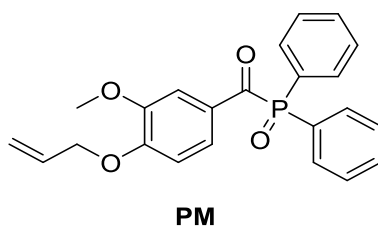


Fig. 60. Chemical structures of (4-allyloxy-3-methoxybenzoyl)diphenyl phosphine oxide (PM).

The grafting of photoreactive functional groups directly onto the structure of the considered dyes allow for the design of renewable photosensitizers playing multiple roles: not only can they efficiently initiate free radical, cationic as well as thiol-ene photopolymerization reactions, but they also act as co-monomer in the overall process. The various dye-based photosensitizers are covalently grafted onto the networks instead of just being embedded within the final polymeric matrices. As a consequence, synthesized coatings no longer progressively release any photoinitiator in their surrounding environment upon application and use, which is a very promising alternative to satisfy environmental and health-related concerns. Since some of the compounds described above also play

the role of antibacterial agents as they enable the generation of bactericidal singlet oxygen in the associated studies, this feature ensures a more permanent antimicrobial effect of the considered coatings.

To date, the design of new PIs and PSs grafted with ether and epoxy groups from sustainable sources has only been scarcely addressed. Comparatively, a series of thioxanthone functionalized macrophotoinitiators have been described over the year in the scopes of free radical, cationic, and thiol-ene polymerization reactions [239,307–313]. However, these functionalized structures are entirely synthetic compounds, which raises economic, environmental as well as health issues in the long-term.

4.3.3. Synthesis of new Water-based Photoinitiating Systems

The addition of low amounts of water to a cationically curable formulation can lead to the acceleration of the CP rate and enhance final conversion. In fact, water may act as a chain transfer agent, thereby leading to polymerization re-initiation through the activated monomer mechanism (Fig. 61) [25,314].

However, high humidity conditions or the use of water as solvent can result in high-localized concentration of water, which is likely to result in excessive chain transfers and thus, to low-molecular weight polymers [25]. Nucleophilic attacks of water on propagating oxonium cations inhibit the polymerization process until it eventually stops [314]. Additionally, in formulations containing vinyl ether derivatives, the presence of water can lead to the hydrolysis of the monomers [25]. As a consequence, cationic photopolymerization is highly sensitive to moisture and water in general, as their excess ultimately slows down or even completely stops the curing process [5,25,314,315]. For these reasons, no suitable water-based cationic photoinitiating system is currently known at this time.

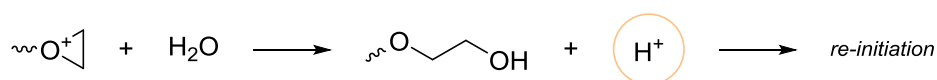


Fig. 61. Activated monomer mechanism involving water.

4.3.4. Cationic Photopolymerization of bio-renewable monomers

In the search for more environmentally friendly technologies and the obtention of greener photoinduced materials, the focus has also been directed toward biosourced, renewable raw materials and their potential to be used as substitutes for petrochemical-based monomers. The number of investigations in the field of photopolymerization encompassing the development of biomass-derived materials skyrocketed in the last decades since these building blocks can be readily extracted from industrial by-products and waste. Excellent reviews describing bio-based photopolymerizable materials and their design strategies have notably been recently published on this matter [22,316,317].

In the framework of cationic photopolymerization reactions, the reactivity of a series of renewable monomers and oligomers have already been investigated among which are the following: a large variety of epoxidized vegetable oils, epoxidized natural rubbers and fatty acids, tannins and polyphenols, starch and sugar derivatives as well as epoxidized terpene monomers [5,186]. Chemical structures of some of the cationically photopolymerizable biosourced monomers further described in this section are shown from Fig. 62 to Fig. 65, except mentioned otherwise.

Vegetable oils are particularly interesting inexpensive building blocks for the synthesis of biobased monomers since a large variety of unsaturated vegetable oils are available from common crop sources. Their chemical structures differ greatly from one another with respect to the plant species, to the related plant within the same species and to the numbers and positions of electron-rich double bonds and already existing possible functional groups along their carbon backbones, such as epoxy groups (vernonia oil) or hydroxyl groups (castor oil) for instance [22]. Thereby, all herein depicted chemical structures of vegetable oils are actually average rather than exact structures. Various functionalization procedures of unsaturated vegetable oils have been developed over the years, epoxidation being one of the most widespread functionalisation reactions. Indeed, unsaturated vegetable oils can be readily epoxidized using environmentally friendly procedures such as previously described in this paper.

In the early 90s, a series of epoxidized vegetable oils, namely soybean, safflower, sunflower, canola, crambe, lesquerella, meadowfoam, vernonia, linseed, rapeseed, and castor oil, was examined in the scope of photoinduced cationic polymerization. Colourless to pale yellow, flexible films were obtained, exhibiting good adhesion, thermal as well as mechanical properties [318–320].

Since then epoxidized triglycerides have been extensively investigated for the study of natural dye photosensitized polymerization reactions [250,251], in the design of photoinduced antibacterial [262], hydrophobic [321,322] and glass fibre-reinforced [245] coatings, combined with petroleum-based epoxy monomers (such as EPOX) [314,323,324], in the preparation of solvent-free and biosourced pressure-sensitive adhesives [325] or for the synthesis of fully biobased nanocomposites [326–328] and thermoset materials [329,330] via cationic photocuring. FRPCP studies [192,227,331] as well as hybrid polymerizations [332] have been carried out on epoxidized soybean, sunflower, corn and linseed oils.

Other studies focused on the further modification of epoxidized vegetable oils, such as the synthesis of norbornyl epoxidized linseed oil (ENLO) and the study of its photopolymerization, which turned out to occur at a higher rate with better monomer conversions compared to the original ELO [333–336]. Cyclohexene as well as epoxidized cyclohexene derivatized linseed oils (ECLo) were reported by the same authors via a Diels-Alder cycloaddition reaction followed by further epoxidation [337,338]. Slightly higher photocuring rates and a higher viscosity were again observed for ECLo than for ELO. Vernolic acid (see chemical structure in Fig. 27) has also been recently grafted onto a hyperbranched hydroxy functional polyether and cationically photopolymerized in presence of different amounts of a vernolic acid ester derivative in order to examine the impact of the resin structure variations on its final thermal and mechanical properties [339]. Another study lately worked on the modification of soybean oil and its incorporation in a biobased composite [340]. The authors successfully synthesized a modified soybean oil with urethane branched chains terminated by epoxy groups via thiol-ene click photochemistry and isocyanate polyurethane reaction. They blended it with EPOX and obtained a homogeneous coating with higher thermal stability.

Finally, natural rubber has also attracted his bundle of interest as the photopolymerization kinetics of epoxidized natural rubber has been studied and described, both alone and combined with other co-monomers [246,341,342].

In the last decade, a few studies described the design and use of photopolymerizable epoxy prepolymers derived from cashew nutshell liquid (CNSL; see chemical structures of the different components of CNSL in Fig. 14). The thermal and mechanical properties of film materials containing epoxidized cardanol derivatives (ECD) and CNSL-based epoxy prepolymers have been investigated [343–348]. Results demonstrated that ECD possess a great potential to be used as humidity blocking reactive ingredients in cationic photoinduced materials while CNSL-based prepolymers allow for an enhancement of film properties such as gel content, drying, hardness and thermal properties compared to conventional photopolymerizable epoxides.

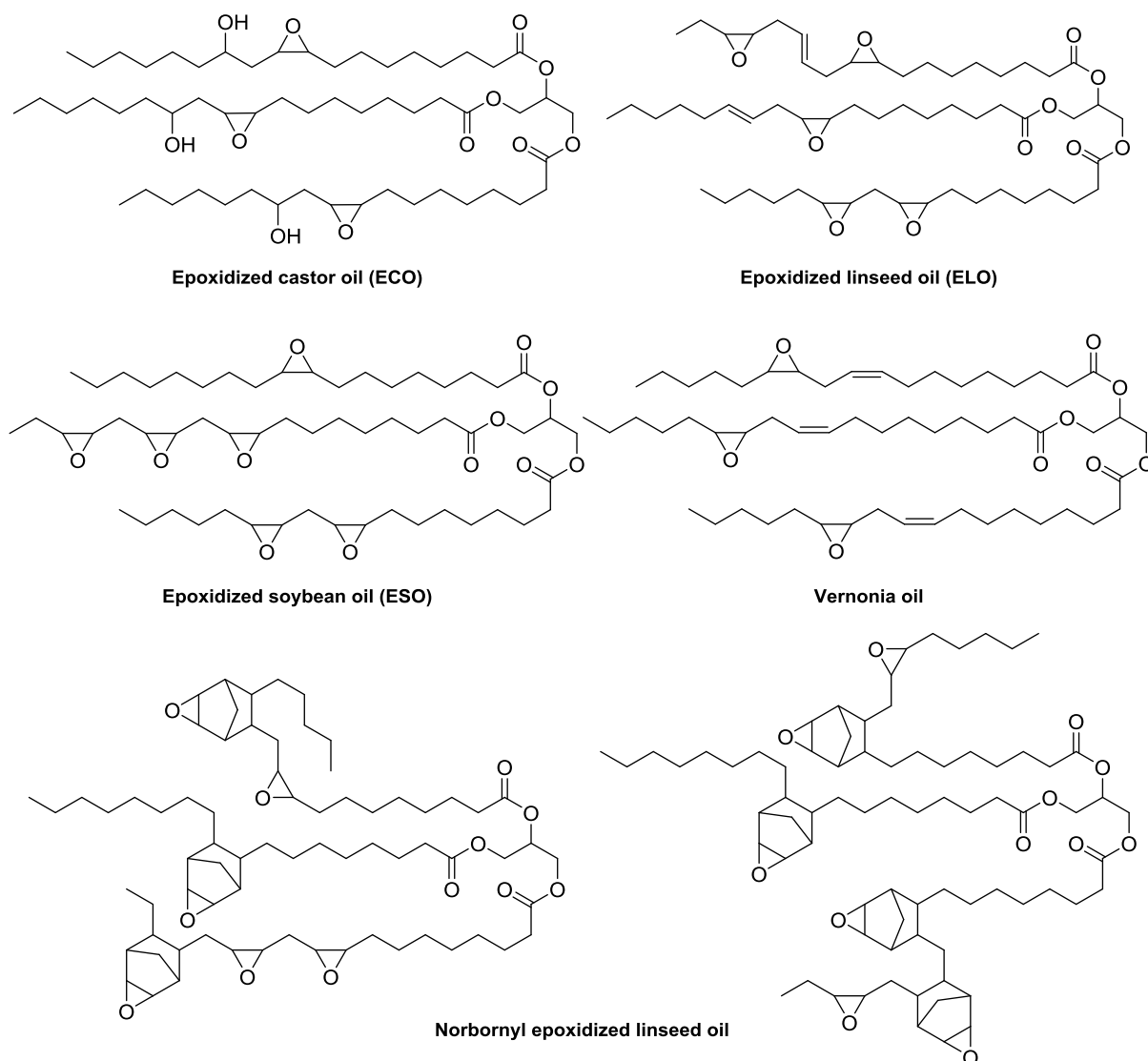


Fig. 62. Average chemical structures of some epoxidized vegetable oils typically used in CP reactions based on biosourced monomers.

