UNIVERSITAT ROVIRA I VIRGILI

INTEGRATING PLANT OILS IN BENZOXAZINE CHEMISTRY.

Alev Tuzun

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INTEGRATING PLANT OILS IN BENZOXAZINE CHEMISTRY

PhD thesis

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Department of Analytical Chemistry and Organic Chemistry

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Prof. Joan Carles Ronda Bargalló, and Assoc. Prof. Gerard Lligadas Puig, of the Departement of Analytical Chemistry and Organic Chemistry of Universitat Rovira i Virgili,

We STATE, that the present Doctoral Thesis entitled "Integrating Plant Oils in Benzoxazine Chemistry", presented by Alev Tuzun for the award of the degree of Doctor, has been carried out under our supervision in the Department of Analytical Chemistry and Organic Chemistry of Universitat Rovira i Virgili, and that it fulfills all the requirements to be eligible for the International Doctorate Award.

Tarragona, February 5, 2015

Doctoral Thesis Supervisors

Prof. Joan Carles Ronda Bargalló   Assoc. Prof. Gerard Lligadas Puig

To my family,

Aileme,

"The most important things are the most hardest to say."

Stephen King - Body

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LIST OF ABBREVIATIONS

ADMET	Acyclic diene metathesis polymerization
$BF_3.Et_2O$	Boron trifluoride diethyl etherate
BPA	Bisphenol A
Bz	Benzoxazine
$CDCl_3$	Deuterated chloroform
CNSL	Cashew nut shell liquid
ΔH	Enthalpy
DCM	Dichloromethane
DDM	4,4'-*bis*-diaminodiphenylmethane
DGEBA	Diglycidyl ether of bisphenol A
DMTA	Dynamic mechanical analysis
DMAC	Dimethylacetamide
DMSO	Dimethylsulfoxide
DP	Degree of polymerization
DPA	Diphenolic acid
DSC	Differential scanning calorimetry
E	End group
E'	Storage modulus
Et_2O	Diethylether
FTIR/ATR	Fourier transform infrared spectroscopy/ Attenuated total reflection
G1st	Grubbs 1st generation catalyst
G2nd	Grubbs 2nd generation catalyst
GC-MS	Gas chromatography-mass spectrometry
HMTA	Hexamethylenetetraamine
H-G2nd	Hoveyda-Grubbs 2nd generation catalyst
H_2PtCl_6	Speier Catalyst'
IPA	Isopropyl alcohol
IF	Insoluble fraction
LOI	Limiting oxygen index
MAI	Maleopimaric acid imidophenol
MB	Metathesis benzoxazine dimers
M_n	Number average molecular weight
M_w	Weight average molecular weight
NHC	N-heterocyclic carbene
NMR	Nuclear magnetic resonance spectroscopy
P	Polymer chain
PBz	Polybenzoxazine

PE	Polyethylene
PDI	Polydispesity
PVC	Polyvinylchloride
PS	Polystyrene
Py	Pyridine
R	Char yield
ROP	Ring opening polymerization
S1	1,1,3,3-tetramethyldisiloxane
S2	1,4-phenylene-*bis*-dimethysilane
SB	Hydrosilylation benzoxazine dimers
SEC	Size exclusion chromatography
SF	Soluble fraction
SM	Self metathesis
TEOS	Tetraethoxysilane
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TPD	Terpenediphenol
THF	Tetrahydrofuran
TMS	Tetramethylsilane
UDM	Methyl-10-undecenenoate
η^*	Complex viscosity

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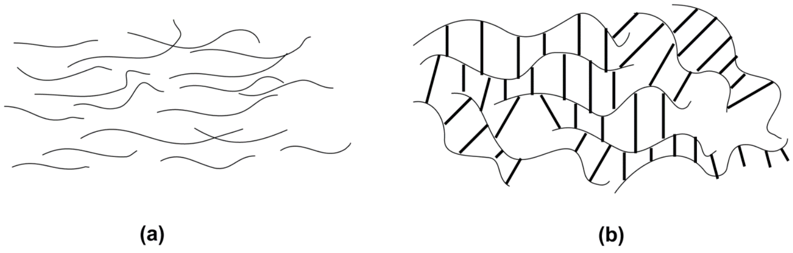
Introduction

1.1 Polybenzoxazines: Background, Preparation and Curing

Since Leo Baekeland[1] synthesized the first synthetic polymer named Bakelite 105 years ago, the development of polymers has increased widely. During the last decades, polymers have been in the focus of scientific and technological world, and is obvious that nowadays they play an important role in modern life.[2] Their advantages as lightweight, low cost, ease of processing, and wide scope of modifications to tailor desired properties have been made them almost irreplaceable materials.[3] Synthetic polymers can be classified into two main categories, based on their response to temperature; thermoplastics and thermosettings (thermosets).

Thermoplastics are two-dimensional macromolecules (Scheme 1.1a). They are constituted by discrete molecules that can be dissolved in appropriate solvents. Moreover, on heating they melt and flow and therefore can be shaped in an appropriate mold after cooling. Usually, the heating and cooling process can be repeated without severe damage, thus, thermoplastics are reprocessable and recyclable materials.[4] Thermoplastics have found a wide variety of applications not only in daily household goods but also in high technology devices. Some examples of commercial available thermoplastics are polyethylene (PE), polyvinylchloride (PVC), and polystyrene (PS).[5]



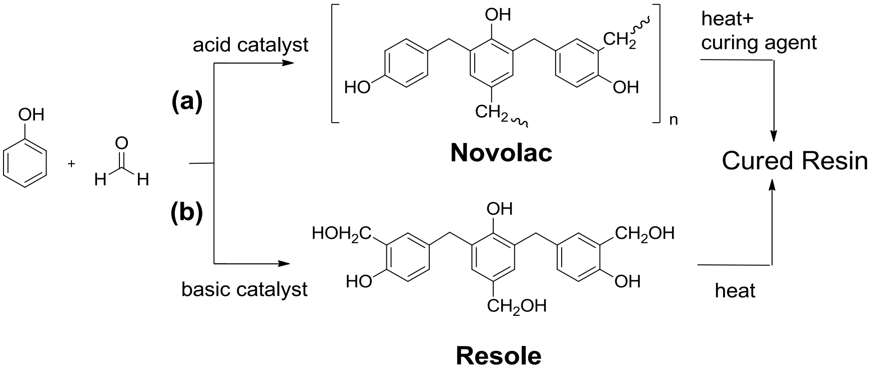
Scheme 1.1. Schematic structures of a) thermoplastic and b) thermosetting resins.

On the other hand, thermosetting resins are three-dimensional macromolecules (Scheme 1.1b) which can be prepared either by direct polymerization of multifunctional monomers or by crosslinking of reactive thermoplastic polymer precursors under appropriate conditions. Due to their network structure, these materials have high dimensional stability, making them attractive for structural applications. Moreover, thermosets are insoluble and infusible materials due to their structure. Properties of thermosets are mainly dependent on their crosslinking density. Thus, lightly crosslinked materials behave as flexible materials showing some elasticity such as rubbers.[6] On the contrary, materials with higher crosslinking density behave as extremely tough and rigid materials. Common high performance thermosetting resins are based on epoxies, urea-formaldehyde, melamine-formaldehyde, polyurethanes, or phenolics based on phenol and formaldehyde.

Phenolic resins were the first fully synthetic polymers produced commercially since the beginning of the 20th century and are nowadays widely used in a broad range of applications. Phenolic resins are synthesized in one or two steps by a step-growth polymerization of phenol, or a phenol derivative, and formaldehyde using either an acid or basic catalyst. They have a complex structure which depends on the ratio of the reactants, pH and temperature used. Thus, there are two types of phenolic resin prepolymers: novolacs and resoles.

Novolacs are produced by the reaction of an excess of phenol with formaldehyde in acidic conditions. The reaction proceeds by electrophilic substitution mainly in ortho and para positions of the phenolic component producing linear or slightly branched condensation products that are linked by methylene bridges (Scheme 1.2a). The production of the final novolac resin requires the addition of a crosslinking agent because the prepolymer has low functionality. The commonly used crosslinking agents are hexamethylenetetramine (HMTA) and paraformaldehyde. Because of the need of a crosslinking agent, novalac resins are also called ‘two-stage’ or ‘two-step’ phenolics.

Resoles are produced by the reaction of phenol with an excess of formaldehyde in basic conditions (Scheme 1.2b). The reaction proceeds through the electrophilic substitution with the more reactive phenoxide ion, leading to the formation of methylol groups mainly in the ortho and para positions (along with some di- or trimethylol phenol units). Due to presence of high amount of methylol groups, resole resins do not require a curing agent and crosslinking is achieved by heating at high temperature. Though, resole resins are called 'one-stage' or 'one-step' phenolics.

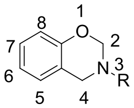


Scheme 1.2. Schematic representation of a) novolac and b) resole resins preparation.

Generally, phenolic materials have been recognized by their low cost, good thermal and dimensional stability, resistance to common solvents, acids and bases, and also by their promising electrical properties.[7] In spite of their good properties, a number of shortcomings are also associated with these materials such as, poor shelf life of the prepolymers, need of harsh reagents and catalysts for their manufacture, release of water and ammonia during the curing process, and brittleness of the final resins. In this context, there is still room to develop improved types of phenolic materials.

Polybenzoxazines are considered an alternative class of phenolic resins, which overcome several of the above mentioned shortcomings of phenolic systems while retaining most of their advantages. Additionally, polybenzoxazines possess unique advantages such as low melt viscosity of the precursors, curing with no need of strong catalyst and non volatile release[8] together with near-zero volumetric change during curing.[9-11] The final materials are characterized by high glass transition temperatures (T_g), low water absorption,[9] high char yield,[12] and excellent thermal and electrical properties.[13] Most of these outstanding properties are related to the presence of high density of inter- and intra-molecular hydrogen-bonding[14] between the phenolic groups and the nitrogen containing Mannich-type bridges (*vide infra*).[15]

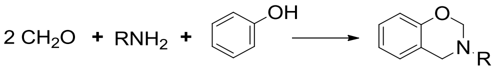
Polybenzoxazine precursors, named benzoxazine monomers, are a class of heterocyclic compounds based on a six-membered heterocycle containing one oxygen and one nitrogen atoms fused to a single aromatic ring. Depending on the relative positions of the two heteroatoms, various isomeric benzoxazines can exist. 1,3-Benzoxazine is the isomer usually used for polybenzoxazine preparations.[16] According to the IUPAC nomenclature 1,3-benzoxazines are numbered as shown Scheme 1.3.[14] Throughout this thesis, we will refer to 1,3 isomer simply as benzoxazine.



Scheme 1.3. 1,3-Benzoxazine molecule, numbered according to IUPAC nomeculature.

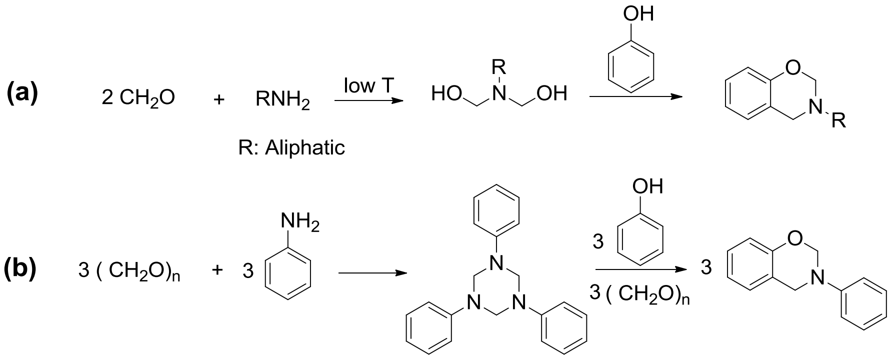
The synthesis of benzoxazine monomers was first reported by Holly and Cope in 1944.[17] Later, Burke[18] extensively investigated the chemistry of benzoxazine ring preparation. During the 70s and 80s, different groups reported on the synthesis of oligomers and polymers from benzoxazine monomers.[19] Even if polybenzoxazines and their applications were reported many years ago, it was not until 1994 when Ning and Ishida reported for the first time an exhaustive study on polybenzoxazine properties.[8] From that date to present, polybenozaxines have been on the spotlight of both academic and industrial researchers.[7,16,20-27]

Benzoxazine monomers are typically synthesized through Mannich type condensation of phenols, amines (aliphatic or aromatic) and formaldehyde or formaldehyde precursors (i.e. paraformaldehyde) in absence of catalysts (Scheme 1.4).