Terpenes and terpenoids compose one of the largest groups of natural products with tremendous industrial impacts. They have been applied in all kinds of purposes, particularly in pharmaceutical, fragrance, solvent, chiral catalysis and fine chemical applications [316]. Terpene derivatives have naturally found their place in recent strategies to design biobased polymeric

materials as a growing number of reports have described the modification of these hydrocarbons to develop innovative renewable monomers. Terpenoid-based monomers are among the most reactive biobased epoxy monomers due to the highly strained epoxy groups located on their cycloaliphatic rings and tend to give highly crosslinked networks.

Among natural monoterpenes, limonene has attracted a lot of attention due to the presence of both endocyclic and exocyclic alkene moieties on its chemical backbone (see Fig. 28). This feature allows for the synthesis of highly reactive epoxidized limonene derivatives, notably limonene-1,2-epoxide, and limonene dioxide (LDO).

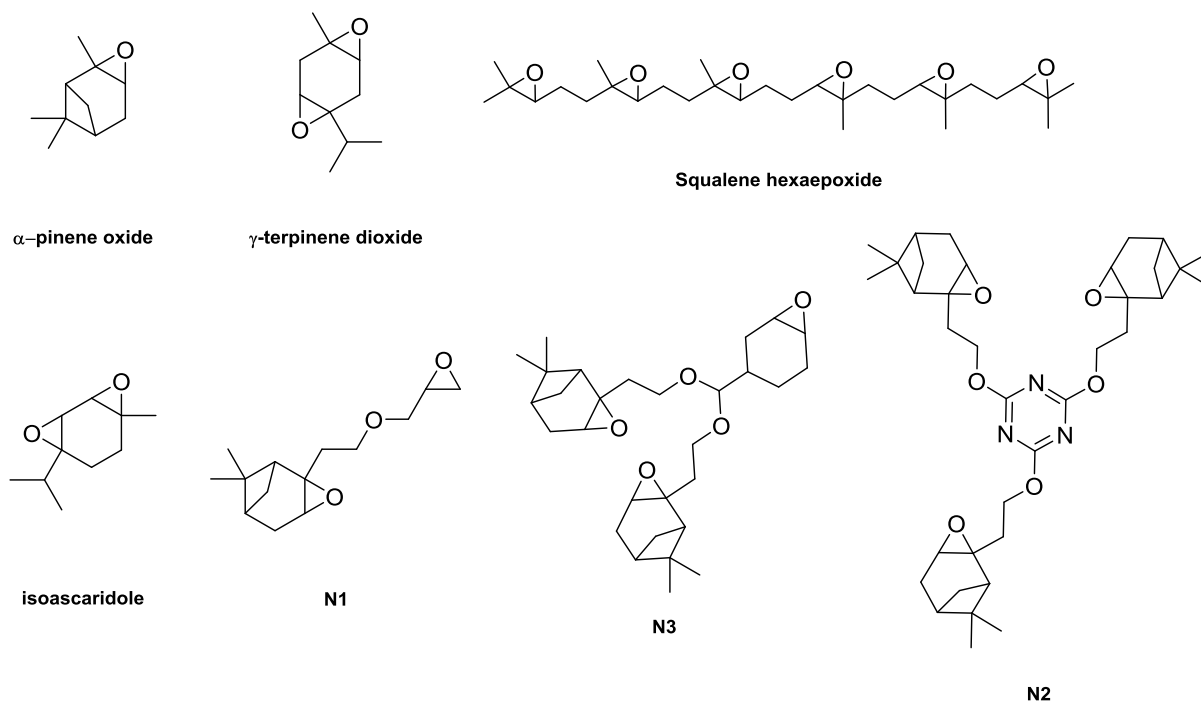


Fig. 63. Chemical structures of cationically photopolymerizable monomers derived from terpenes.

LDO is one of the most reactive monomers since the ring-opening process is highly favourable, exhibiting higher polymerization rates than those observed when using epoxidized fatty acids and vegetable oils [186]. Taking advantage of this attractive feature, a few studies investigating the photosensitization of cationic polymerization reactions with natural dyes used limonene-1,2-epoxide and limonene dioxide as renewable monomers [230,251,275]. In recent investigations, LDO has also been combined with a silane derivative in three-component PISs for the FRPCP of biobased monomers under various low intensity visible light sources [192,227,247]. The photopolymerization rates of limonene-1,2-dioxide and LDO have been compared respectively to that of α -pinene oxide, another monoterpene derived from coniferous trees [349], and to diepoxides of isoascaridole and γ -terpinene [319,350]. In 2020, the synthesis of biosourced epoxy monomers derived from nopol, a β -pinene-based intermediate, and their subsequent photopolymerization profiles have been reported (see structures N1, N2 and N3 in Fig. 63) [351]. Total monomer conversions of 54%, 58% and 62% after 10 minutes of irradiation have been obtained for N3, N2 and N1 respectively.

Polyterpenes on the other hand have not been sidelined either, since the epoxidation of squalene and poly(*cis*-isoprene) allowed for the development of squalene hexaepoxide and epoxidized natural rubber [319,352]. Cationic photopolymerization experiments carried out on these

epoxidized elastomers resulted in colourless, transparent, flexible, highly crosslinked biobased polymers.

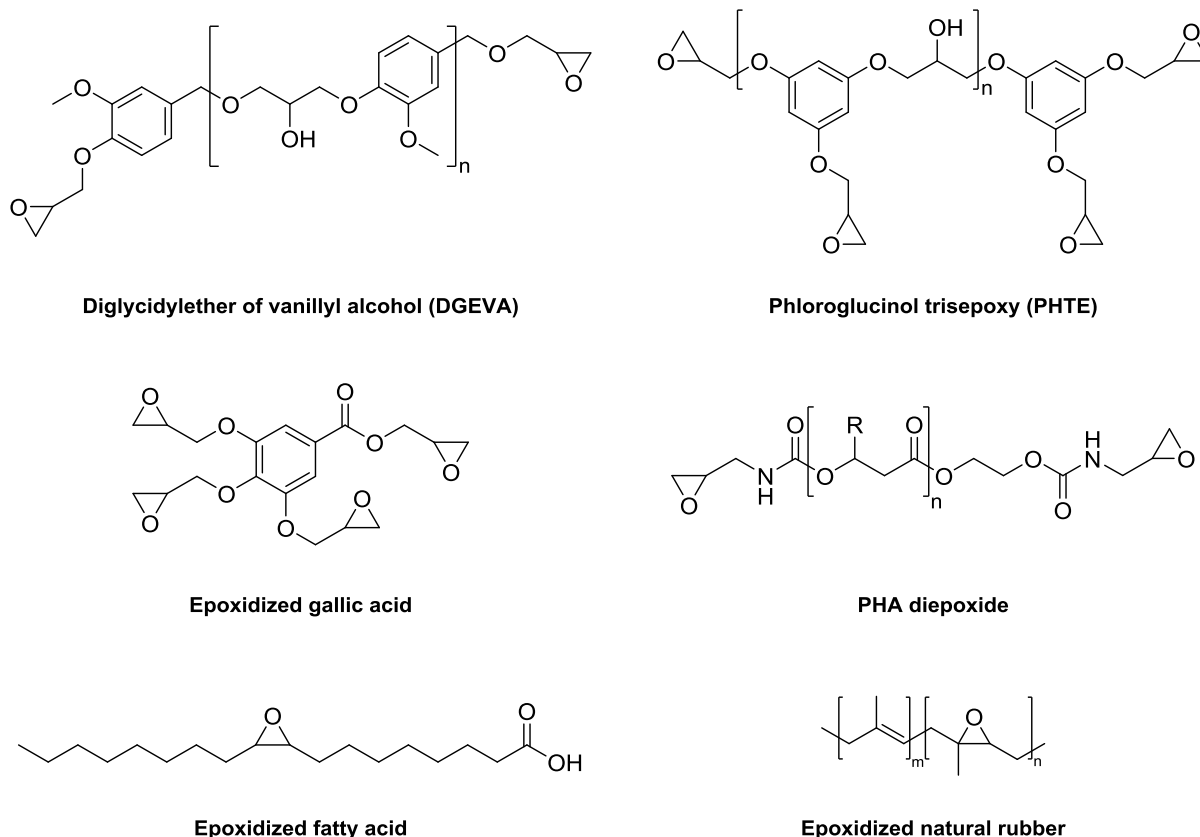


Fig. 64. Chemical structures of typically used biosourced cationically photopolymerizable monomers.

A series of other epoxidized biobased monomers can be obtained starting from phenolic lignin-derived compounds, such as eugenol, gallic acid, phloroglucinol, vanillin and resorcinol.

Eugenol naturally possesses a terminal alkene, allowing for immediate use in thiol-ene, free radical and cationic polymerization reactions. In this regard, Breloy et al. took advantage of this natural allyl moiety for the concomitant thiol-ene and cationic copolymerization of eugenol with limonene-1,2-epoxide and LDO in the development of a β -carotene-based antibacterial coating [230]. Alternatively, eugenol can also undergo further functionalization either via the alkene group or through the phenolic part [316], such as described by Modjinou et al. With the aim of designing a photoinitiated epoxy co-network of resorcinol diglycidyl ether and eugenol for antibacterial and antioxidant purposes, they reported the successful synthesis of an epoxidized eugenol-based monomer as well as its first time use in a photoinduced cationic polymerization process [353].

Extracted from lignocellulosic biomass, resorcinol and its derivatives, namely resorcinol diglycidyl ether (RGDE), resorcinol glycidyl furfuryl ether and resorcinol glycidyl dihydroxyl ether, have been investigated for the preparation of durable epoxy resins as efficient substituents to bisphenol A-based epoxy monomers. Yet, they did not attract much interest in the field of cationic photopolymerization until the studies recently published by Nguyen et al. [354,355]. They were the first to process RGDE in bulk photoinduced epoxy resins, both alone and combined with diatomite, for the synthesis of fully biobased composites exhibiting a great application potential in the

construction industry. They investigated the benefits of dual UV-thermal curing to increase final monomer conversions and successfully obtain highly crosslinked materials.

Finally, in the class of phenolic compounds, an epoxidized monomer derived from gallic acid involved in a photocationic polymerization process has been recently reported for the first time [231]. Via a simple two-step procedure, Sautrot-Ba et al. obtained a tetra-epoxidized gallic acid-based monomer which they used for the photoinduced synthesis of paprika-derived antibacterial coatings. Other sustainable epoxy monomers based on vanillin and phloroglucinol, namely diglycidylether of vanillyl alcohol (DGEVA) and phloroglucinol trisepoxy (PHTE), have been successfully synthesized through quick and environmentally-friendly processes [356]. Cationic photopolymerization experiments evidenced high final monomer conversions, reaching values as high as 85%.

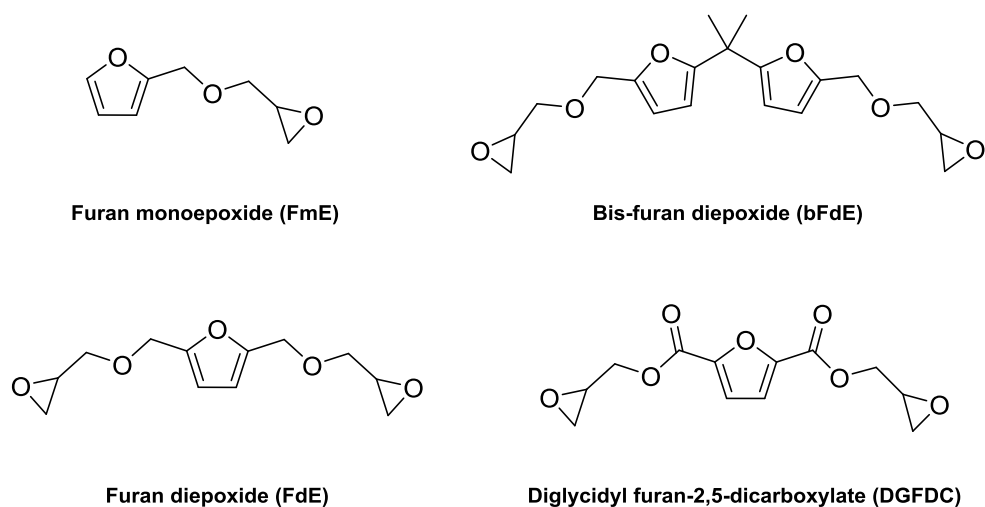


Fig. 65. Chemical structures of some furan-based epoxidized monomers used in CP.

Starch and sugars represent a particularly interesting pool of raw material as they are inexpensive, very abundant and exhibit substantial structural and stereochemical diversity [316]. Through chemical or enzymatic processes, polysaccharides can be broken down to monosaccharides, unsaturated carboxylic acids, furanic derivatives, polyesters and polyols, which can be in turn transformed into polymerizable monomers.

In this regard, glycerol has recently been investigated as a cationic building block for the photoinduced synthesis of antibacterial coatings [267]. It was first readily transformed into its glycidyl ether derivative and then successfully combined to quercetin, resulting in a tack-free coating featuring good adhesion and antibacterial properties.

In a similar procedure, isosorbide was used and transformed into a diepoxide derivative (see chemical structure in Fig. 25) to be cationically co-photopolymerized with a poly(3-hydroxyalkanoate) (PHA) diepoxy monomer for biodegradable purposes [357]. In this matter, PHAs are biopolyesters also receiving increasing interest for their biodegradation ability and great potential for biobased drug delivery systems and tissue engineering applications. Alternatively, allylation and subsequent isomerization steps carried out on isosorbide afforded highly reactive vinyl and propenyl ether derivatives of isosorbide [196,319]. These monomers exhibited high reactivity in cationic photopolymerization experiments, with final monomer conversions higher than 60%.

Furanic compounds on another hand constitute an additional class of carbohydrate biomass derivatives that are particularly interesting candidates for the replacement of petroleum-derived aromatic compounds. They can be obtained from polymeric carbohydrates such as cellulose and hemicellulose via hydrolysis, dehydration and oxidation/reduction steps such as shown in Fig. 66. In 2013, Cho et al. described the synthesis of epoxy derivatives of furan, namely furan monoepoxide (FmE), furan diepoxide (FdE) and bis-furan diepoxide (bFdE), starting from 2-furan methanol (FM), 2,-furan dimethanol (FDM) and 2-furan carboxylic acid (FCA) respectively [358]. They studied the cationic photocuring kinetic profiles of the newly-developed furanic epoxy monomers by photo-differential scanning calorimetry (photo-DSC) while irradiating the samples in the near-UV-visible light range. More recently, Nameer et al. expanded the scope of furanic monomers by reporting the synthesis of diglycidyl furan-2,5-dicarboxylate (DGFDC) and its photo-copolymerization with different epoxidized fatty acid methyl esters (EMX) derived from linseed oil [359]. The CP experiments were carried out at 85 °C for an hour, enabling the obtention of fully cured films featuring flexible and hydrophobic structures, provided by EMX monomers, as well as enhanced rigidity and mechanical stability, thanks to DGFDC.

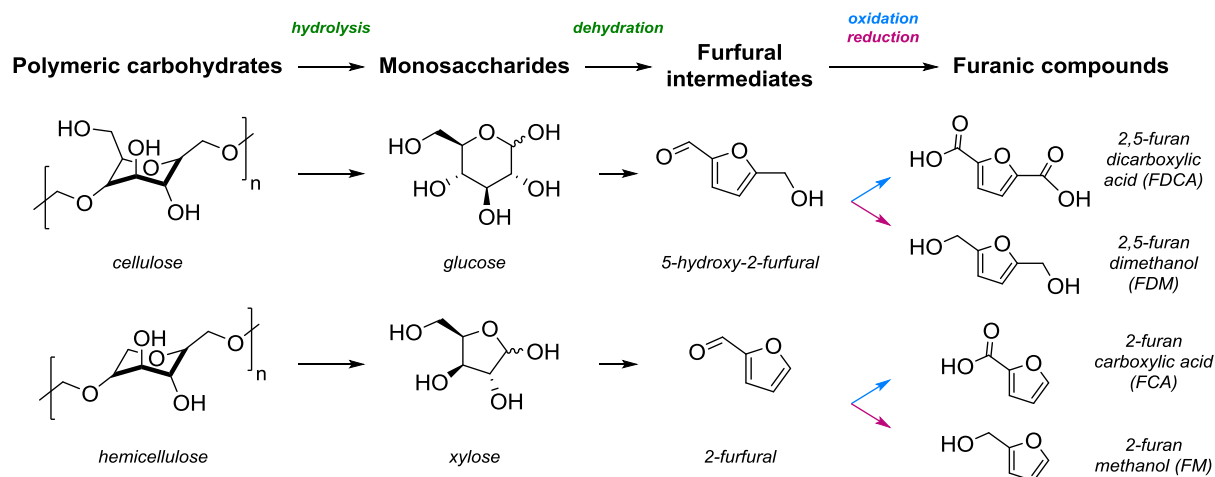


Fig. 66. Synthesis routes for the preparation of furanic compounds derived from carbohydrate biomass polymers.

In another study, starch has also been modified into a cationically photopolymerizable monomer by means of graft functionalization, without being broken down to monosaccharide units first. Glycidyl methacrylate was indeed successfully grafted onto starch in aqueous medium using ceric ammonium nitrate, as depicted in Fig. 67, and subsequently photo-copolymerized with EPOX [360]. The use of starch is all the more interesting for CP as its hydroxyl groups can act as chain transfer agents and are potential sites for the generation of inter penetrating polymer network.

In the upcoming years, one of the challenges around the topic of renewable monomers will be the economically-viable and environmentally-friendly modification of these biosourced building blocks into usable reactants [22]. Recent progress in the epoxidation of vegetable oils and in the enzymatic degradation of starch and wood pulp to produce various monomers open the way in the field of biomass valorisation. Nonetheless, these processes should themselves be energy-efficient and limit the production of waste and volatile organic compounds. Some species of plants have been brought to light as they are able to produce epoxidized triglycerides in high yields, such as *Vernonia galamensis* and *Euphorbia lagascae* [251].

Over 60 species in 12 families of plants have been described as botanical sources of natural epoxidized oils in total [318]. Exciting prospects in the field of genetics and plant biology described the successful cloning and expression of the genes responsible for the natural epoxidation of fatty acids in *Vernonia galamensis* in other plants. Common and highly productive crops could be expressly designed for the production of targeted monomers [251,361].

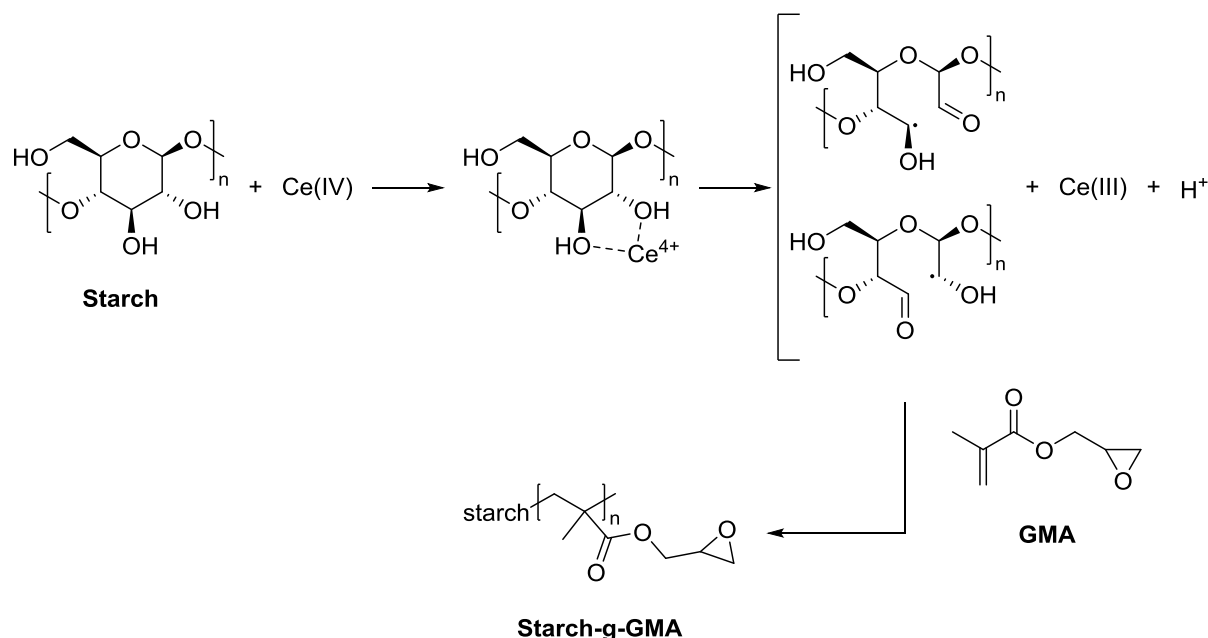


Fig. 67. Reaction mechanism of the starch-g-GMA graft copolymer.