Scheme 1.4. General synthesis of benzoxazine monomers.

This synthetic method can be accomplished either in solution[28] or melt-state,[29] being the later particularly interesting. According to Ishida,[29] in the solventless method all reactants are mixed together, heated to above their melting point, and maintained at this temperature to complete the reaction. It should be noted that in this method, the use of paraformaldehyde is beneficial because helps to maintain the reaction stoichiometry. In some cases, the high melting point of reactants makes necessary the utilization of solvents such as toluene, 1,4-dioxane or chloroform.[30,31] Several modifications of this general method have been reported. Thus, in the case of using aliphatic amines, better results in terms of yield and purity were obtained following a two-step procedure consisting on the reaction of the amine and formaldehyde at low temperature and subsequent addition of the phenolic reagent (Scheme 1.5a).[32] On the other hand, Ishida reported that in the case of the aromatic derived benzoxazines the one-step synthesis proceeds through the formation of an intermediate 1,3,5-triarylhexahydro-1,3,5-triazine.[33] Thus, an alternative synthetic method was proposed consisting of the previous synthesis of the triazine derivative by condensation of the aromatic amine and

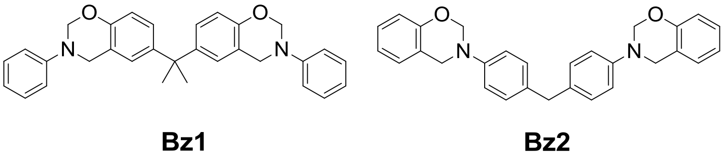


Scheme 1.5. Alternative synthesis of benzoxazine monomers based on two-step procedures.

formaldehyde and the subsequent condensation with the phenol in the presence of more formaldehyde (Scheme 1.5b).[34]

One of the main problems associated to benzoxazine monomers synthesis is the extensive formation of oligomers, which reduces the yield and offers a difficult purification. This undesired side-reaction has been reported to be favored mostly by water, polar solvents and high temperatures.[8,29,33,35,36] Interestingly, the use of of 1,3,5-triarylhexahydro-1,3,5-triazine and paraformaldehyde instead of the formaldehyde solution as reagents in bulk conditions or in the presence of low polarity solvents such as toluene or xylene has been described to minimize the formation of oligomers.[30,31] In any case, phenolic oligomers can be efficiently eliminated with a sodium hydroxide solution final work-up. It is important to point out that a three-step synthetic method involving an imine intermediate has also been reported.[37] This method allows obtaining functional monomers with high structure complexity minimizing the formation of oligomers.

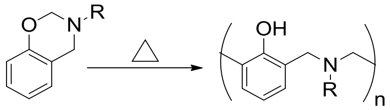
The wide variety of available phenols and amines combined with all the above mentioned synthetic methodologies definitely allow a tremendous molecular design freedom which permits to tune the properties of the final resins.[14,20] According to that, almost any combination of a mono-, di- or multifunctional phenol and amine can be used. Usually, monofunctional benzoxazines upon curing lead to linear or lightly crosslinked materials incapable of displaying the necessary toughness and strength required for structural application by themselves. On the contrary, di- and multifunctional benzoxazines lead to highly crosslinked materials with better mechanical and thermal performance. Combinations of bisphenol-A (BPA) with aniline (Bz1, Scheme 1.6), and 4,4´-*bis*-diaminodiphenylmethane (DDM) with phenol are by far the most studied benzoxazine systems are based on (Bz2, Scheme 1.6).[8,35,38-41]



Scheme 1.6. Chemical structure of the two most studied *bis*-benzoxazine monomers based on BPA and DDM.

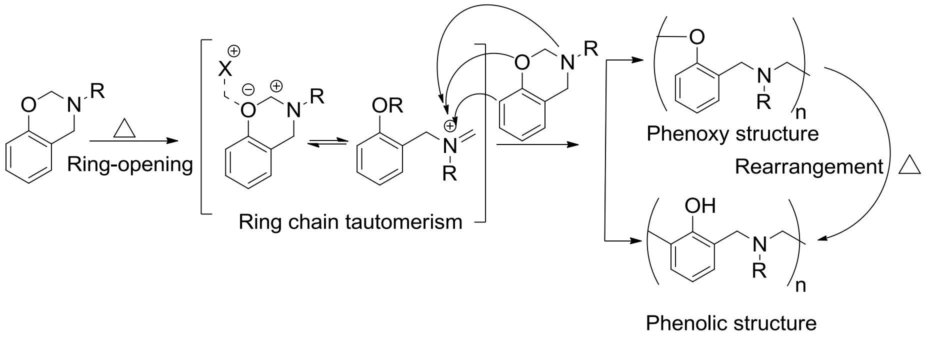
BPA based benzoxazines exhibit unique mechanical properties whereas DDM-derived benzoxazines are superior in heat resistance and electrical insulation. The interest in benzoxazine chemistry is not merely academic as evidenced by the fact that several benzoxazine monomers have been commercialized by companies such as Huntsmann and Shikoku.[42] Polybenzoxazine polymeric materials as prepregs, composites, and resins have also been launched to the market by Henkel[43] and Huntsman.[44] These materials have a promising feature in many application fields such as electronic packaging, aerospace, automobile, adhesives, coatings, and composites.[45]

Polybenzoxazines can be obtained *via* thermally activated ring opening polymerization (ROP) of benzoxazine monomers without adding any initiator or catalyst (Scheme 1.7).[13,46,47]



Scheme 1.7. Classical thermal ROP of benzoxazine monomers.

In fact, it has been demonstrated that this polymerization is initiated by traces of remaining phenolic impurities and proceeds through a cationic mechanism.[8,48] The thermally induced polymerization of benzoxazines typically occurs at high temperatures (220-280ºC) and gives the corresponding polymers having phenolic moieties bridged by Mannich-type linkages. ROP of benzoxazines can be performed at lower temperatures in the presence of acidic substances,[49-51] metallic salts,[52] thiols[53,54] or photoinitiators[55] as catalysts. Since the ring opening reaction of the benzoxazines was first reported by Burke et al.,[18,32,56] several attempts to explain the polymerization mechanism have been described.[57] Simplified ROP mechanism for benzoxazine monomers is shown in Scheme 1.8.



Scheme 1.8. Simplified mechanism of the ROP of the benzoxazine monomers.[57]

It is considered that there are two main steps involved in the polymerization; a ring opening and a subsequent electrophilic substitution step through N, O or free aromatic ortho and para positions. Depending on the polymerization conditions and the structure of the monomer, the final polymer may have phenolic structure,[39] phenoxy structure[58] or both of them.[59] The phenoxy structures are mainly obtained in the case of highly substituted monomers or certain catalysts. For the rest of the monomers it has been proposed an intermediate phenoxy structure that rearranges to the final phenolic structure on heating.[59,60]

As mentioned above, polybenzoxazines have a variety of superior properties when compared to traditional phenolics. However, these systems also suffer from some important drawbacks. Recent developments on benzoxazine technology have focused on addressing these shortcomings while retaining their benefits. Thus, main efforts have focused on: a) decreasing the high temperature required for curing, b) increasing the crosslinking density, and c) improving the toughness and flexibility of the final resins. In addition, due to the rapid depletion of petroleum-based products, polybenzoxazine technology is now finding a breakthrough through the preparation of their monomers from renewable resources in the same way as other petroleum-based polymers. Therefore, nowadays polybenzoxazine technology faces four main challenges to improve practical applications and developing more environmentally friendly materials.

1.2 Decreasing Polymerization Temperature of Benzoxazine Monomers

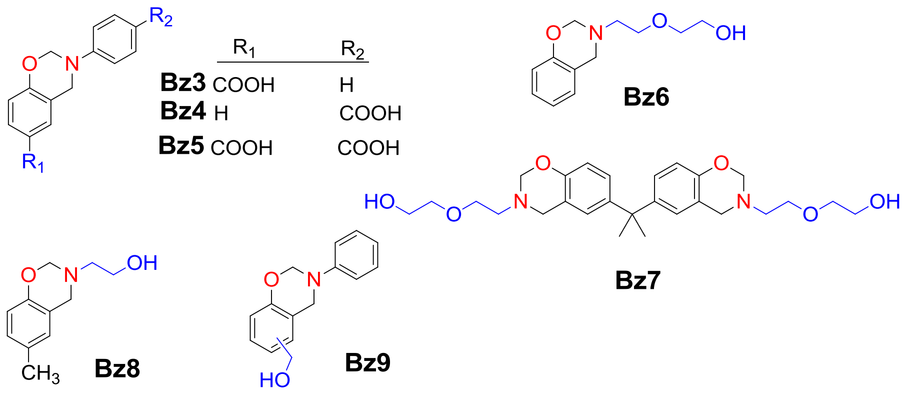
As mentioned previously, the ROP of benzoxazine monomers usually requires relatively high temperatures at around 220-280ºC. This high temperature curing may destroy the inner hydrogen bonding interactions, resulting in polymer degradation, and furthermore limits its wide range of applications.[39,47,61] Therefore, in some cases it is mandatory to decrease the polymerization temperature. For this aim, two general strategies have been described: the utilization of catalytic systems that promote the ROP of benzoxazines and the design of active hydrogen-containing benzoxazine functional monomers (i.e. carboxylic acids, phenols or alcohols) as auto-catalytic systems.

1.2.1 Catalytic Systems for Benzoxazine Monomers

Many catalysts have been tested as promoters for the thermal ROP of benzoxazine monomers. Ishida and Wang[59] demonstrated that Lewis acids such as halides (PCl_5, PCl_3, $POCl_3$, $TiCl_4$, and $AlCl_3$) and metal trifluoromethane sulfonates under solvent conditions promote the polymerization of benzoxazines. PCl_5 and $AlCl_3$ showed the best results for the polymerization of Bz1 *bis*-benzoxazine. For both systems, a $CHCl_3$ soluble fraction of around 50% was obtained at 20ºC using a monomer-catalyst molar ratio of 20:1. The same research group also reported that transition metal salts such as CuCl, $CrCl_2$ initiate the ring opening but do not catalyze the polymerization of benzoxazines.[52] On the other hand, various strong carboxylic acids and phenols have been demonstrated to be effective in the curing temperature reduction of benzoxazines.[50,62] *p*-Cresol/methyl amine-based benzoxazine was polymerized to high conversion (>90%) with 10 mol% trifluoroacetic acid at temperature as low as 130ºC. Endo and co-workers[60] effectively combined a Lewis acid (*p*-toluenesulfonic acid) with a nuchleophilic catalyst (2-ethyl-4-imidazole) to promote the polymerization. Also they reported a series of acetylacetonato complexes of 4th period transition metals from vandanium to zinc, as highly efficient catalysts.[63] Sudo et al.[64] reported efficient promoting effects of some aromatic urethanes, derived from phenolic compounds such as resorcinol and phenyl isocyanate, on the thermal ROP of benzoxazines. Such urethane-type promoters are particularly interesting because of their metal-free character that can minimize undesired conductivity in some specific applications such as electrochip-bonding. Moreover, the neutral nature can avoid the presence of residual highly acidic or basic species that can cause deterioration of the resulting polymers and other materials that contact with them.[64] Possible mechanisms for this promoting effect would involve the thermal dissociation of these urethanes into resorcinol and phenyl isocyanate as the real active species. Andreu et al.[51] reported that boron trifluoride diethyl etherate ($BF_3.OEt_2$) in combination with alcoholic solvents is an efficient initiator system for the cationic ROP of aromatic benzoxazines in alcoholic solution under mild conditions (60ºC). Finally, Liu et al.[57] recently reported lithium iodide as a very active and effective catalyst for the ROP of a *p*-cresol/aniline-based benzoxazine. In the presence of 1 mol% LiI the maximum temperature of the polymerization decreased from 269 to 197ºC.

1.2.2 Auto-catalytic Benzoxazine Systems

Usually, when catalytic activators are used, they remain embedded into the polymer network. This behavior is undesirable, if we take into account relatively high catalyst/initiator ratios used in some of the above mentioned examples. This free additives compounds can not only act as plasticizers, but they can also migrate to the surface and produce brittle materials.[65] Functional benzoxazine monomers with active hydrogen-containing groups (for examples COOH[65] or OH[66,67]) have been demonstrated to be effective reactive co-monomers to decrease polymerization temperature of oxazine ring. Acidic functional groups are belived to activate the benzoxazine ring by coordinating either to oxygen or nitrogen center (see Scheme 1.8). In this way OH and COOH functional groups are the most studied. Some examples are shown in Scheme 1.9.



Scheme 1.9. Chemical structure of benzoxazine monomers with OH and COOH functionalized side groups.

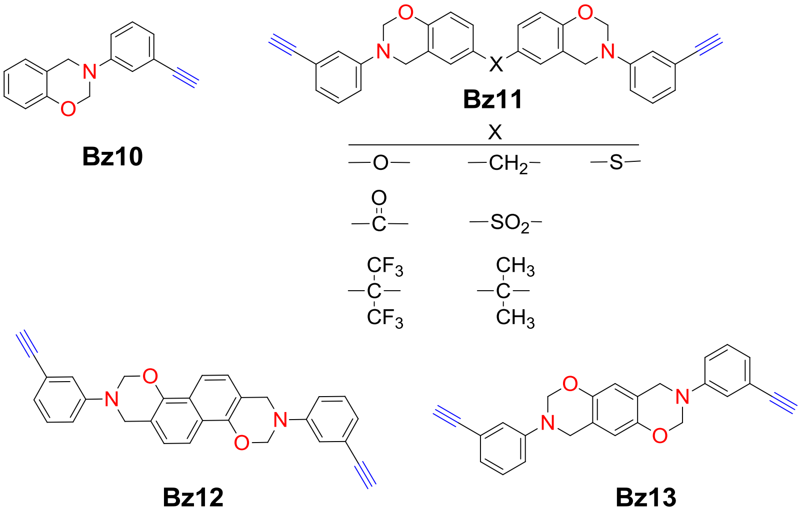
Andreu et al.[65] reported the auto-catalytic thermal polymerization behavior of three benzoxazine monomers containing carboxylic acid functionalities (Bz3-5, Scheme 1.9). The acid character of these reactive benzoxazine monomers increases the concentration of oxonium species, thus catalyzing the ROP of the benzoxazine ring. Consequently, the polymerization of Bz3-5 occurs at 180, 204, and 208ºC, respectively, which are 50-70ºC lower than the benzoxazine without carboxylic functionality. FTIR/ATR analysis revealed that thermal polymerization of these monomers proceeds with a partial decarboxylation, which in the case of monomer (Bz3) is almost complete. The decarboxylation of the COOH groups located at the aromatic benzoxazine ring proceeds faster than those located at the aromatic ring attached to the N.[65]

Yagci and co-workers[66] synthesized hydroxyethyl terminated ether chain-functional mono- and difunctional benzoxazine monomers (Bz6, Bz7) which exhibited curing temperature peaks with maximum at 193 and 202ºC, respectively. The authors reported the reduced polymerization temperature of these monomers in comparison to ordinary unfunctional benzoxazine monomers. Further, Kudoh et al.[67] has demonstrated the role of the hydroxylethyl group in activating the thermally ring opening of Bz8 monomer. As reported, the polymerization of Bz8 monomer was performed at 120ºC with 90% conversion after 6h, while the conversion of the non-functional benzoxazine monomer was 20%. Ishida and co-workers[68,69] has studied mechanistic aspects of the polymerization and the accelerating effect of methylol groups in the ring opening of methylol-functional benzoxazine monomers (Bz9). The differential scanning calorimetry (DSC) results exhibited that exothermic peaks due to condensation reaction of methylol groups and ROP of benzoxazine were 231, 214, and 196°C for monomers with methylol group placed on para-, meta-, and ortho- position, respectively. However, the exothermic peak of unfunctionalized monomer exhibited a higher value of 255°C.[68] Obviously, such alcohol functional benzoxazines have relatively lower ring opening reaction temperature compared to classical benzoxazine monomers due to the activation effect of phenolic OH groups.[70]

1.3 Increasing Crosslinking Density of Polybenzoxazines

Crosslinking improves the chemical, thermal, and dimensional stability of polymers. Despite the tremendous advantages of polybenzoxazines, due to a large amount of intra- and relatively weak intermolecular hydrogen bonding,[14] their crosslinking densities are considered quite low. Further tightening of the polybenzoxazine network structure is expected to improve both thermal and mechanical performance. The design of benzoxazines with acetylene as additional polymerizable side functional group was envisioned in 1988 by Ishida and co-workers as an effective strategy to enhance the crosslinking density and consequently improve the properties of the final resins (Scheme 1.10).[71-73]

It is well-known that acetylenic groups can react under cationic, coordination, free radical, photolytic, and thermal inducement. The reaction of the acetylenic group leads to chain extension, branching or crosslinking of the polymer by thermal treatment.[74] For acteylenic - functional benzoxazines

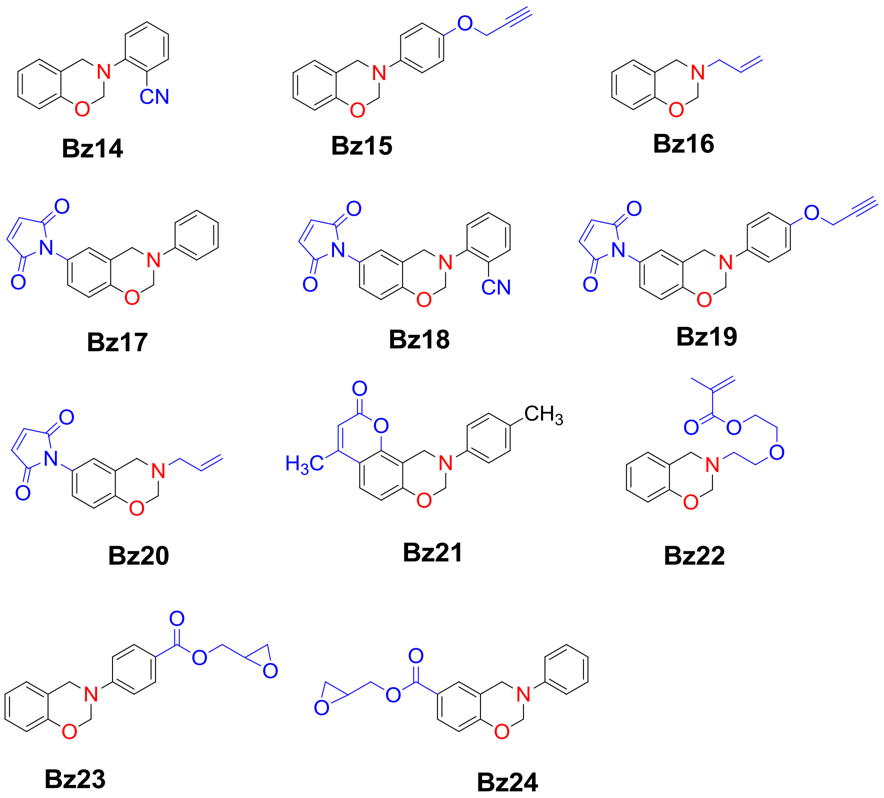


Scheme 1.10. Chemical structure of benzoxazine monomers containing acetylene functional polymerizable side groups.

two types of thermally initiated polymerization were expected to occur during thermal curing process: polymerization of the acetylene-functional group and oxazine ROP. The authors reported the synthesis and polymerization of a series of acetylene containing benzoxazine monomers (Bz10-13) and compared their thermal and mechanical properties with analogous polybenzoxazines without acetylene functional groups. Bz10-13 monomers were reported to polymerize at moderate temperatures (190ºC) without any added catalysts. The storage modulus at room temperature of those acetylene terminated polybenzoxazines was in the range of 1.9-2.2 GPa. The resulting T_gs were in the range of 330-368ºC, which were significantly higher compared to the analogous polybenzoxazines and, also, much higher than their polymerization temperature. Their higher T_gs and also high char yield, in the range of 70-80% in nitrogen at 800ºC were attributed to the formation of additional crosslinking sides due to the presence of polymerizable acetylene functional groups.

Taking advantage of the tremendous molecular design freedom of benzoxazine monomers, the incorporation of other polymerizable functional groups such as nitrile (Bz14),[75,76] maleimide (Bz17),[77] and epoxy (Bz23-24)[78] has also been reported. Scheme 1.11 summarizes the chemical structures of monofunctional benzoxazine monomers containing one or two additional polymerizable side groups.

In general, significant improvements on thermal and mechanical properties were observed in all these systems. However, it is important to point out that better results in terms of thermal stability were observed when the additional polymerizable group is introduced *via* the amine fragment. This was attributed to the fact that the decomposition of the polybenzoxazines is well-known to mainly proceeded by volatilizing amine fragments.[47,61]



Bz14 **Bz15** **Bz16**

Bz17 **Bz18** **Bz19**

Bz20 **Bz21** **Bz22**

Bz23 **Bz24**

Scheme 1.11. Chemical structure of benzoxazine monomers containing nitrile (Bz14), phenyl propargyl (Bz15),[79] allyl (Bz16),[80] maleimide (Bz17-20), coumarin (Bz21),[81] methacrylate (Bz22),[82] and epoxy (Bz23-24) additional polymerizable functionality.

Brunovska et al.[75,76] by adding nitrile groups such as phthalonitrile and phenylnitrile functionalities to benzoxazine monomers obtained high thermal stable polybenzoxazine materials (Bz14 Scheme 1.11). All nitrile-functional polybenzoxazines showed high thermal stability with high T_g (>300ºC) and high char yield up to 80%. Propargyl ether group is another thermally reactive end-capping agent investigated and it has been demonstrated that preparation of the propargyl ether functional group containing benzoxazine monomers such as Bz15 is much more cost effective than acetylenic systems. As reported, the first degradation stage due to the volatizing aniline fragment was decreased by the propargyl ether crosslinking unit. The T_g of these polymers were 100-140ºC higher than typical polybenzoxazines. To address the same aim, thermosets derived from allyl-functional benzoxazines have been studied by several groups. Agag et al.[80] prepared allyl-based benzoxazines such as Bz16. T_g values of the polybenzoxazines was as high as ca. 300ºC by the introduction of allyl group. In addition, storage modulus and the thermal stability of these polybenzoxazines increased compared to traditional aniline-based polybenzoxazines. Liu et al.[77] prepared benzoxazine containing maleimide functionalty (Bz17). Depending on the polymerization temperature, high T_g values were observed (84-204ºC). Fully cured polybenzoxazine from Bz17 exhibited high char yield (50%) and limiting oxygen index (LOI) value over 33. Further, several groups synthesized functional benzoxazine monomers containing combinations of maleimide and nitrile,[83,84] propargyl ether, or allyl groups[85] (Bz18-20). In all cases, except maleimide-allyl functional benzoxazine system Bz20, char yield of resulting thermosets increased in comparasion with Bz17. All polymerized difunctional benzoxazines exhibited higher T_g than maleimide functional polybenzoxazine. Yagci and co-workers[81] studied the incorporation of a photodimerizable coumarin group into benzoxazine structure (Bz21). After irradiation at 300nm and curing, the corresponding polybenzoxazine exhibited higher char yield (42%) than only thermally cured coumarin functional polybenzoxazine (36%). The same group synthesized a monofunctional benzoxazine monomer with methacrylate functionality, Bz22 and investigated the copolymerization with styrene.[82] The resulting copolymer showed improved thermal properties and a higher first stage degradation temperature. Andreu et al.[78] incorporated an epoxy group functionality into benzoxazine monomer (Bz23-24). Thermal and mechanical properties of these polybenzoxazine resins have yet to be studied, but interesting results may be obtained.