In a nutshell, biobased sustainable monomers are successfully used for the photoinduced CP carried out upon exposure to a broad range of excitation wavelengths and light intensities, delivered by both polychromatic and monochromatic irradiation devices, and sun. They constitute adequate and promising candidates for the partial substitution for petroleum-based monomers, if not to replace them completely. Yet, they need to be designed according to the final applications and targeted material properties [186].

4.3.5. Biodegradability, Mechanical Properties, Chemical and Thermal Resistance of the Photoinduced biosourced Materials vs Toxicity

Released unpolymerized monomers and non-covalently bound molecules from materials are responsible for the decrease of material biocompatibility. These substances diffuse throughout the final material and by contact can elute into the organism, thereby causing adverse effects. Several investigations focused their attention on the cytotoxicity, mutagenicity, estrogenicity or allergic reactions of material components, essentially (meth)acrylate derived monomers or free radical type I photoinitiators. However, scarce literature is available on the toxicity of epoxy-based monomers and PISs for CP.

4.3.5.1. *Biodegradability, mechanical properties, chemical and thermal resistance of biobased materials obtained via CP*

Epoxidized vegetal oils (EVOs) often lead to thermosets featuring low thermal and mechanical properties because of their aliphatic structure [317]. Coatings prepared from epoxidized triglycerides are reported to range from colourless to pale yellow and are transparent and flexible with good general adhesion to steel, aluminium and glass. Both early and recent studies identified that their thermomechanical performances linearly increased with the epoxy content of the vegetal oil starting monomers [318,319,329]. The higher the epoxy percentage, the harder the polymer, the lower the impact strength. Mechanical experiments also demonstrated that the tensile storage modulus (E') as well as the shear storage modulus (G') gradually increased with increasing epoxy content [329,330]. Additionally, polymer films synthesized using epoxidized triglycerides exhibit good thermal stabilities since cured coatings are reported to be stable up to 370 °C, reaching between 10 and 50% of weight loss at this point, before they are thermally degraded in the 420-470 °C range [262,318,325]. The glass transition temperatures of films made out of EVOs usually range from -34 to 36 °C and depend on epoxy content, as they shift towards higher temperatures when increasing the epoxy index of the EVO raw materials [322,325,329,330,356,359]. Nanoindentation and scratch tests performed on coatings synthesized using ESO evidenced a quasi-viscoelastic behaviour, meaning that the polymer film is in a rubber-like state at room temperature [262]. Overall, coatings obtained by CP using EVOs can be tuned from hard and brittle to soft and resilient by carefully selecting the starting raw materials. All the data suggest that the main factors driving the thermomechanical properties of a considered EVO-based coating are the epoxy content of EVOs as well as the possible presence of additional functionalities, such as hydroxyl groups for ECO [329,330]. Biodegradation experiments showed evidence of bacterial and hydrolytic degradation of EVO-derived films after being buried in soil for 6 months [318].

On the other hand, EVOs can also be used as copolymers in combination with petroleum-based epoxy monomers, biobased fibres or in blends with inorganic diluents for the synthesis of polymer networks with enhanced mechanical properties [317]. Indeed, the glass transition temperature, thermal stability, pencil hardness, tensile strength, crosslink density, tensile as well as shear storage and loss moduli of a given composite increase as the weight fraction of highly flexible, aliphatic EVOs in blends with relatively rigid resins decreases [245,321–324,326,328,335–337,340,359]. Alternatively, the incorporation of epoxidized vegetal oils in rigid resins allows for the transformation from a plastic polymer exhibiting a great stiffness to a rubbery material. EVO-based composites are able to undergo considerable elongation before breaking as compared to relatively rigid petroleum-based resins which usually exhibit a greater hardness. All these characteristics can be tuned depending on EVO content and on their use in blends with other additives, such as tackifiers for the design of pressure-sensitive adhesives [325] or with sol-gel precursors such as tetraethylorthosilicate (TEOS) for the synthesis of hybrid coatings [336,337]. Glass transition temperature values have notably been reported to increase from the aforementioned [-34; 36] °C range to 89.2 °C for films made out of epoxidized norbornyl-functionalized linseed oil alone, and to 92.1 °C for organic-inorganic hybrid coatings made out of ENLO mixed with 20 wt% of TEOS. As EVOs consist mainly of hydrophobic fatty acid methyl esters, their incorporation with other epoxy monomers also enables the improvement of chemical resistance of the final coating, especially towards water, indicating waterproof and hydrophobic characteristics [314,321,322,335]. It is important to mention that the mechanical and thermal properties of a composite are likely to change over time due to the dark cure effect. One way to overcome this undesirable effect is to accelerate the post-cure period by an additional thermal curing step [245]. This process is usually called “dual curing” in the literature.

In parallel, coatings obtained after the photo-copolymerization of natural rubber tend to feature high stiffness and flexibility at the same time [246,341]. They are elastomeric materials that are able to sustain chocks, scratches, impacts and abrasion. The dark cure effect tends to particularly impact crosslinked networks of epoxidized natural rubber since the coatings hardness continues to increase in the 24 hours following the photoinduced crosslinking [341]. Some copolymer blends of natural rubber, such as a natural rubber/EPOX copolymer, even reach hardness values as high as these of purely petroleum-derived crosslinked polymers while remaining highly flexible and resistant to impact [342].

The use of epoxidized cardanol derivatives in blends with petroleum-derived epoxy resins enable the obtention of coatings featuring higher toughness [317]. However, as for EVOs, ECD-based polymers are rubbery, transparent and highly flexible, though autoxidation at side chains enhance hardness over time. In fact, gel content, colour indices, T_g and dynamic viscoelasticity data all suggest that the curing reaction still proceeds even after 3 months due to the autoxidative behaviour of unreacted side chains, resulting in an increasing hardness and glass transition temperature [346]. Simultaneously, ECD act as “humidity blockers”, as their use helps overcoming the negative effect excess humidity can have on the CP [343]. Incorporating ECD within an epoxy resin actually allows for a high increase of the film hydrophobicity without sacrificing its flexibility nor significantly changing other properties such as hardness, solvent and impact resistance [343,347]. These results are attributed to the combination between the long and flexible hydrocarbon chains and the more rigid aromatic structure of ECD. The ECD-based photoinduced polymers exhibit glass transition temperatures ranging from -7 to 53 °C, which is a slightly bigger temperature interval than for EVOs [346–348]. It appears that T_g values also increase along with the epoxy content in the photocurable cardanol resin or by taking advantage of a potentially polyaromatic starting structure [348]. Overall, the thermo-mechanical properties of the final coatings can be tuned by thoroughly selecting the epoxy content or the chemical structure of the starting photocurable cardanol resin, or by copolymerization with other polyfunctional epoxide resins.

Regarding terpenoid-based monomers, the photoinduced polymerization of LDO and γ -terpinene dioxide usually results in highly crosslinked polymers while the photopolymerization of isoascaridole gives rise to unreactive epoxy ketones via side reactions [319]. Other terpene-derived monomers, such as α -pinene oxide and limonene-1,2-dioxide, also undergo side reactions, resulting in a large number of nonpolymeric products, thus inhibiting their use for the production of homopolymers [349]. On the other hand, squalene hexaepoxide has been reported to give a rigid and glassy polymer [319]. A glass transition temperature of 12 °C has been described for a monofunctional terpene-based polymer, whereas T_g values around 61-66 °C have been found for polyethers obtained from trifunctional nopol-derived monomers (see chemical structures of N1, N2 and N3 in Fig. 63) [351]. These moderate T_g values are attributed to the early vitrification of the polymeric network, potentially due to the voluminous nopol moieties producing free volume in the crosslinked structures, resulting in average conversions of the epoxy groups. Degradation temperatures ranged between 214 °C and 302 °C, depending on the crosslink density of the network. Although studies conducted on the cationic photopolymerization of biobased terpene epoxides highlighted the high reactivity of such monomers due to their highly strained epoxy groups, none of them actually dealt with the investigation of their mechanical properties, thermomechanical and chemical resistance yet.

Epoxidized phenolic lignin-derived compounds tend to exhibit visco-elastoplastic behaviour once polymerized. Polymer networks obtained via CP of epoxidized gallic acid exhibited an elastic modulus of 5.45 +/- 0.77 GPa [231]. Scratch resistance tests confirmed high adherence on stainless

steel as well as good resistance to fracture. Simultaneously, it has been reported that the incorporation of eugenol within polymeric matrices composed of epoxides of limonene improved the hydrophobicity of the tack-free films [230]. However, when combined with RGDE in a co-network, the increase of eugenol derivative proportion leads to a decrease of the water contact angle, evidencing an improvement of the hydrophilicity [353]. The introduction of eugenol in the formulation also induced an increase of the strain and tensile stress as well as a decrease in storage modulus, thereby evidencing a better network flexibility and lower mixture functionality [353]. The monofunctional and liquid nature of epoxidized eugenol allows for a larger and more homogeneous formation of crosslinks in the polymeric network, thus enabling tuneable mechanical and thermal properties. Eugenol blending also resulted in a 63 °C decrease of the glass transition temperature between a structure made entirely out of RGDE and a 50-50 blend of RGDE with epoxidized eugenol, which is attributed to the reduced crosslink density [353]. RGDE on the other hand has been especially investigated in CP studies for the replacement of DGEBA in epoxy resins [354,355]. Materials derived from RGDE exhibited higher mechanical and thermal performances than commercial DGEBA, with evaluated flexural modulus and strength of 4.5 GPa and 105 MPa respectively, while being both amine-type hardener and solvent free [354]. However, the incorporation of diatomite in a RGDE-derived resin led to a 50 °C drop in terms of glass transition temperatures, to an enhancement of its flexural modulus as well as to lessened mechanical properties [355]. Overall, RGDE-based structures featured T_g included in the 99-153 °C range [353–355] while coatings obtained by CP of DGEVA and PHTe featured T_g of 86 and 75 °C respectively [356]. The increase in glass transition temperature values between EVO-derived coatings and phenolic compound-based films in general is attributed to the higher rigidity of aromatic structures in the polymeric backbone, although the possible presence of hydroxyl groups in the starting monomers can result in better epoxy conversions as well as a polymer network flexibilization [356]. In terms of thermal stability, gallic acid, eugenol and RGDE-derived coatings have been reported to stable up to 300 °C [231,353–355].