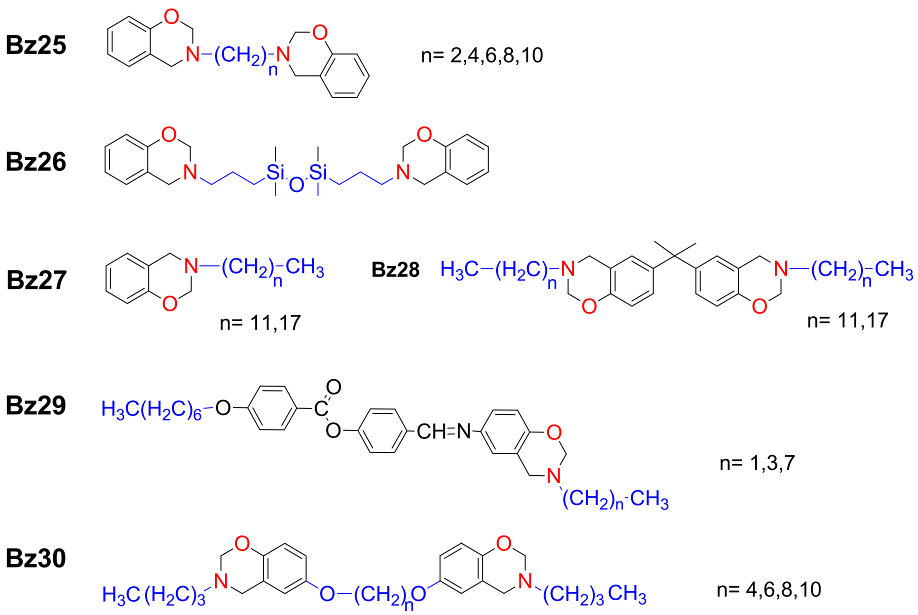
1.4 Improving Polybenzoxazine Toughness and Flexibility

In recent years considerable efforts have been made to improve polybenzoxazine toughness and flexibility because of the brittleness that plagues most of conventional thermoseting resins. Brittleness is an intrinsic characteristic polybenzoxazine resins due to the their rigid core. The classical approach to enhance polybenzoxazine toughness is to incorporate elastomeric or thermoplastic polymers (i.e. epoxy,[86,87] polyurethane,[88-90] and polysiloxane[91]) into the thermosetting matrix to form a phase-separated morphology. Even more attractive is the design of inherently toughed and flexible polybenzoxazines by preparing benzoxazine monomers or preferable prepolymers containing flexible segments. In this way, polybenzoxazine precursors with low melting point or even liquid systems are obtained, thus also improving the processability of the formulations.

1.4.1 Benzoxazine Monomers Containing Flexible Segments

A series of benzoxazine monomers containing flexible segments have been described in the literature and are summarized in Scheme 1.12.

The preparation of *bis*-benzoxazines with an intercalated aliphatic segment was repoted by Ishida and Allen.[92-94] The monomers were prepared combining a series of linear aliphatic diamines with phenol using the classical one-step solventless method (Bz25 Scheme 1.12). The resulting *bis*-benzoxazines had melting points that decreased from 112 to 49ºC as a function of diamine chain length.[93] Interestingly, these monomers could be easily processed into thin films by a solvent-free processing. The rate of polymerization was found to be inversely proportional to the aliphatic chain length. The properties of the final polybenzoxazines were also dependent on the length of the linear aliphatic chain but in all cases flexible materials were obtained. Liu et al.[95] reported the preparation of a silicon containing benzoxazine (Bz26) *via* hydrosilylation between an allyl functional benzoxazine and 1,1,3,3-tetramethyldisiloxane. This flexible benzoxazine was



Scheme 1.12. Chemical structure of benzoxazine monomers containing aliphatic chains.

demonstrated to be a high performance modifier for conventional benzoxazine polymers producing a simultaneously enhancement of T_g as well as toughness.[95]

Alternatively, Agag et al.[96] designed two BPA derived benzoxazines from N-dodecylamine and N-octadecylamine (Bz27, Bz28) as flexible aliphatic end groups. A consequence of the long aliphatic chains (C12 and C18), these monomers possess low melting points (53ºC for Bz27 and for Bz28 44ºC), respectively, and excellent solubility in all common organic solvents, which facilitate their processability. Furthermore, integration of the long aliphatic chain into the polybenzoxazine network structure provided flexible polybenzoxazine resins. While incorporation of pendent aliphatic chains improved flexural properties, thermal properties of these polybenzoxazines were not improved compared to aniline-based polybenzoxazines due to the low thermal stability of aliphatic chains. These new class of benzoxazine monomers possess the potential to be used as reactive diluents to enhance the processability and flexibility of other polybenzoxazines.[96] Similarly, Kawauchi and Ito et al.[97,98] reported a series of *bis*-benzoxazines containing different end aliphatic chains but focused their attention only on the liquid crystal properties (Bz29).

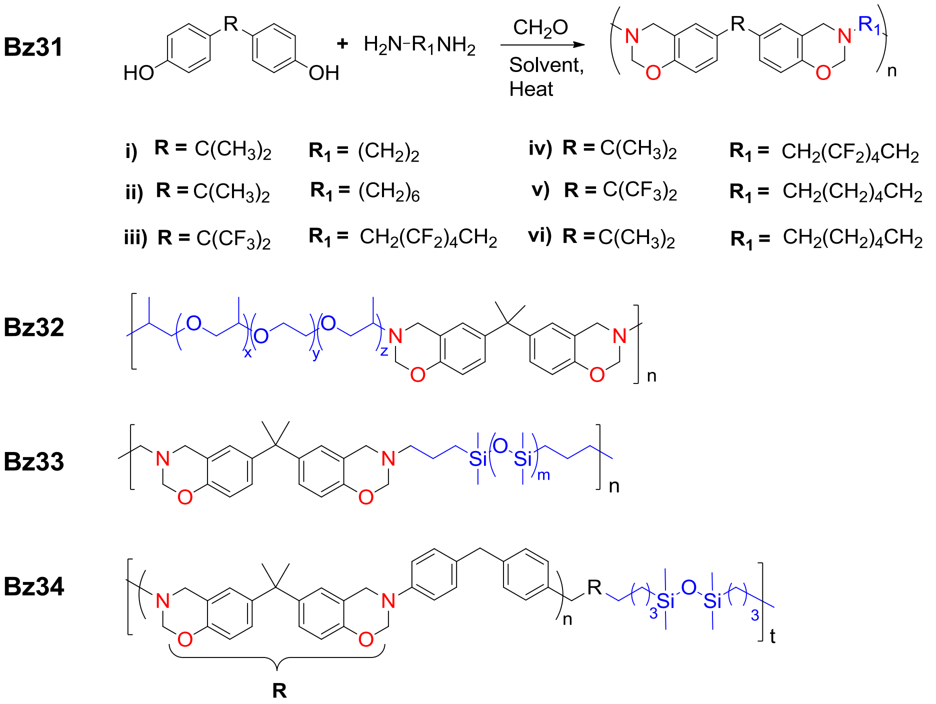
The incorporation of both intercalated and end groups aliphatic was reported by Patton's group.[99] Authors developed a series of long aliphatic chain-based benzoxazine monomers (Bz30) *via* integration of aliphatic chains into the phenolic and in the amine component. The resulting monomers have low melting point that allowed processing into thin film by solvent-free method. These *bis*-benzoxazine monomers showed high polymerization temperatures which slightly increased with the length of the aliphatic linker. The resulting polybenzoxazine thin films were flexible, transparent, and showed low T_g dependent on the chain length. These materials were proposed for membrane and coating technologies where improved flexibility and tunable thermomechanical properties are beneficial.

1.4.2 Benzoxazine Oligomers and Polymers Containing Flexible Spacers

Another promising strategy described to improve toughness and flexibility is the incorporation of flexible segments into polymeric precursors either in the main or side chain.[100-103] In this way, soluble, relatively high molecular weight, and easily processable into thin films polybenzoxazine precursors are also obtained. Polymeric benzoxazines have the typical advantages of ordinary thermoplastic polymers and are able to yield thermosets after heating. Thus, resulting polymers may present properties that are the combination of thermoplastic and thermoset polymers such as processability, flexibility, high crosslinking density after curing, and reduction in the vapor pressure is another advantage during the processing of the precursor material.

Mannich-type polycondensation is attractive for the synthesis of benzoxazine polymers containing flexible segments. Takeichi et al.[100] and

Chernykh et al.,[101] independently reported the synthesis of high molecular weight polybenzoxazine precursors through the polycondensation of BPA and aliphatic (ethylene and hexamethylene) diamines in the presence of formaldehyde to produce linear polymers with a benzoxazine ring as repeating unit in the main chain (Bz31(i-ii) Scheme 1.13). The resulting relatively high molecular weight viscous polymers (6000-8800 Da) contained a percentage of ring opened structures and were easily processed into films by the solvent casting method. After curing, material properties were much better when compared to those of the obtained from monomeric *bis*-benzoxazines. For example, T_g of polybenzoxazines from the high molecular weight precursors were 239-260ºC, much higher than the T_g of the typical polybenzoxazines



Scheme 1.13. Chemical structure of benzoxazine oligomers and polymers containing flexible spacers prepared *via* Mannich condensation.

from *bis*-benzoxazine Bz1 (see Scheme 1.6) (171ºC).[101] Moreover, the toughness and the tensile strength of the crosslinked polymers were also enhanced. Velez-Herrera et al.,[102] synthesized a series of highly fluorinated main chain polybenzoxazines with molecular weights in the range of 6400-13300 Da (Bz31(iii-vi)). The curing conditions strongly affected the value of the T_g of the materials. The introduction of fluorinated segments not only increases the processability but also reduces the dielectric constant and improves the thermal stability.[102]

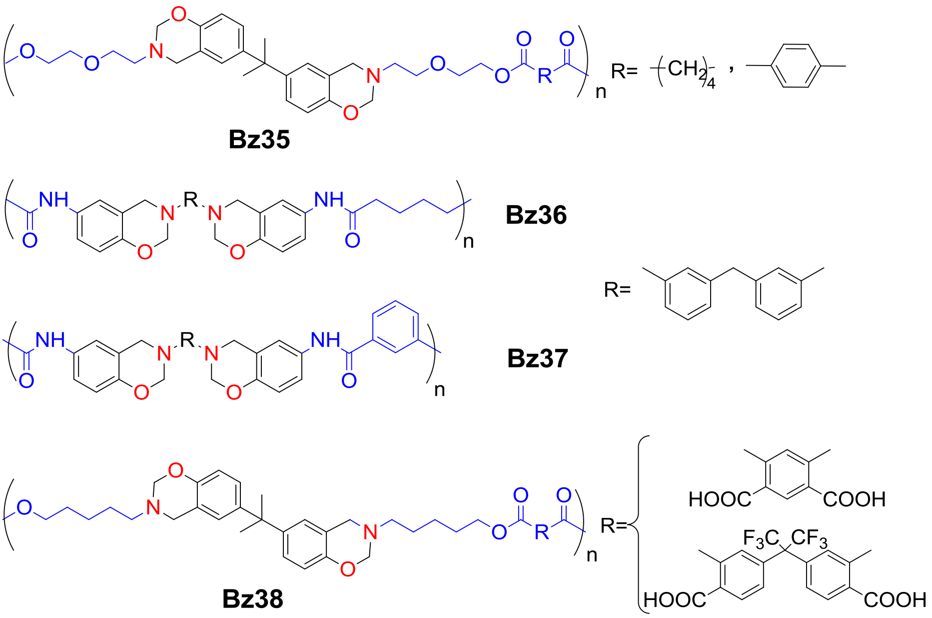
BPA has been also combined with poly(ether diamine), (Jeffamines ED-600, ED-900, and ED-2000) to give a series of benzoxazine prepolymers with low viscosity at room temperature (Bz32).[103] All synthesized polymers were soluble in common solvents such as toluene, chloroform, and dioxane. The length of the polyether chain was demonstrated to modify the properties of the polymer precursors and also those of the cured polymers. By increasing the poly(ether diamine) length, viscosity of the prepolymers and the onset and maximum of the thermal ROP temperature was increased. On the other hand, the total enthalpy decreased and a low T_g were obtained -19ºC, -40ºC and -45ºC, respectively.[103,104]

Mannich polycondensation has also been used to prepare siloxane containing polybenzoxazine oligomeric precursors. Takeichi et al.[105] combined BPA, α,ω-bis(aminopropyl)polydimethylsiloxane of different molecular weights and paraformaldehyde to produce a series of thermally curable systems (Bz33). The resulting polymeric precursors exhibited relatively high molecular weight between 5700 and 8900 Da. After curing, these novel polybenzoxazine films exhibited improved toughness due to the polysiloxane unit. Higher elongation at break values were obtained for polybenzoxazines containing longer siloxane units. The dynamomechanical analysis of the films revealed that the storage modulus and T_g were decreased with increasing the molecular weight of siloxane unit.[105] Surprisingly, the T_g of the lower molecular weight siloxane unit containing polybenzoxazine was higher than that without siloxane unit. This was explained by the beneficial effect of linear long backbone which restricted the movement of polymer chain.[105] On the other hand, Wang et al.[106] synthesized main-chain polybenzoxazine-*block*-

polydimethylsiloxane multiblock copolymers based on BPA *via* Mannich polycondensation (Bz34). The phenol was combined in two-steps first with DDM and subsequently with aminopropyl-terminated polydimethylsiloxane in the presence of paraformaldehyde. The resulting prepolymers showed molecular weight ranging from 4560 to 7730 Da. The cured silioxane containing polymers exhibited high thermal stability. However, when the siloxane content increased above 46% the initial temperature of polymer degradation decreased. These results could be explained on the basis of the formation of microphase-separated morphology and the insulation effect of siloxane microdomains. Similar results have been found in other siloxane-containing benzoxazine-hybrids.[107,108,116]