Vinyl ether derivatives of isosorbide are readily photopolymerized into colourless and transparent films [319]. Coatings obtained via CP of glycidyl ether derivatives of isosorbide have been reported to be thermally stable up to 300 °C with a T_g at 125 °C, although the integration of PHA-diepoxy in the network lowered the thermal stability to 210 °C and the glass transition temperature to 81 °C [357]. The incorporation of oligomers of PHA in the isosorbide epoxy network hence improved its flexibility as well as enabled its hydrolytic degradation. Antibacterial and tack-free coatings obtained via CP of triglycidyl ether derivatives of glycerol are also thermally stable up to 300 °C, with a 50% weight loss at 375 °C [267]. The final polymer exhibits a viscoelastic behaviour at room temperature with an elastic modulus and a hardness of 189 +/- 18 MPa and 12 +/- 1 MPa respectively [267]. Overall, results showed a good adhesion to stainless steel along with a good resistance during the scratch tests. For adhesive applications, the tensile-shear strengths of polycarbonate joints bonded by biobased furanic compounds, namely FmE, FdE and bFdE, have been investigated [358]. Although furan diepoxide and bis-furan diepoxide exhibited lower tensile-shear strengths because of their more rigid structures and hydrophobicity, biobased furan monoepoxide appeared to give better results as an adhesive than petroleum-based phenyl glycidyl ether. Furanic compounds also appear to be adequate candidates for the replacement of petrol-derived monomers, such as DGEBA, since their blending in 1:1 epoxy molar ratio systems with EVOs generated coatings via photo-curing exhibiting similar thermal properties [359]. The evaluated T_g values were indeed only around 10 °C lower for furanic and EVO-based coatings compared to their DGEBA analogues, which is probably due to DGEBA possessing two aromatic rings instead of one. DMTA analyses demonstrated performances of EVO/furanic composites to be similar to common commercial plastics

such as PET [359]. Last but not least, replacement of cycloaliphatic diepoxide by starch-g-GMA resulted in a decrease in pendulum hardness from 142 to 112, which is due to the improved flexibility brought by starch-g-GMA [360]. As previously mentioned, the latter acts as chain transfer agent during the cationic photocuring process, getting thus grafted into the polymer network while enabling the formation of interpenetrating networks, thereby functioning as internal plasticizer. Additionally, its core-shell structure contributes to better water resistance performances.

Even though biobased monomers appear to be increasingly studied for the replacement of synthetic and petroleum-based building blocks in the obtention of cationically photo-crosslinked polymer networks, their mechanical properties as well as thermal and chemical resistance have only been scarcely investigated so far. Promising prospects in terms of biodegradability, thermomechanical performances as well as chemical resistance should be available on this matter in the years to come.

4.3.5.2. *Short overview on the toxicity of free radical-photoinduced resin-based composites*

Most of the investigations related to toxicity of (meth)acrylate derived monomers and free-radical photoinitiating systems dealt with dental applications. Increasing numbers of monomers in dental restorations have been designed over the past twenty years. In the meantime, the toxicity issue and the adverse effect of the leachable unbonded chemical compounds caused by dental resin degradation or erosion over time gained increasing interest. Some individual molecules (monomers, additives or photoinitiators) of resin-based materials have been tested for cytotoxicity, genotoxicity/mutagenicity and carcinogenicity in various cell culture systems. However, it seems difficult to compare toxicity data due to a non-standardization of the biological experiments. For instance, Ratanasathien et al. investigated the synergistic effects of four acrylate monomers (Bisphenol A-glycidyl dimethacrylate (Bis-GMA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxy-ethyl-methacrylate (HEMA)) and their cytotoxicities to Balb/c3T3 mouse fibroblasts by MTT assays [362]. The toxicity of the acrylate monomers in terms of TC_{50} values increase with exposure time as follows: Bis-GMA > UDMA > TEGDMA >>> HEMA (least toxic). The high cytotoxicity of Bis-GMA, UDMA, and TEGDMA was corroborated by other studies [363,364]. Particularly, Manojlovic et al. used MTT assays on foetal lung MRC-5 fibroblasts to evaluate cytotoxicity of Bis-GMA, UDMA and TEGDMA [364]. They concluded that the liposolubility of acrylate monomers is the main parameter affecting their cytotoxicity, thus causing effective cell penetration. Urcan et al. have confirmed these results and reported acrylate cytotoxicity as follows: Bis-GMA > UDMA > TEGDMA. They used the sensitive γ -H2AX DNA repair focus assay to demonstrate a greater genotoxic effect of UDMA compared with TEGDMA in human gingival fibroblasts [365]. TEGDMA was proved to induce lipid peroxidation of dental pulp microsomes in rabbits and caused the lipid bilayer solubilization of cell membranes [366]. Similar results were demonstrated by Rakich et al. [367]. Furthermore, the lipid peroxidation intermediates may lead to DNA damages according to COMET assays [364] and TEGDMA revealed a high level of genotoxicity on human salivary gland tissues, peripheral lymphocytes [368] and on human oral keratinocytes [369]. Geurtsen et al. also demonstrated a complete inhibition of 3T3 fibroblast cell growth with the release of high concentrations of TEGDMA [370]. This was later proved to promote proliferation of *S. sobrinus* and *L. acidophilus* and can significantly induce growth of cariogenic pathogens [371,372]. Recently, it was reported that TEGDMA is implied in DNA sequence deletions in the hprt gene of V79 cells. Such deletion reactions are common for acrylates and methacrylates according to Schweickl and Schmalz [373]. Heil et al. also revealed the genotoxic effect of Bis-GMA and UDMA [374].

Furthermore, it has been reported that methyl methacrylate (MMA) may be teratogenic and responsible for damaging cardiovascular effects in animals [375,376]. Subcutaneous poly(methyl methacrylate) implants may lead to malignant tumours in some animals [377]. In addition, mutual cross-sensitivity to methacrylates was observed. For instance, HEMA, EGDMA, MMA, Bis-GMA and TEGDMA are frequently cited as allergenic components [378]. In light of these observations, some dental technicians have developed allergic contact dermatitis to HEMA due to the handling of dentin composites and some of them had to stop the practice of their profession [379–381].

The increasing use of photoinitiating systems in medical applications means that researchers are paying greater attention to the evaluation of photoinitiators toxicity. However, to date, few data about the cytotoxicity of photoinitiators and photosensitizers are available. Williams et al. have studied the toxicity of three Norrish type I PIs, namely 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959, I2959), 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, HPK), and 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, I651) against six different types of mammalian cell species with WST-1 assay [382]. The results show that I2959 is well tolerated over the studied cell lines despite the observed differences of sensitivity among the cell lines. This difference is explained by the capability of cells to express antioxidant enzymes protecting themselves from oxidative damage. Among the three cited photoinitiators, the most hydrophobic one (I651) led to the most toxic effects. Indeed, the authors suggested that the permeability through cellular membranes increased with the hydrophobicity of the PI. These results are in accordance with the investigation of Bryant et al. which demonstrated a particularly good acceptance of I2959 by NIH/3T3 fibroblast cell line [383]. The toxicity of bisacylphosphine (BAPO) was also investigated and some authors indicated obvious cytotoxic and genotoxic issues [384–386]. Even if 0.5 wt% and 1 wt% are the maximum concentrations of BAPO tolerated by osteoblast-like cells and MC3T3 pre-osteoblasts respectively, its tolerance level is much lower for other cell lines. Popal et al. highlighted a significant cytotoxic effect of BAPO but also of 2,4,6,-trimethylbenzoyldiphenyl phosphine oxide (TPO, a phosphine oxide derivative) on human oral keratinocytes (OKF6/Tert2) and Chinese hamster lung fibroblasts (V79) at low micromolar concentrations [387]. However, the toxicity of BAPO is more pronounced than TPO on OKF6/Tert2 and V79 at 25 μ M and 10 μ M respectively. The same results were evidenced by Van Landuyt with TPO on human pulp-derived cells (tHPCs) [388]. Popal et al. explained that the non-polar structures of BAPO and TPO may increase their diffusion across cell membranes, and thereby enhance their interaction with amino acids groups of proteins as previously described for other diphenyl phosphine oxides [387]. Phosphine oxide groups may be also reduced by electron transfer reaction to form anion radical which could interact in cellular redox state. Moreover, the micronuclei (MN) assay, which detects irreversible chromosomal transformations in cell lines, has revealed that BAPO induced some genomic damages in V79 cells on the contrary to TPO. These results seem to be in contradiction with those of Nikolic et al. [364]. Indeed, they demonstrated that 0.04 ng/mL is the lowest TPO concentration leading to genotoxicity effects on foetal lung MRC-5 fibroblasts.

Interestingly, even the most frequently used photosensitizer in visible-light curable dental materials, namely camphorquinone (CQ), showed cytotoxic effects in various primary cells [389–391]. However, the cytotoxic results from Manojlovic and Van Landuyt showed that TPO was respectively 7 times and 10 times more toxic on human cell line of foetal lung fibroblasts MRC-5 than CQ [364,388]. Furthermore, CQ is responsible for mutagenicity in bacterial umu test as well as genotoxicity in the Comet assay performed on human oral and intestinal cell lines [374,392]. It was shown that CQ induced the generation of intracellular reactive oxygen and nitrogen species (ROS/RNS), causing damage of DNA in cultured primary human gingival fibroblasts [393], apoptosis and/or necrosis [394,395]. Based on Comet assays, CQ is responsible for oxidative stress leading to

genotoxic effects on MRC-5 fibroblasts at the lowest concentration of 75 $\mu\text{g}\cdot\text{mL}^{-1}$ [364]. Additional studies also described the toxicity of CQ/amines photoinitiating systems [393,396], which remain less cytotoxic than TPO ones [388].

As a conclusion, the toxicity of photoinduced materials is reduced by increasing the degree of polymerization of resins or minimising the leaching of PIs by grafting them to dendritic or hyperbranched polymers [397]. Some authors also attempted to add photopolymerisable functions to the chemical structures of PIs to covalently graft them into the polymer network during the irradiation process [235,259,275,282]. As an alternative, some PIs are replaced by riboflavin, a water-soluble vitamin [277] or chlorophyll derivative PIs. Finally, acrylates could be replaced by less toxic methacrylates or thiol-ene systems [398]. However, CP seems to be actually an interesting alternative to radical light curing [24]. Nonetheless, this needs to be put into perspective. The following section describes the main advantages and drawbacks of using epoxy-based resins and cationic photoinitiating systems with respect to materials toxicity.

4.3.5.3. *Overview on the toxicity of cationic PISs (monomers, onium salts, type II PSs)*

To date, few studies described the cytotoxicity of epoxy-based resins. The first crucial point about the epoxy-based resins concerns their synthesis. Indeed, double bond oxidation remains a burning issue for the development of new epoxy resins. The main epoxidation reaction of the alkene double bond actually uses oxone or m-CPBA, which are either expensive or toxic (as described in the first part of this review). Therefore, some greener oxidants such as hydrogen peroxide should be deeply envisaged. As an alternative, bio-based epichlorohydrin may be the solution but still remains toxic.

The second point deals with the suitable formulation of epoxy-based resins to overcome their cytotoxicity. Indeed, some epoxy monomers (i.e. 4-vinyl cyclohexane dioxide, EPOX and DGEBA) have revealed severe cytotoxic effects according to MTT assays on mouse connective tissue (L929 cell line) [399]. Among expanding monomers that have been designed, spiroorthocarbonates (SOCs) appear as the most promising candidates for improving biocompatibility of epoxy-based materials [400]. Yourtee designed a series of SOC comonomers and demonstrated their potential for the development of biocompatible non-shrinking composites [399,401,402]. Based on Yourtee's results, the SOC monomers did not show neither mutagenic nor cytotoxic issues respectively in the *Salmonella* microsome assay for strains TA100 and TA98, and in the MTT assay using the fibroblast cell line L-929 [401]. Besides, the incorporation of selected SOC into epoxy-based resins significantly reduced the cytotoxicity of the final photocured epoxy-based materials [399]. The authors suggested that SOC participated to the cationic photopolymerization, resulting in an increase of the polymerization degree, thus decreasing the toxic leachables.

The third point concerns the cationic photoinitiating systems based on onium salts. Hypervalent iodonium salts derivatives, besides the versatility and diversity in their chemical behaviour, demonstrated biocidal properties against a wide spectrum of microorganisms (bacteria, fungi, and yeast) but also showed remarkable cytotoxicity in vitro. According to the investigation of Menkissoglu-Spiroudi et al., some iodonium salts revealed to have antibacterial activities against ice nucleation active (INA) *Pseudomonas syringae* by decreasing their growth rates [403]. Their potency is similar to that of either known bactericides or some promising biocide agents (essential oils and derivatives). Their results are in accordance with Goldstein et al. against dental and periodontal bacterial pathogens [404]. Interestingly, a series of iodonium salt derivatives have also demonstrated

NADPH oxidases and ROS inhibition activity, preventing the progression of inflammation-associated disorders [405,406]. However, despite their promising use in biological applications, Shibata et al. recently highlighted the cytotoxicity of several fluorinated diaryliodonium salts on human lymphoma cell line (U937) [407]. These results should be in accordance with the high oxidation potential of iodonium salts. For instance, the toxic concentration (TC_{50}) of a iodonium salt derivative ((4-octylphenyl)phenyliodonium hexafluoroantimonate) reached for killing 50% of L929 cells was evaluated at $1\mu\text{g/mL}$ which is extremely high [399].

As a conclusion, investigations on the cytotoxicity and genotoxicity activities of resin-based materials mainly include commonly used (meth)acrylate monomers and free-radical photoinitiators separately. However, to date, the toxicity studies of epoxy-based materials are scarce despite the growing interest of scientists for cationic photopolymerization. Additional biological studies are needed, not only on monomers/photoinitiators used alone, but also on their combination. Indeed, the combination of several toxic compounds may cause various other unexpected toxic effects compared to their sole actions. This is particularly important to highlight synergistic toxic effects of mixed photopolymerizable and photoinitiating components, which could potentially produce higher toxic effects than those observed for compounds alone. Therefore, toxic synergistic effects should be evaluated by varying the range of the concentration of the mixture components. Last but not least, the cytotoxicity and genotoxicity assays should be normalized to allow relevant comparisons between the toxicity of the photoinduced materials further described in literature. Some alternative solutions to the use of free-radical and cationic photoinitiators exist and will be partially described in the following section.

4.3.6. Photoreactive Bio-based compounds for Cyclo-addition Reactions: an Alternative

Photoreactions are widely applied in tissue engineering, regenerative medicine, and drug delivery systems. In particular, bio-based hydrogels using natural polymers, such as proteins and polysaccharides, are highly useful because of their high cytocompatibility and biocompatibility. Due to the simplicity of the process, biopolymer-based hydrogels are often prepared by free-radical polymerization of acrylates and/or acrylamides under light irradiation.

However, there are several challenges to their use in biomedical applications, such as the cytotoxic effects of residual monomers and photoinitiators due to the relatively low degree of polymerization. Therefore, other photo-crosslinking methods, such as photocycloaddition and photooxidation, are used to improve the safety and functionality of biopolymer-based hydrogels. Photoresponsive functional groups can be introduced into the structure of natural polymers by a one- or two-step reaction and straightforward purification process (Fig. 68 and Fig. 69). In particular, the amino, carboxyl, and hydroxymethyl groups of the natural polymers are widely used to introduce photoresponsive groups i.e., furan, coumarin and cinnamate groups.

Fig. 69. Introduction of photo-responsive units on natural polymers.

4.3.6.1. From furan derivatives

In the past ten years, visible light-photoactive natural polymers have been designed [408–410]. Particularly, natural polymers conjugated with furan appear as a new class of photo-crosslinked polymers [411]. The furan derived polymers can be crosslinked using a photooxidation reaction implying the furan moiety in the presence of photosensitizers, such as rose bengal or riboflavin [412,413]. For instance, photosensitizers produce singlet oxygen upon visible light irradiation, leading to endoperoxide bonds on the furan ring through a photooxidation process as described (Fig. 70).

An interesting review from Caillol et al. [414] described the different synthetic methods to prepare furanic building blocks by various coupling methods based on reductive and carbonyl-aromatic reactions from furfural and 5-hydroxymethylfurfural obtained by the biorefining of fructose, cellulose or sucrose [411]. Owing to the high reactivity of furan derivatives, the synthesis of high-added value polymers is expected.

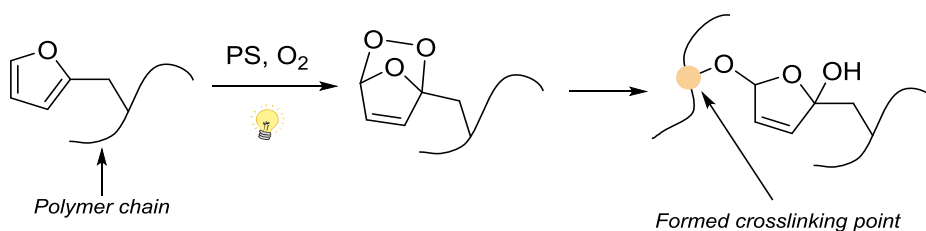


Fig. 70. Photo-crosslinking of furan-based polymers using a PS.

Some examples of bio-based polymers such as DNA [415], gelatin [416], chitosan [417,418], alginate [419,420], and hyaluronic acid [421] have been previously described and are mainly used for tissue engineering applications [422], wound healing dressings [418,419,423], bio-sealant [412], anti-adhesion material [416,420], regenerative medicine [424,425] and as cell laden hydrogel for 3D bioprinting [422,426].

4.3.6.2. From coumarin derivatives

Coumarins are naturally present in many plants and commonly consumed fruits, and proved to have health benefits as they exhibit antioxidant, anti-inflammatory and antimutagenic properties [427]. They are produced *via* ortho-hydroxylation, trans-cis isomerization of the side-chain double bond and lactonization of cinnamic acids [428]. Interestingly, some studies highlighted their role in the synthesis of polymers under light activation. Indeed, the photoinduced dimerization of coumarins has been known for 40 years. Upon UV-light irradiation, coumarins undergo a $[2\pi + 2\pi]$ cycloaddition reaction to form a cyclobutane ring [242]. The structure of the dimers are *anti* head-to-head, *anti* head-to-tail, *syn* head-to-head, and *syn* head to-tail types. Additionally, the photocycloaddition reaction of coumarin unit is reversible by irradiation with wavelengths shorter than 300 nm (Fig. 71) [242,429–433]. The addition of coumarin group on polymer side chains leads under light activation to

insoluble polymer networks. Delzenne and Laridon attached coumarin groups on poly(hydroxyl ethers) and poly(vinyl butyral) backbones and investigated their reversible photoreaction properties in 1,4-dioxane under 254 and 350 nm (or 300 nm) light exposure [434,435].

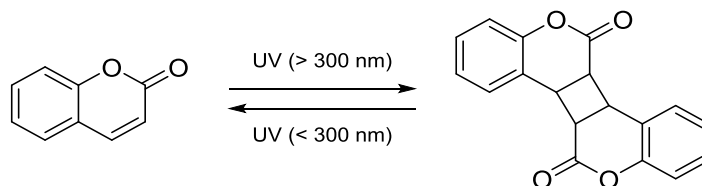


Fig. 71. Photo-reversible cycloaddition of coumarin.

Chujo et al. demonstrated the possibility to control the reversible gelation reaction of photodimerization of coumarin-based polyoxazolines by means of UV irradiation [436]. Other reversible and photocrosslinking of coumarin derived polymers based on acrylates and acrylamides have been also reported [437,438]. In 2007, Kiskan and Yagci were the first to insert coumarin units into benzoxazine structures which exhibited a high increase of glass transition temperature after photodimerization [439]. Since then, a multitude of studies have described the synthesis of photocrosslinkable coumarin-derived polybenzoxazines [440–444]. The advantage of this photocrosslinking system is initiator-free so that the formation of photoreaction by-products is minimized. These systems are mainly applied for biological applications, particularly as drug delivery systems, for the synthesis of hydrogels for migration of vascular endothelial cells [445–447].

4.3.6.3. From cinnamate derivatives

Cinnamic acid is an organic acid extracted from cinnamon bark and commonly used as a food additive thanks to its antibacterial, antifungal and antiparasitical activities [448,449]. They have attractive properties particularly in macromolecular synthesis due to the presence, in the main or side polymer chains, of the photoresponsive cinnamoyl group. Similar to coumarins, cinnamic derivatives undergo $[2\pi + 2\pi]$ photo-dimerization upon UV light irradiation (> 260 nm) to yield a cyclobutane ring structure [450]. The cross-linked cinnamoyl group is reversible and can be dissociated by UV treatment at $\lambda < 260$ nm (Fig. 72). These photocrosslinkable cinnamoyl-conjugated bio-based polymers are widely prepared by condensing the carboxylic acid of cinnamic acid with hydroxyl or amino groups of bio-based building blocks [451]. Cinnamoyl moieties were therefore associated with biodegradable polyesters such as poly(lactic acid) and poly(ϵ -caprolactone) [452], gelatin [453–455], hyaluronic acid [456–458], alginate [459,460] and hydroxypropyl cellulose [460], but also benzoxazines, lithocholic acid [461], oil-based ricinoleic acid [462], acrylate monomers [463] and butyl rubber derivatives [464].