Although Mannich polycondensation has allowed a successful preparation of some thermally curable benzoxazine polymers containing flexible segments, this synthetic methodology has also some disadvantages. Polybenzoxazine polymeric precursors obtained *via* Mannich route have relatively low molecular weight. This is attributable to the difficulty of maintaining the stoichiometry during the polycondensation reaction since there is some ring opened benzoxazine structures as a result of side reactions. The poor solubility of some *bis*-phenols is another common disadvantage. To overcome these drawbacks, other polycondensation and step-growth chemistries have also been considered to achieve this goal.[104]

Yagci and Ishida,[109] reported the synthesis of a benzoxazine containing diol with oxyethylenic spacers suitable to further polyester synthesis *via* polycondensation with diacid chlorides. Thus, using adipoyl chloride and terephthaloyl dichloride a series of polyesters with molecular weights around 34000 Da were obtained (Bz35, Scheme 1.14). Flexible transparent films of the polyester were obtained by solvent casting from dichloroethane solution. Due to the presence of soft ether ester segments, these films preserve shape and to some extent toughness after thermal curing between 140 and 220ºC. Combining benzoxazine diamine also with dicarboxylic acid chloride produced main chain type polybenzoxazines with



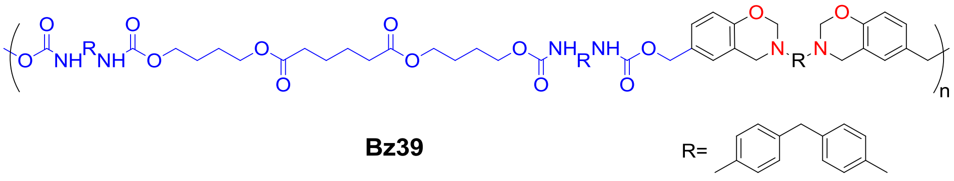
Scheme 1.14. Chemical structure of polyetherester, polyamide, and polyester containing benzoxazine units in the main chain.

amide and benzoxazine groups repeating group in the main chain (Bz36-Bz37).[110] Polymers from both adipoyl and isophtaloyl dichlorides were isolated as white solids and were soluble in aprotic organic solvents at room temperature with approximately 20% solid content.

The crosslinking of aliphatic poly(amide-benzoxazine) took place at slightly lower temperature than the aromatic polymer due to the flexibilizing effect of the aliphatic segment in the main chain (Bz36, Bz37). But on the other hand, crosslinked aromatic polymer exhibited higher thermal stability than aliphatic cured polymer. These crosslinked poly(amide-benzoxazine)s showed good thermal stability compared to the uncrosslinked aromatic amide.[110]

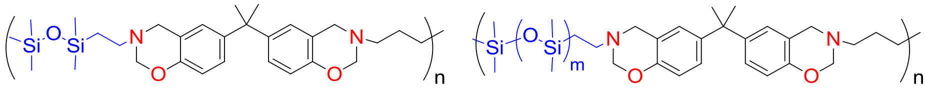
Polyester containing benzoxazine units in the main chain (Bz38) were also obtained by Tuzun et al.[111] *via* polycondensation of another diol benzoxazine and pyromellitic dianhydride or 4,4'-(hexafluoroisopropylidene) diphatalic anhydride. The diol monomer was synthesized *via* a Mannich-type reaction based on BPA and 5-amino-1-pentanol to introduce a flexible chain. Polyesters with molecular weight between 5800 and 7000 Da were obtained and further thermally crosslinked in the absence of any catalyst to produce films that exhibited high flexibility and adhesion on tin plates.

Hydroxyl/urethane reaction to produce urethane linkages has also been explored to prepare linear poly(benzoxazine-*co*-urethane) materials (Bz39, Scheme 1.15).[112] These copolymers were prepared through one-pot synthesis *via* the reaction of dimethylol-functional benzoxazine monomer with 4,4´-methylenediphenyldiisocyanate and a poly(1,4-adipate). Structure of copolymers was characterizated by FTIR and ^{1}H-NMR. These copolymers were further thermally crosslinked to produce a network structure. Resulting films exhibited superior thermal stability compared to previously reported polybenzoxazine/polyurethane blends.[88-90] Excellent mechanical integrity was stemmed from high tensile modulus and tensile strength due to the presence of benzoxazine groups as part of the main-chain. Additionally, their mechanical and thermal properties are comparable to the well-known high performance poly(urethane-imide)s.[113,114]



Bz39

Scheme 1.15. Chemical structure of main chain type poly(benzoxazine-*co*-urethane)s.

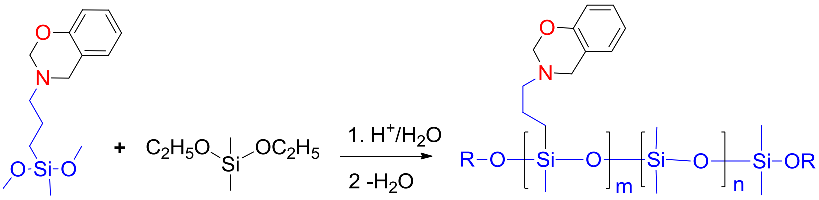


Bz40 **Bz41**

Scheme 1.16. Chemical structure of siloxane containing benzoxazine polymers.

Hydrosilylation reaction was also demonstrated to be a valid tool to introduce flexible siloxane units in the main chain of polybenzoxazine polymeric precursors (Bz40, Bz41 Scheme 1.16). Particularly, Yagci and co-workers[115] reported the Pt-catalyzed hydrosilylation reaction between 1,1,3,3-tetramethyldisiloxane and benzoxazine structurally equipped with allyl groups. Although the chain growth was limited and only oligomers were formed (M_n SEC below 2600 Da) the process showed high selectivity and products exhibited properties of both segments. Siloxane segments introduce flexibility and transparent thin films were easily obtained by casting. On the other hand, the benzoxazine groups readily underwent thermally activated ROP in the absence of added catalyst to form a crosslinked polymer network. The chain elongation of the above mentioned oligosiloxane containing benzoxazine moieties was also investigated by reacting them with readily available cyclic oligomers (2,2,4,4,6,6,8,8-octamethyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane and decamethyl-1,3,5,7,9,2,4, 6,8,10-pentaoxapentasiloxane) in the presence of tetramethylbutylamonium salts as catalyst.[116] In this way, it was possible to prepare polysiloxanes without affecting benzoxazine moieties under anionic polymerization conditions. Crosslinked siloxane-containing networks exhibited much more thermal stability than those of the structurally similar low molecular weight analogous up to 450ºC.

An alternative pathway for the preparation of polysiloxane oligomers bearing functional benzoxazine side groups (Bz42, Scheme 1.17) was based on the hydrolysis and polycondensation of a benzoxazinyl siloxane with

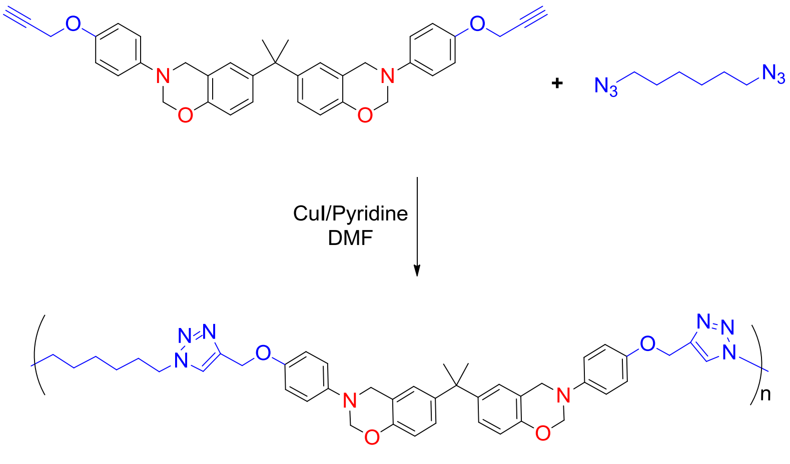


Bz42

Scheme 1.17. Synthetic route to poyl(benzoxazine-*co*-siloxane)s.

dimethyldiethoxysiloxane.[117] The structure of the obtained oligomers was characterized by FTIR and NMR spectroscopy. Average molecular weights were estimated to be in the range of 2000-4000 Da. The oligomers gave crosslinkable transparent films by casting in tetrahydrofuran (THF) solution. Tensile test of cured films revealed that the elongation at break increased with siloxane content and therefore proved the success of this approach to improve the flexibility of polybenzoxazines.[117]

Copper(I)-catalyzed azide-alkyne cyclo addition[118,119] (Huisgen type click reaction) is another effective synthetic route for the preparation of main chain polybenzoxazine containing flexible segments. This reaction together with many other highly efficient reactions has recently collectively termed click chemistry and has attracted attention due to its various advantages including high selectivity, facile experimental set-up, applicability in aqueous and aerobic systems, tolerance to variety of functional groups, quantitatively yields, and minimal synthetic workup.[119] Although Yagci group was the first group that used Huisgen type click reaction in polybenzoxazine chemistry,[120-122] the preparation of linear polymers with benzoxazine rings and flexible segments in the main chain were reported also by Chernky.[123] A propargyl containing benzoxazine was polymerized with 1,6-diazidohexane at room temperature in the presence of copper iodide (Bz43, Scheme 1.18). The number average molecular weight estimated from size exclusion chromatograpghy (SEC) was around 50000 Da which is significantly higher



Bz43

Scheme 1.18. Synthesis of main chain type benzoxazine prepolymer *via* Huisgen type click chemistry.

than the similar benzoxazine polymers prepared *via* Mannich reaction and the other above mentioned synthetic methodologies. Unfortunately, no discussion about elastic properties was reported for these systems.

As summarized above, main chain benzoxazine polymers can be prepared by various approaches to enhance their flexibility, processability, and thermal and mechanical properties. These linear polymers exhibit thermoplastic behavior that can undergo thermoset conversion when they are further thermally polymerized and crosslinked. Moreover, high performance thermosets can be prepared by playing structure-property relationship for specific applications.

1.5 Benzoxazine Monomers from Renewable Resources

In recent years, the choice of raw materials for chemical purposes has been a key subject of interest to researchers due to strong environmental incentives to reduce consumption of petroleum and its derivatives. In this context, polymer researchers are devoting increasing attention on the utilization of renewable resources as raw materials for the production of the majority of synthetic polymer building blocks.[124,125] The interest in bio-based polymers is not merely academic as evidenced by the fact that some polymers with high renewable content are already on the market. Rilsan®, a polyamine based on castor oil, sugar-derived polyesters such as Sorona®, Hytrel®, and the Pearlthane® ECO thermoplastic polyurethane ranges marketed by Merquinsa are successful examples. Polybenzoxazines are by no means an exception and have recently become new players in the bio-based polymers arena.

Taking into account that formaldehyde is within the area of influence of biomethanol, the two remaining benzoxazine monomers building blocks, phenols and amines, are right now in the spotlight. Although the first attempt to incorporate natural components to benzoxazine-based materials dates from 1999,[126] it was not until recently when both academia and industry have focused their efforts to exploit renewable resources, paying special attention to naturally occurring phenolics and other bio-based phenols. Renewable amines have otherwise received limited attention probably due to its lower natural stock. A facile and efficient benzoxazine monomer synthesis protocol combined with the characteristic structural wealth of these natural compounds offers a palette of possibilities to design polybenzoxazine precursors with comparable and in some cases superior properties than well-studied petroleum-based polybenzoxazines. The purpose of the following section is to comprehensively overview recent efforts for either partial or complete replacement of petro-based feedstocks from polybenzoxazine precursors.