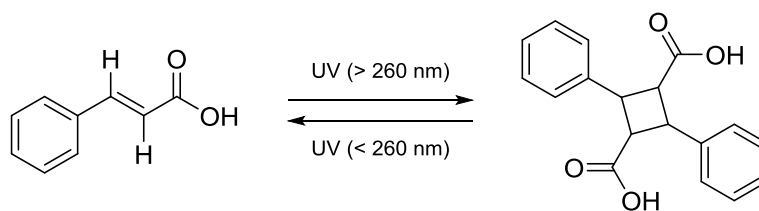


Fig. 72. Photo-reversible cycloaddition of cinnamic acid.

Polymers containing cinnamoyl moieties have been used in a wide range of applications to produce photo-crosslinked polymer materials [465–470], photo-crosslinked hydrogels [471–473], materials for photoinduced alignment of liquid crystals [474–478], in advanced microelectronics [479], in photolithography [480], in non-linear-optical materials [481], and for the synthesis of photocurable coatings [482]. To date, some reports have also described the efficiency of cinnamoyl derived photo-crosslinked materials to promote cell proliferation [456,464,483–485] despite the low toxicity of cinnamoyl groups [486,487].

5. Expanding the Scope of Applications

In this finale section is reported the wide variety of applications associated with the cationic photopolymerization of biosourced monomers.

Photoinduced materials have attracted exponential attention over the years because of the multiple advantages brought by photopolymerization reactions. They indeed allow to avoid costly and environmentally harmful solvents, they can be carried out at room temperature and high conversion rates are achieved in a short irradiation time [488]. These reactions enable the synthesis of materials for a large variety of applications such as coatings, composites, adhesives or inks [25]. Photochemistry is also used in other interesting fields such as microelectronics [489–494] or the automotive and aerospace industry [495–497].

However, most areas of application to date are based on FRP. Additionally, the use of bio-based building blocks is not yet widely developed in these fields. As a consequence, the combination of CP with renewable PISs is still scarce and the applications are not yet very diverse. So far, the properties achieved by biosourced cationically photoinduced materials can only fulfil requirements in the fields of coatings, films and adhesives [317]. The application expansion of biobased cationically photopolymerizable monomers to possible new fields represents nowadays a considerable challenge with promising prospects.

In the following sections, examples of applications in the medical field, in durable construction, in the recycling of natural resources, in the synthesis of coatings and films and in adhesives will be provided.

5.1. Medical applications

Hospital-acquired infections are infections that patients contract within 48 hours or more in hospitals or care centres. According to the World Health Organisation, out of every hundred hospitalized patients, seven in developed and ten in developing countries will acquire at least one health care-associated infection at any given time [498]. Due to the appearance of multidrug-resistant microorganisms, these infections can be fatal [353]. The bacterial strains most responsible for nosocomial infections are *E. coli*, *S. aureus*, *Enterococci*, and *Pseudomonas aeruginosa* [499,500]. These bacteria became increasingly resistant to methicillin over the years [501]. In this respect, partially or fully bio-based antibacterial materials have been recently successfully synthesized via CP for biomedical purposes.

Modjinou et al. worked on the synthesis of a crosslinked co-network of resorcinol diglycidyl ether and an epoxidized eugenol derivative by cationic polymerization under ultra-violet irradiation [353]. As previously stated, eugenol is a natural, aromatic, phenolic molecule found mostly in cloves. The phenolic groups confer natural bactericidal properties to eugenol as they lead to the permeability of the bacteria membrane and ultimately to cell lysis [502]. The epoxidation of eugenol allows for its incorporation within the polymeric matrix, thereby avoiding eugenol diffusion and ensuring long-term antioxidant as well as antibacterial properties. The efficiency of this material has been demonstrated for two types of bacterial strains: *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria). A reduction of more than 90% of the bacteria population has been observed, regardless of the bacteria strain. Lately, the same research group further investigated eugenol for its interesting antibacterial properties as they synthesized all-green limonene-derived polymer networks incorporated with eugenol using β -carotene as a photosensitizer [230]. They obtained tack-free coatings with effective antibacterial properties against both Gram-negative and Gram-positive bacteria strains (Fig. 73). Limonene and eugenol-derived polymer films showed low toxicity as well as promising features for their use in biomedical applications.

Upon irradiation, natural dyes are able to generate cytotoxic singlet oxygen, among other reactive oxygen species [503,504]. They are therefore particularly interesting in the field of photoinduced polymerization since they enable the synthesis of antibacterial coatings with promising applications in photodynamic therapy. Taking advantage of this attractive feature, some studies recently demonstrated the antibacterial properties of bio-based coatings derived from quercetin [267], curcumin [262], β -carotene [230], paprika [231], purpurin [235] and quinizarin [259]. These newly-developed coatings have a great potential to avoid bacteria proliferation on one-time usable disposable medical devices.

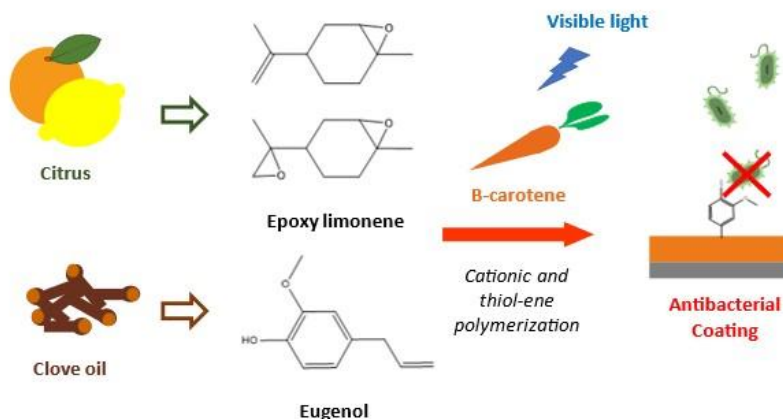


Fig. 73. Synthesis of bio-based antibacterial coatings using β -carotene, eugenol and epoxidized limonene. Reprinted with permission from Breloy et al. [230]. Copyright 2019 American Chemical Society.

In their work on quercetin, Condat et al. combined the naturally-occurring flavonoid with glycerol triglyceride ether in the design of bio-based antibacterial coatings [267]. Antibacterial assays showed a greater antibacterial efficacy against *S. aureus* than *E. coli*, with a 99% decrease of the *S. aureus* population under irradiation after 2 and 6 hours of incubation. In a similar approach, the same authors developed a bio-sourced antibacterial film composed of curcumin and ESO [262]. Results demonstrated the successful antibacterial action of the polymeric coatings, thus evidencing their potential for biomedical applications.

In their work on paprika, Sautrot-Ba et al. developed an antibacterial material with paprika as a photoinitiator in presence of bio-sourced epoxidized gallic acid [231]. They showed that the coating was 100% effective against *E.coli* and *S. aureus* strains under irradiation after 2 and 6 hours of incubation. The same authors also used an allylic purpurin derivative as photoinitiator for the synthesis of antibacterial materials. This material showed more than 99% of efficiency against bacteria regardless the number of cycling experiments [235]. Likewise, they developed allylic and epoxidized derivatives of quinizarin, which demonstrated photoreactive properties as well for antibacterial applications [259]. Crivello et al. developed crosslinked coatings using curcumin as PI, combined with different monomers, such as limonene-1,2-epoxide, LDO, ELO, 3-ethyl-3-phenoxy-methyloxetane and vernonia galamensis linseed oil. Since the monomers and photosensitizers used in this study are nontoxic and visible light does not damage living tissues, these coatings are particularly interesting for diverse medical applications such as adhesives for catheters, casts, splints, and for dental composite fillings [251].

However, it is currently difficult to use CP processes for some biomedical fields, especially for biocompatible applications. In fact, strong protonic acids generated by cationic photoinitiators during initiation negatively impact cell cultures and tissues [315].

5.2. Coatings and films

The synthesis of coatings is one of the most common applications in the CP field and using renewable resources as building blocks is increasingly recurrent, especially owing to the efficiency of vegetable oils. The review written by Noè et al. [317] lists some studies in this regard, notably the

work of Malburet et al. on the epoxidation of 12 different vegetable oils used as monomers in CP, in order to obtain bio-sourced coatings with high epoxy conversions (90%, regardless of the EVO used) [329]. The coatings had different thermomechanical properties according to the vegetable oil used in the formulation. They demonstrated that the T_g value increased linearly with the raise of epoxy group content in the considered EVOs (from -19 to 50°C). Some other investigations were carried out combining vegetable oils with synthetic compounds. In fact, Thames et al. worked on the combination of castor oil glycidyl ether (between 10 and 40 wt%) with EPOX to obtain smooth films with good water resistance [324]. Wan Rosli et al. combined epoxidized palm oil with EPOX to obtain a gel film with a tendency to increase hardness and gel content values with the raise of epoxy concentration [323]. EPOX was used in an additional study carried out by Han et al. on the copolymerization of a starch copolymer [360]. Using a starch-g-GMA comonomer in the formulation enabled a more flexible film with higher water-resistant performance without influencing hardness and gel content.

Noè et al. worked simultaneously on the synthesis of bio-renewable epoxy building blocks such as PHTe, DGEVA and ECO for coating applications. Using PHTe led to 80% of epoxy conversion due to the presence of alcohol functions (activated monomer mechanism) while the use of DGEVA induced only 60% of conversion because of its aromatic and rigid structure. In addition, ECO enabled to reach 85% of epoxy conversion thanks to its flexible chains [356]. ECO has also been used for the synthesis of a self-cleaning and hydrophobic bio-sourced coating. Indeed, carbon powder was deposited on the coating. After dropping water on the film, they noticed that neither carbon powder nor water stayed on the surface [505]. Additionally, tung oil has recently been used in formulations to synthesize potentially waterproof bio-based coatings [321,322]. The higher the tung oil concentration, the greater the hydrophobic properties. Another oil was used by Sung et al. for the synthesis of green coatings. Dihydroxy soybean oil (DSO) was indeed copolymerized with ESO on one hand, and with EPOX on the other hand. The mechanical properties of these two materials were compared and the effect of the amount of DSO was investigated. Coatings containing DSO copolymerized with EPOX were harder than those copolymerized with ESO. The mechanical properties were related to the amount of DSO, which plays a role as a plasticizer in the different formulations [506].