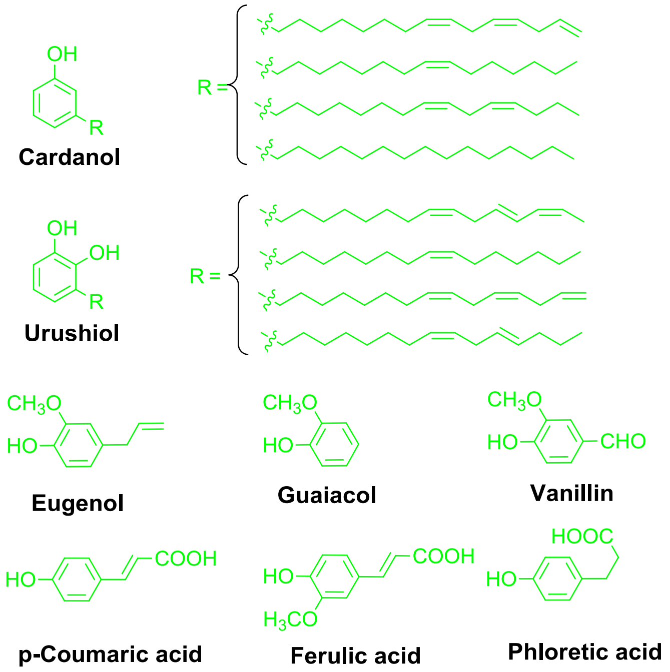
1.5.1 Plant-derived Phenolics as Platform Chemicals for Benzoxazine Technology

Phenolics are broadly distributed in the plant kingdom and are the most abundant secondary metabolites in plants.[127] They exist with an incredible diversity of several thousands of structures ranging from simple single-ring molecules with, for example, C_6, C_6-C_1, or C_6-C_3 basic skeleton to highly polymerized substrates. Biogenetically, these compounds arise from two main pathways: the shikimate pathway, which directly provides phenylpropanoids such as hydroxycinnamic acids and coumarins, and the polyketide (acetate) pathway, which can produce simple phenols and also lead to quinones. The flavonoids, by far the largest group of phenolics, are derived by combination of these two pathways.

The fact that natural phenolics are found in large amounts either in natural existing plant sources or wastes generated from agro-based industries makes them potential substitutes for phenolic petrochemicals. However, it is important to point out that only abundant and easily isolable phenolics are economically feasible. In this context, the incorporation of abundant plant-derived phenolics into benzoxazine building blocks has been considered the simple and straightforward approach to reduce benzoxazine chemistry reliance on petroleum. Monomeric phenols derived from lignocellulosic biomass have also been considered. Chemical structures of all plant derived phenolics exploited for such purposes are shown in Scheme 1.19.

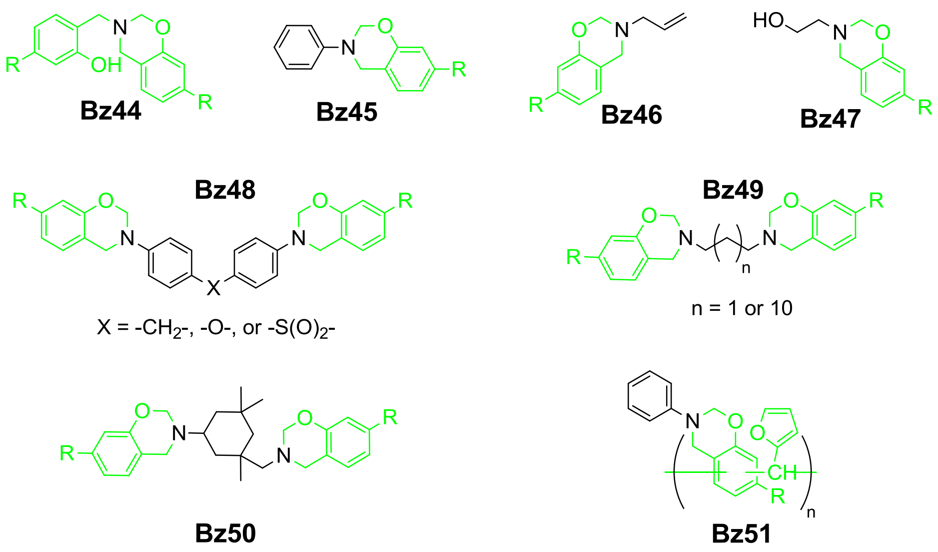
1.5.1.1 *Benzoxazine monomers from naturally occurring phenolics*

Cardanol, urushiol, and eugenol are three naturally occurring single-ring phenols that have been used as building blocks of benzoxazine monomers. Cardanol and urushiol belong to the phenolic lipids class of chemical compounds composed of a long hydrophobic alkyl chain linked to a phenolic ring, whereas eugenol is a member of the C_6-C_3 phenylpropanoids, synthesized by plants from the amino acid phenyalanine via shikimate



Scheme 1.19. Chemical structure of plant-derived phenolics used as benzoxazine monomer precursors. Only the most abundant side alkyl chains are shown in R.

pathway. Urushiol and eugenol can be considered abundant naturally occurring phenols because exist in high percentage in the sap of Chinese and Japanese lacquer tree (60-65%)[128,129] and the essential oil extracted from cloves (72-90%), respectively. Although cardanol is also considered a sustainable and largely available natural resource, its case is quite special. In fact, cardanol is naturally found in cashew nut shell liquid (CNSL), a byproduct of the cashew nut industry. However, natural CNSL contains other three components: anacardic acid, cardol, and 2-methyl cardol, being anacardic acid the main component (~75%). Nevertheless, cardanol is the main component of commercial grade CNSL because anacardic acid descarboxylates to cardanol during the roasting process used industrially to extract the oil from cashew nuts.



Scheme 1.20. Chemical structure of cardanol and cardanol-based mono- and bis-benzoxazines.

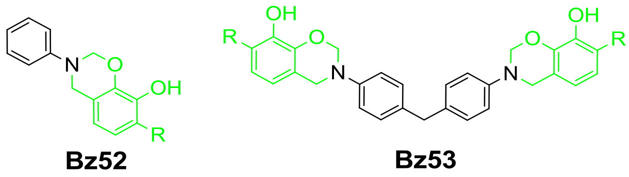
Clearly, cardanol is the most widely exploited plant-derived phenol for bio-based benzoxazine synthesis purposes. The literature reports several examples of cardanol-based benzoxazines (Scheme 1.20, where biobased part is highlighted in green).

The pioneer work, reported by Mele and coworkers, described the preparation of the benzoxazine Bz44 using cardanol, ammonia and formaldehyde as starting materials.[130] Interestingly, Bz44 contains two molecules of cardanol per oxazine unit, leading to a monomer with high biobased content value. DSC analysis of Bz44 showed a exothermic peak associated with curing from 160ºC to 275ºC with a peak maximum of 243ºC. Compared to, for example, phenol/aniline benzoxazine monomer, the curing of Bz44 takes place at much lower temperature. This lowering of cure temperature is due to catalysis of phenolic group as reported in the literature.[131] Cardanol has also combined with other amines such as aniline[132-135] (Bz45, Scheme 1.20), allylamine[136] (Bz46), ethanolamine (Bz47) and a series of aromatic[137,138] and aliphatic diamines[139] such as DDM (Bz48 with X =

-CH_2-) and isophorone diamine (Bz50) to yield different benzoxazines with a broad range of applications. Additionally, cardanol-furfural phenolic resins were also used to prepare oligomeric benzoxazine precursors (Bz51).[140] Furfural is also green platform product derived from a variety of agricultural by-produtcs such as corncorbs and wheat bran.

In comparison with classical systems, most of cardanol-derived benzoxazines are liquid monomers with low viscosity at room temperature. This characteristic feature has been exploited technologically to develop cardanol-based benzoxazine reactive diluents for petroleum-based epoxy and benzoxazine resins. For example, Gu et al.[137] recently demonstrated that Bz48 *bis*-benzoxazines containing different bridging groups are able to significantly reduce the melting viscosity of DDM/phenol-based *bis*-benzoxazine and improve the toughness of the copolymers due to the plasticizing effect and flexibility of their alkyl side chains. Some cardanol-derived benzoxazines have also shown good performance as thermosetting matrix for natural fiber-reinforced composites and organic-inorganic hybrid materials.[130,134,136,141] For example, Li et al.[142] successfully synthesized Bz47-based polybenzoxazine/SiO_2 hybrids by the sol-gel procedure. The preparation of the hybrids mainly included the hydrolysis and the following condensation of tetraethoxysilane (TEOS) at room temperature, further condensation reactions of silanol groups and the ring-opening reaction of benzoxazine moieties at high temperature. As can be seen in Figure 1.1, flexibility of films improved for 5:1 and 5:3 Bz47:TEOS (w/w) content. Dewetting and UV resistance properties also improved with silicon content.

Figure 1.1. Photographs of the bending for a) polybenzoxazine Bz4 and polybenzoxazine/SiO_2 hybrids with Bz4:TEOS (w/w) ratios b) 5:1, c) 5:3, and d) 5:5. Reproduced from Ref. [142] with permission from Wiley-VCH.

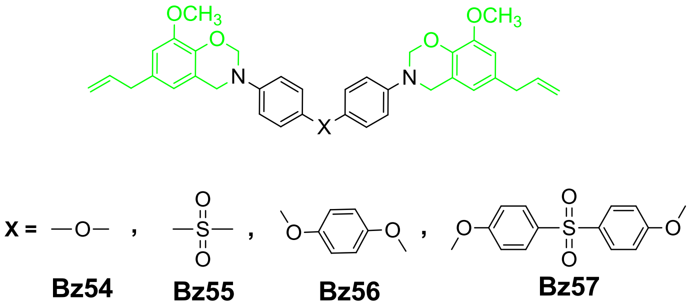


Scheme 1.21. Chemical structure of urushiol-based mono- and *bis*-benzoxazine monomers.

Similarly to cardanol, urushiol-based mono- and *bis*-benzoxazine monomers and derived polymers showed properties dominated by the presence of the hydroxyl group and the alkyl side chain that remain in the benzoxazine structure (Scheme 1.21).

Thus, for example, Bz52, prepared *via* condensation reaction of urushiol, aniline, and paraformaldehyde in dioxane, was isolated as a liquid and showed relatively low curing temperature (180ºC) without addition of catalyst.[143] Moreover it produced polybenzoxazines with low T_g, superb toughness and extraordinary elongation at break. In this case it is important to point out that FTIR analysis of the curing process showed that oxazine polymerization takes place simultaneously with crosslinking of olefins in the side chains yielding a highly crosslinked polymer. Futhermore, the *bis*-benzoxazine Bz53 and DDM/phenol *bis*-benzoxazine were copolymerized into hybrid polybenzoxazines, where the alkyl chains in Bz53 improved the ductility of the materials.[144]

Eugenol has only been considered in the preparation of *bis*-benzoxazines. A series of eugenol-derived monomers (Bz54-57, Scheme 1.22) were prepared from various aromatic diamines and paraformaldehyde.[145] As reported, Bz54-57 were isolated as powders with high melting temperatures at around 100ºC. Interestingly, Bz56 and Bz57 showed wider processing window, defined as the temperature difference between the melting point and onset of polymerization, indicating good processability. FTIR data support that Bz54-57 shows similar curing behaviour



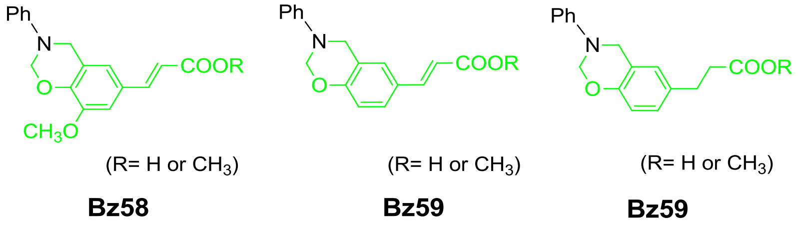
Scheme 1.22. Chemical structure of eugenol-based *bis*-benzoxazines.

than urushiol-derived systems, with allyl moieties also participating during the curing process. Polybenzoxazines prepared by heating up monomers Bz54-57 to 250ºC, to ensure benzoxazine and allyl groups crosslinking, produced materials with T_g values ranging from 120 to 155ºC although flexible ether and sulfone linkages in Bz54 and Bz55 produced lower T_g materials. In all cases, polymers with high char yield in the range of 23-36% at 800ºC in N_2 and good flame retardance in terms of their LOI values were obtained.

1.5.1.2 *Benzoxazine monomers from lignin-derived phenols*

Lignocellulosic materials, which can be found in either the natural existing plant sources or wastes generated from agro-based industries, are one of the most attractive biomass resources in nature and therefore have not gone unnoticed by benzoxazine researchers. Lignocellulosic biomass is composed of cellulose (40-50%), hemicellulose (20-40%) and lignin (20-30%).[146] Proteins, oils, and ash make up the remaining fraction. Cellulose and hemicellulose are polysaccharides whereas lignin is a highly branched phenylpropanoid polymer framework assembled by oxidative coupling of p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.[147] In recent years, conversion of lignocellulosic biomass to fuel and chemicals is globally gaining significant prominence.[148,149]

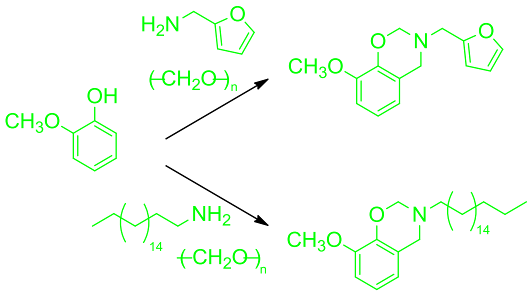
Hydroxycinnamic acids, principally ferulic acid and *p*-coumaric acid (see Scheme 19), are abundant molecules in lignocellulose materials with the function to bind lignin to the hemicellulose and cellulose in plant cell walls. Altough *p*-coumaric and ferulic acids are present in relatively large quantities in vegetables like peanuts, tomatoes, fennel, coffee, or artichokes, as main components of lignocellulose, they are commercially produced mainly by chemical or enzymatic transformation of corn, sugarcane, and other agricultural bagasses.[150-152] Our group recently investigated the preparation of polybenzoxazines based on *p*-coumaric, ferulic, and phloretic acids.[153] Phloretic acid can be obtained by hydrogenation of *p*-coumaric acid but it is commonly produced by chemical or enzymatic treatment of phloretin, a dihydrochalcone present in the apple tree leaves. Monomers Bz58-60 synthesis was carried out using 1,3,5-triphenylhexahydro-1,3,5-triazine and paraformaldehyde as reagents to minimize oligomers formation (Scheme 1.23). Unfortunately, the high melting point of free acids prevented to use bulk conditions and toluene had to be added as solvent. In the case of methyl ester derivatives, reactions could be carried out in bulk with a significant shortening of the reaction time. Benzoxazines with conjugated unsaturated chains exhibited unusual poor thermal stability and partially degrade at the polymerization temperature making necessary the use of a $BF_3{\cdot}Et_2O$ catalyst to low the polymerization temperature and prevent degradation.



Scheme 1.23. Chemical structure of benzoxazine monomers based on ferulic, *p*-coumaric, and phloretic acids and their corresponding esters.

Polybenzoxazines from Bz58-60 and the corresponding methyl esters were obtained as hard and brittle materials with T_g values ranging from 120 to 150ºC. These high T_g values, compared to phenol/aniline benzoxazine, were attributed to the occurrence of additional esterification and transesterification reactions between the phenolic hydroxyl groups resulting from the oxazine ring opening and the free carboxylic or methyl ester groups.

Lignin is a valuable source of chemicals, particularly phenols, when selectively depolymerised *via* pyrolysis, hydrogenolysis, hydrolysis or enzymatic disassembly reactions.[154,155] Guaiacol is a typical lignin breakdown product that has been recently used as phenolic building block to prepare benzoxazine monomers. Using a solventless synthesis procedure and starting materials entirely derived from biobased feedstocks, guaiacol was combined with furfurylamine and stearyl amine in the presence of paraformaldehyde to prepare benzoxazine monomers Bz61 and Bz62 (Scheme 1.24).[156] Furfurylamine has also been incorporated into other petroleum-based polybenzoxazine systems.[157,158] Industrially, furfurylamine is obtained from furfural. On the other hand, stearylamine can be produced from vegetable oils. Bz61 and Bz62 were obtained in high yields as white solids with melting points at 97 and 59ºC, respectively. Homopolymerization of both monomers was investigated. Bz61 and Bz62 homopolymers exhibited T_g values of 150 and 93ºC, indicating that furfurylamine-based benzoxazine has higher crosslinking density and backbone rigidity. In fact, the furan moiety of Bz61



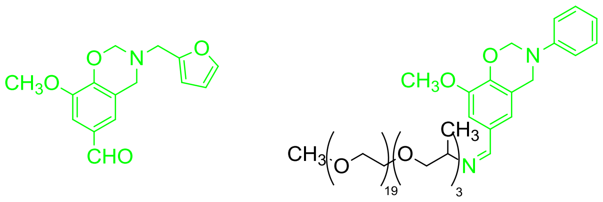
Bz61

Bz62

Scheme 1.24. Synthesis of fully biobased guaiacol-derived benzoxazines.

participates in ROP of benzoxazines *via* electrophilic aromatic substitution. Finally, both benzoxazines were copolymerized in order to improve the crosslinking density of the resins and therefore enhance properties such as T_g, thermal stability and char yield. Thermogravimetric analysis (TGA) results showed a remarkable improvement of the char yields for the copolymers, with the char yields of all the copolymers exceeding that of the neat polybenzoxazine derived from Bz62. Furthermore, the addition of methyl *p*-toluensulfonate to Bz61 demonstrated to significantly improve its polymerization behaviour, producing a decrease in the polymerization temperature from 240 to 174ºC, a shortening of the time required to reach the gel point on heating at 200ºC from 47 to 20 min, and an increase in the char yield at 800ºC of the cured resin from 53 to 62%.[159]

Another renewable natural resource that can be obtained in large quantities from lignin is vanillin.[160,161] Vanillin is of great interest for benzoxazine chemistry because contains an aldehyde group that is not expected to be consumed during benzoxazine synthesis. In fact, Varma et al.[162] synthesized and characterized a renewable benzoxaine monomer from vanillin, furfurylamine and paraformaldehyde using a solventless method (Bz63, Scheme 1.25). Interestingly, DSC analysis of Bz63 shows a low temperature curing behaviour, showing a curing exhotherm in the range of 179-232ºC with a maximum at 205ºC. This low curing temperature was attributed to the oxidation of formyl group to carboxylic groups which catalyses the ROP of benzoxazines. On the other hand, Ishida et al.[163]



Bz63 **Bz64**

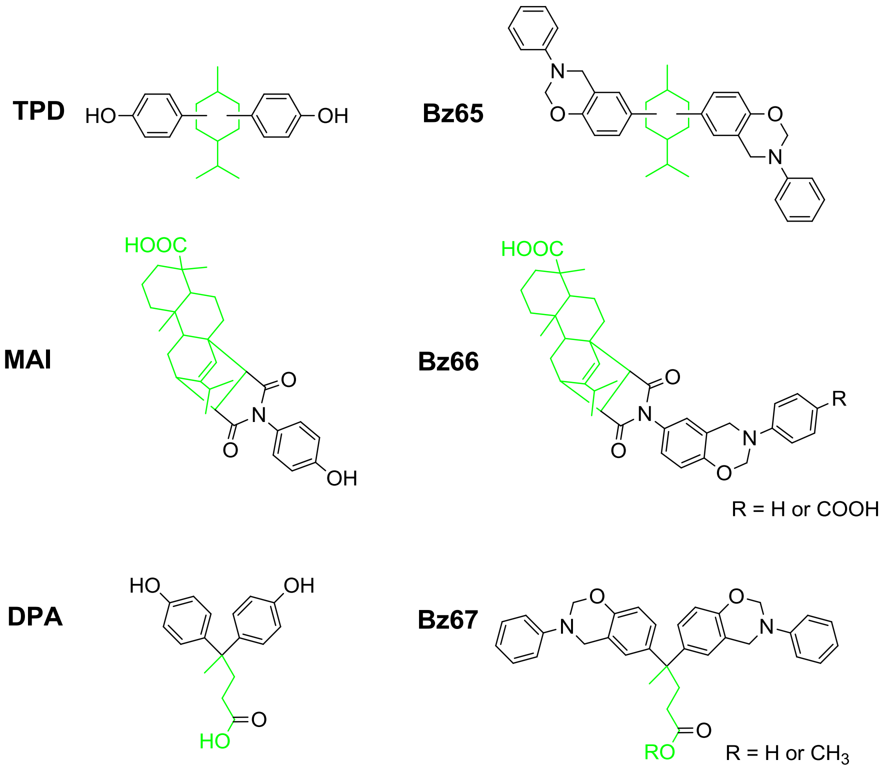
Scheme 1.25. Chemical structure of vanillin-based mono-benzoxazines.

exploited the aldehyde group of vanillin/aniline benzoxazine to expand benzoxazine applications as surfactants. The aldehyde of N-phenyl vanillin-derived benzoxazine monomer was further reacted with amine terminated poly(ethylene oxide) to form a benzoxazine surfactant Bz64. Emulsification using Bz64 was successful in producing polystyrene particles of 627 nm in average diameter with a polydispersity of 1.24, determined by dynamic light scattering (DLS). The miniemulsion was stable for up to 2 weeks without significant deposition.

1.5.1.3 *Biobased synthetic phenols as platform chemicals for benzoxazine technology*

The utilization of partially biobased phenols is an alternative approach to incorporate natural components into benzoxazine monomers. Terpenediphenol (TPD) and maleopimaric acid imidophenol (MAI) are succesfull examples; altough diphenolic acid (DPA) is the product that has received much attention (Scheme 1.26).

TPD is one of the most important derivative of terpenes, which are important natural compounds widely produced by various plants, typically conifers. TPD, synthesized from terpene compounds that are continued in pine or orange rind, and excess phenol has a rigid molecule structure of the aromatic and cyclohexane rings, thus TPD is expected to be a monomer for high T_g and high dimensional stability bioplastics. With the aim to improve the mechanical and water resistance properties of benzoxazine/epoxy resins, 1,3- and 2,8-TPD-derived N-phenyl benzoxazine monomers were synthesized in 1,4-dioxane or THF as a solvent from a TPD mixture containing 2:1 ratio of both structural isomers.[126] 1,3- and 2,8-Bz65 were copolymerized with equimolar amounts of diglycidyl ether of bisphenol A (DGEBA), and the cured resins had superior heat resistance, electrical insulation and especially water resistance, compared with the cured resin from BPA type novolac and epoxy resin. The percent of water absorption after boiling for 2h was improved from



Scheme 1.26. Chemical structure of terpendiphenol (TPD), maleopimaric acid (MAI), and diphenolic acid (DPA) as well as their corresponding *N*-phenyl benzoxazines.

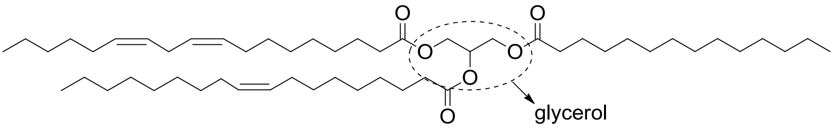
0.54 wt-% for BPA benzoxazine/epoxy mixture to 0.28 wt-% for 2,8-Bz65/ DGEBA resin. In fact, the polybenzoxazine rigidity, inferred by the inclusion of the TPD rigid hydrocarbon ring into the network structure, contributes to decrease water absorption. MAI is another rigid structure that has been used as partially biobased phenolic component in benzoxazine monomers (Bz66, Scheme 1.26).[164] MAI was obtained from rosin, which is a versatile natural mixture of unsaturated polycyclic carboxylic acids, especially abietic acid, obtained from pines and some other plants, in two steps: Diels-Alder reaction with maleic anhydride and reaction with *p*-aminophenol with a global yield of 41%. Bz66 could not be prepared by a solventless method due to the high melting point of MAI. Thermal polymerization behaviour of Bz66 was influenced by the steric hindrance of the hydrogenated phenantrene ring, showing higher polymerization temperatures than conventional mono-functional benzoxazines. On the other hand, the resulting polymers exhibited outstanding thermal stability and char yield.