The CP efficiency of ELO and epoxynorbornane linseed oil was investigated and compared in 2003 by Zong et al. who showed that ELO reacted more quickly than ENLO [334]. Two years later, they deepened their investigation with the combination of ENLO with linseed oil oligomers containing TEOS for the synthesis of sustainable films. Adding TEOS oligomers allowed for the increase of pencil hardness (H to 6H) and crosshatch adhesion (1B to 2B) [335] and enabled the synthesis of more thermally stable films than those only made out of ENLO [336]. On the same principle, Zou et al. worked on the study of organic-inorganic hybrid films containing epoxidized cyclohexene linseed oil and TEOS [337]. Hybrid films demonstrated to have greater hardness, tensile modulus and strength and to be more thermally stable than pure epoxidized cyclohexene linseed oil films. In 2021, two functionalized PIs derived from lawsone (HNQA and HNQE) were synthesized by Elia et al. in order to obtain lawsone-based monomers [275]. They were combined with EPOX to form sustainable coatings under visible irradiation.

5.3. Durable Materials in Construction

Research increasingly focuses on the synthesis of bio-products for construction purposes, such as the work done recently by Nguyen et al. [354,355,507]. They synthesized a porous material with

acoustic absorption properties via the incorporation of sodium chloride (NaCl) particles [507] or diatomite [355] to RDGE. The porosity is then generated by removing the NaCl particles. According to the porosity, the material absorbs different frequencies. The more porous the material, the more it absorbs low frequencies [507]. Besides, RDGE with the incorporated diatomite showed to be an optimal flame-retardant material when the amount of diatomite is the highest (60 wt%) [355].

In 1996, Crivello et al. developed coatings by mixing epoxidized botanical oils with synthetic epoxy resins. Their results indicated that the coatings were flexible and transparent with an interesting adhesion ability on aluminium and glass surfaces. This suggests potential coatings applications for housing, boats, water and sewage systems as well as many other articles of common usage [319]. The same group also synthesized films out of functionalized vegetable oils (ESO, ELO), which mechanical properties are suitable for interesting low-performance applications, such as piping, roofing, culverts and boats construction [245]. More recently, they have also reported the synthesis of biomaterials upon solar irradiation which could be useful for the fabrication of boats, building, roofing panels and conduits for water and sewage [251].

5.4. Adhesives

Adhesives are regularly used in daily life, often in its commercial form such as tapes or in packaging. However, commercial pressure-sensitive adhesives (PSA) are generally synthesized with petrochemical compounds. However, a 97% bio-sourced PSA was recently developed by the UV cationic photocuring of ESO, DSO and rosin ester (Sylvalite). The weight ratio of ESO/DSO/rosin ester was optimized to 1/1/0.7 and this sustainable PSA showed similar tack and peel properties as the commercial PSA tape (Scotch Magic Tape), but with 1.7 times higher peel strength [325]. Simultaneously, novel epoxidized furanic compounds derived from carbohydrates, namely monoepoxidized, diepoxidized furan compounds and a bisphenol A derivative, were synthesized in order to form bio-based adhesive films. According to the tensile-shear strength studies, the mono epoxidized compound showed a better performance as adhesive (4.7 MPa) than the petroleum-based phenyl glycidyl ether (2.6 MPa) [358].

As previously mentioned, ENLO was used to synthesize organic-inorganic hybrid bio-sourced coatings with TEOS oligomers. The pencil hardness, impact resistance, adhesion, chemical resistance and contact angles of the films were investigated and largely depended on the amount of TEOS in the formulations. Experiments showed that the introduction of 10% TEOS was the most optimal for coatings resistance. The research group came to the conclusion that using ENLO in coatings synthesis could be attractive for adhesive applications [335].

On the other hand, Crivello et al. prepared new mono-, di-propenyl and divinyl ethers derived from sustainable resources which seem to be attractive for adhesives purposes due to some of their properties (low viscosity, low molecular weights and high boiling points) [196]. They also studied some epoxidized terpenes as building blocks for CP, such as LDO and γ -TO, which proved to be highly reactive and could be used for adhesives synthesis [319]. LDO was also used in a photo-curable formulation with α -pinene as a comonomer. As α -pinene is a compact monomer undergoing double ring opening photopolymerization, it led to a substantial volume shrinkage, which could be an interesting property for adhesives as well [349].

Finally, an epoxy acrylate rubber was investigated as a building block for CP under sunlight exposure. Due to their high reactivity under visible light irradiation, this rubber presents an interest in different applications including adhesives [246].

5.5. Possible new Applications

Additional applications have been lately reported in the literature exploiting bio-sourced materials by CP processes. According to Crivello et al., their films synthesized with vegetal oils (ESO, ELO) would not only be interesting for construction, but also for electronic applications due to their low water absorption. The materials reached 0.6% of weight increase after immersion in water for 6 days. This value is lower than that of materials commercially made using DGEBA (0.8-1%) [245]. ESO was also used with (R)-12-hydroxystearic acid (HSA) derived from castor oil to form nanocomposites. By replacing ESO by thermoplastic polymers it could be possible to obtain various composites exhibiting easy-to-recycle features. The interest of ESO/HAS nanocomposites was their ability to be fused at low temperature [326]. In the field of biodegradable epoxy networks, Lorenzini et al. worked on the photopolymerization of PHA-diepoxy and isosorbide diglycidyl ether. The resulting coatings incorporated with PHA were more degradable than pure isosorbide epoxy films. Increasing the PHA amount from 0 to 25 wt% led to a rise of hydrolytic degradation with a weight loss increasing from 9.2 to 21.6%. This high degradation property would also enable these coatings to be useful as thermoset films [357].

As previously stated, films synthesized by Crivello et al. with epoxidized vegetal oils and synthetic epoxy resins could be used for housing, boats, water and sewage systems but also for photocurable inks production [319]. Likewise, synthesized mono-, di-propenyl and divinyl ether building blocks would also be interesting for inks applications [196]. In 2005, the effect of substituted benzyl alcohols on the rate of CP in presence of epoxidized oils was studied. Ortiz et al. showed that the use of substituted benzyl alcohols led to the acceleration of the polymerization curing rate via an activated monomer mechanism, which could be attractive for various applications like high speed coatings and printing inks [331]. Other natural oils have been mentioned to be potential suitable candidates for the replacement of synthetic epoxides in the inks field, such as ENLO [335].

By using epoxidized vegetable oils, Malburet et al. developed coatings for 3D-printing owing to their low viscosity, stability and flexibility [329]. Overall, the use of EVOs in photopolymerization studies opens new perspectives in the preparation of bio-coatings and sustainable raw materials for the synthesis of biobased polyurethanes, non-isocyanate polyurethanes and vinyl ester resins. On the other hand, with promising textile production applications, films obtained via hybrid polymerization of ELO with an acrylated epoxidized soybean oil (AESO) have been recently developed on a pilot scale [332].

With industrial purposes in mind, Decker et al. used epoxidized liquid natural rubber (ELNR) combined with DVE or other epoxy resins to form three-dimensional coatings. Their kinetics and mechanical properties were tested for matching as adequately as possible the industrial fields of coatings, adhesives and photoresists production [342].

6. Conclusion

This review aims at underlying the increasing importance of cationic photopolymerization in combination with bio-based photopolymerizable monomers, and describes the numerous reactive species derived from bioresources that can lead to innovative materials through cationic photopolymerization reactions.

In the search for more environmentally friendly technologies and the obtention of greener photoinduced materials by cationic photopolymerization, the focus has been directed toward biosourced, renewable raw materials and natural dyes, and their potential to be used as substitutes for petrochemical-based monomers and synthetic photoinitiators/photosensitizers. The number of investigations in the field of photopolymerization encompassing the development of biomass-derived materials skyrocketed in the last decades since these building blocks can be readily extracted from industrial by-products and waste. The diversity of renewable resources and the different performing strategies developed by chemists allow to screen a large number of backbone structures able to be cationically polymerized under light irradiation. The bio-based macromolecules can be easily modified by functional groups to form cationic photoreactive monomers. Many synthetic routes for the addition of epoxy groups on macromolecules have been reported. On one hand, the epoxidation of unsaturations of vegetal oils, fatty acids, terpenoids and resin acids can be carried out enzymatically in the presence of acetic acid, by oxidation in the presence of hydrogen peroxide or m-CPBA. On the other hand, the hydroxyl groups of tannins and polyphenols, eugenol, cardanol, lignin and derivatives can be substituted by either bio-based ECH in basic medium or allyl bromide followed by an oxidation with enzyme lipases in the presence of hydrogen peroxide or m-CPBA. Such epoxy-biobased macromolecules are now used for a large variety of applications with high-added-value such as coatings for durable products in construction, coatings for automotive, adhesives, microelectronics or medical devices.

Last but not least, the burning issue of the nature of photoinitiators used in epoxy cured materials and their migration remains a key point of further research. The development of non-hazardous photoinitiators and/or photosensitizers usable in cationic photopolymerization is a new opportunity for scientists. As a result, natural products have attracted the spotlight for the design of photoinitiators addressing environmental and safety concerns, since onium salts and metal-based PISs usually involved in photoinduced CP reactions are synthetic compounds which can be rather toxic in some cases and not environmentally friendly. There is hence a growing interest for the use of naturally derived photoinitiating systems. For example, new natural and photopolymerizable dyes have been designed to be covalently grafted on the polymer backbone during the photopolymerization process, thus avoiding their release through the materials. Natural dyes promise indeed the supply of cheap, available, abundant and renewable photoinitiators while being visible light-sensitive and responsive even under low light intensities. Over the years, several natural compounds have been identified as interesting and efficient photosensitizers of onium salts to induce cationic photopolymerization reactions, such as anthraquinones, carotenoids, various derivatives of chlorophyll, curcuminoids, flavonoids, naphthoquinones, riboflavin and lignin derivatives.

Despite these new trends and the growing interest of scientists for cationic photopolymerization, the toxicity studies of epoxy-biobased materials are scarce. Additional biological studies are needed, not only on monomers/photoinitiators used alone but also on their combination. In fact, the combination of several toxic compounds may cause various other unexpected toxic effects compared to their sole actions. This is particularly important to highlight synergistic toxic effects of mixed photopolymerizable and photoinitiating components, which could potentially produce higher toxic effects than those observed for compounds alone. Therefore, toxic

synergistic effects should be evaluated by varying the range of the concentration of the mixture components in photosensitive formulations. Additionally, the cytotoxicity and genotoxicity assays should be normalized to allow relevant comparisons between the toxicities of the photoinduced materials further described in literature. Interestingly, some alternative solutions based on photo-crosslinking methods, such as photocycloaddition and photooxidation from furan, coumarin or cinnamic acid derivatives, already exist and should be further explored. These photo-crosslinking systems are advantageously initiator-free so that the formation of photoreaction by-products is minimized. The photoresponsive system is also reversible but can be dissociated only by UV treatment.

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