As mentioned above, DPA is the most outstanding example of synthetic partially biobased phenol exploited by benzoxazine technology. DPA is a condensation product of phenol and levulinic acid, a cheap platform chemical that can be commercially produced from cellulose-rich biomass (especially from waste biomass).[165] The research interest resulted from that DPA has a structure similar to BPA, a key industrial monomer under health concerns. Our group reported the preparation of two benzoxazine monomers Bz67 (R=H and CH_3) from DPA and DPA methyl ester, respectively.[166] The thermal activated polymerization of both monomers was investigated and compared to BPA-derived benzoxazine. As expected, Bz67 (R=H) could be polymerized at lower temperatures due to the presence of carboxylic acid group. Interestingly, both DPA-derived monomers afforded thermosetting polybenzoxazines with higher T_g, 270 and 208ºC respectively, and higher crosslinking density compared to BPA-derived system (T_g= 172ºC). These results were attributed to the transesterification or esterification reactions occurred during curing process on basis to FTIR data. In addition, Bz67 (R=H) enabled the preparation of rigid foams as well as flame retardant counterparts through a self- induced foaming process.[167,168] The foaming approach described relies on the *in situ* generation of CO_2 *via* decarboxylation during the thermal curing.[169] Moreover, by adding neat carbon nanotubes, nanocomposite materials were prepared with low percolation threshold and improved thermal and fire properties.[170]

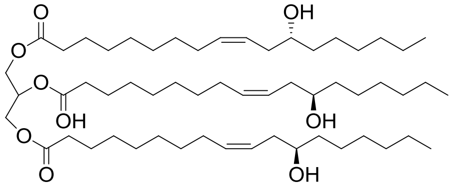
1.6 10-Undecenoic Acid as a Biobased Aliphatic Block for Flexible Polybenzoxazines Preparation

As reviewed above, several examples of benzoxazine monomers prepared from renewable resources have been reported but only structures coming from cardanol,[130-140] urushiol,[143] and sterylamine[156] incorporate flexible aliphatic moieties. Vegetable oils are attractive and versatile platform chemicals when aliphatic moieties are needed in the monomer design. Vegetable oils are one of the cheapest and most abundant biological resources available in large quantities and are predominantly a mixture of triglyceride molecules.[171] Triglycerides are made up of three fatty acids joined at a glycerol junction (Scheme 1.27). Most of the common oils contain fatty acids vary from 12 to 22 carbons in length, with 0 to 3 internal double bonds per fatty acids. Numerous examples of vegetable oils and fatty acid-based polymers have been described until now. [172,173]

The first generation of plant oils polymers was mainly based on edible feedstocks. However, as the food-versus-chemicals debate ascended, the focus is progressively diverterting to non-edible oils. Among them, castor oil (Scheme 1.28) is one of the most versatile, being its end user market already quite diverse. Castor oil is a plant-oil obtained from extracting or expressing the seeds of the castor bean plant *Ricinus communis* (Euphorbiaceae),[174] which grows in tropical and subtropical areas. The main producer of castor oil all over word is India, after that China and Brazil are following.



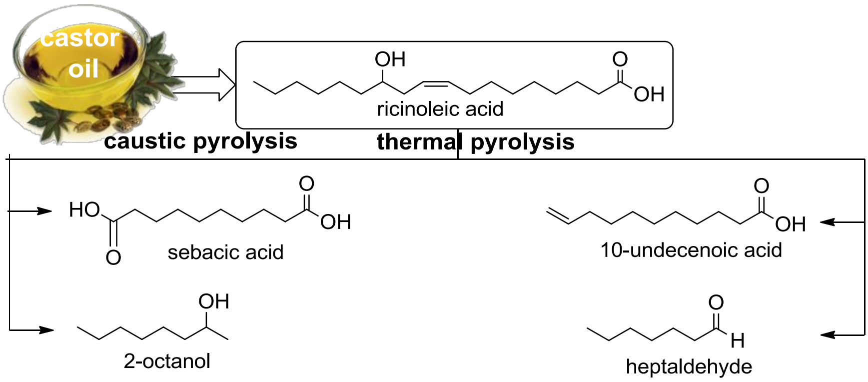
Scheme 1.27. Reprensentative chemical structure of trigylcerides.



Scheme 1.28. Reprensentative chemical structure of castor oil.

Castor oil is possibly the plant oil industry's most underappreciated asset.[175] With new applications being explored, especially in areas such as pharmaceuticals and biopolymers/bioplastics, the end user markets for castor oil and its derivatives are expected to expand significantly over the next few years.[176] This non-edible oil has tremendous future potential as a bioenergy and industrial feedstocks because of its high oil content, potential modifications in fatty acid composition, very high oil yields, wide range of adaptation, and ability to be grown on marginal sites subject to drought and saline conditions.[177] Consequently most of the international scientific community working on castor oil, believe that this crop will become a major crop used for production of plant lipids for both energy and industrial applications

The originality of castor oil relies in its chemical nature. The specificities come from: the high content (up to 85%) of a particular fatty acid, the ricinoleic acid, which has a unique structure that combines a double bond and additional hydroxyl functionality inside its linear chain comprising 18 C atoms (Scheme 1.29). After alcoholisis of castor oil, the resulting ricinoleic acid can be subjected to various treatments.[178- 181] The oldest and more usual is to crack under alkaline conditions (caustic pyrolisis) leading to capryl alcohol (2-octanol) and sebacic acid (decanodioic acid).[178] In an alternative process the methyl ester of ricinoleic acid is cleaved by steam cracking (pyrolisis at elevated temperature) into n-heptaldehyde and methyl 10-undeceneoate.



Scheme 1.29. Caustic pyrolisis of castor oil and thermal pyrolisis of ricinoilec acid.

Both processes are basically carried out to produce sebacic acid for the polyester industry (EcoPaxx® from DSM, Oleris® from Arkema) and 10-undecenoic acid for the polyamide industry (Rilsan® range of products from Arkema).

Nowadays, 10-undecenoic acid and derivatives are in the spotlight of polymer chemistry community and are already considerd valuable, renawable building blocks for design of monomers and polymers.[182-188] In particular, academic research has exploited 10-undecenoic acid *via* metathesis and thiol-ene coupling reactions to produce a broad palette of polycondensate precursors such as hydroxyesters, diesters, diols, and diacids.[189-204] However, to the best of our knowledge 10-undecenoic acid has not yet been used in benzoxazine technology. The incorporation of this biobased product into benzoxazine monomers and polymers as flexible aliphatic block is envisioned as a novel route to improve toughness, flexibility, and processability as well as incorporate renewable resources into polybenzoxazines.

Scope And Objectives

Scope and Objectives

Polybenzoxazines are a relatively new class of polymeric phenolic resins, having a wide range of interesting features and the capability to overcome several shortcomings of conventional novolac and resole type phenolic resins. As mentioned in the introduction, in recent years polybenzoxazine research has focused on four main topics. Three of them; the decrease of polymerization temperature, increase of crosslinking density, and improvement of toughness and flexibility, are related to intrinsic properties of these materials, whereas the fourth debates on the possibility to prepare their precursors from renewable resources. To address two of these topics, the general purpose of this thesis is the preparation and characterization of novel flexible and tough polybenzoxazine materials from renewable resources. To achieve this goal, we propose the incorporation of fatty acid derivatives into benzoxazine monomers and polymers as flexible biobased segments. In particular, we have focused on 10-undecenoic acid because is a non-edible oil (castor oil derivative) with an aliphatic skeleton that contains two α,ω reactive points.

These general objectives have been applied to three groups of polybenzoxazine precursors as described below:

a) α,ω-*Bis*-benzoxazine monomers obtained by hydrosilylation reaction.

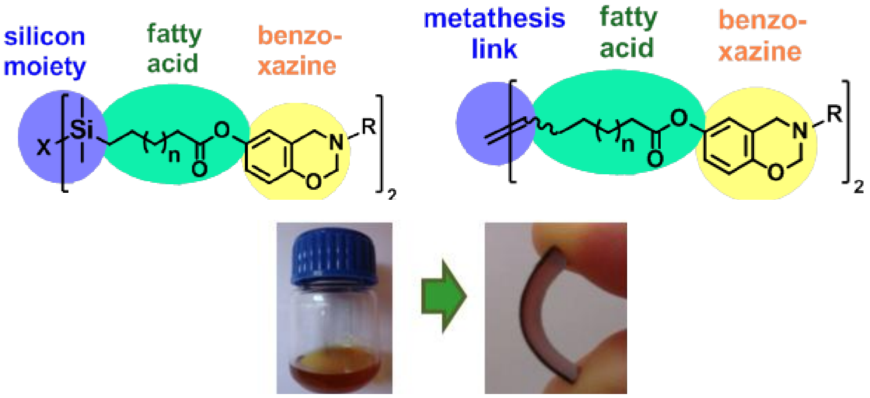
b) α,ω-*Bis*-benzoxazine monomers obtained by metathesis reaction.

c) Main chain benzoxazine polymers obtained by acyclic diene metathesis polymerization.

Results And Discussions

3.1 Synthesis, Polymerization and Properties of α,ω-*bis*-Benzoxazine Monomers Obtained by Hydrosilylation or Metathesis

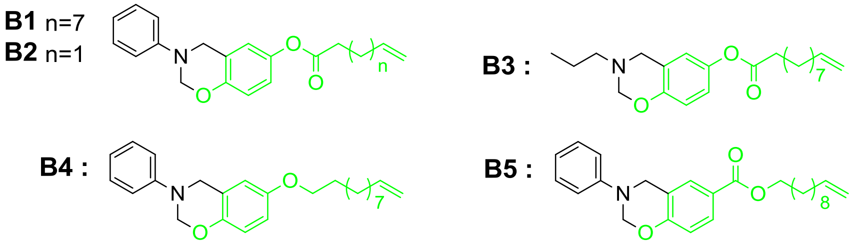
The synthesis, polymerization behaviour, and material properties of α,ω-*bis*-benzoxazine monomers containing biobased aliphatic spacers of different chain legth are described. First, a series of monofunctional benzoxazine monomers with terminal unsaturated alkyl chains were synthesized by combining *via* a Mannich-type reaction two castor oil derivatives (10-undecenoic acid and 10-undecenol) and 4-pentenoic acid with hydroquinone or 4-hydroxybenzoic acid. In the second step, the monofunctional monomers were dimerized under mild conditions by hydrosilylation reaction using two difunctional silanes, 1,1,3,3-tetramethyldisiloxane and 1,4-phenylene-*bis*-dimethylsilane, or metathesis reaction. Both dimerization proceses were optimized in terms of catalysts, reaction temperature, and time to produce the desired dimers in good yield and high purity. Finally, the characteristics and thermal polymerization behaviour of the resulting α,ω–*bis*-benzoxazines were studied. The properties of the resulting flexible materials were evaluated by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and dynamomechanical thermal analysis (DMTA).



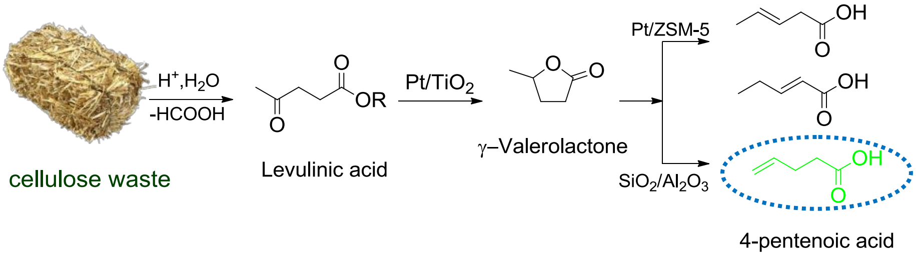
3.1.1 Monofunctional Benzoxazine Synthesis

A set of five ω-unsaturated alkyl benzoxazines have been synthesized combining two castor oil derivatives (10-undecenoic acid and 10-undecenol) and 4-pentenoic acid with hydroquinone or 4-hydroxybenzoic acid *via* a Mannich-type reaction (Scheme 3.1).

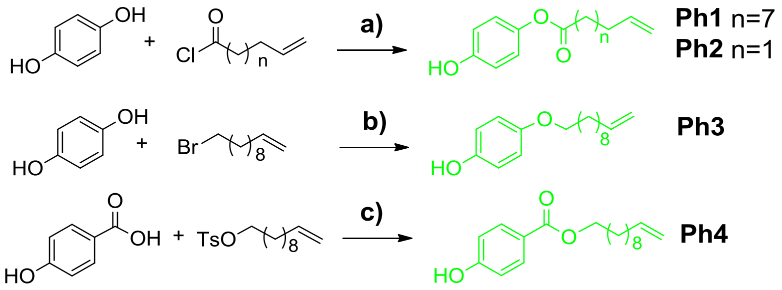
4-Pentenoic acid, hydroquinone, and 4-hydroxybenzoic acid can also be considered biobased products. They are currently produced from petrochemical feedstock's but recently alternative green processes have been described to produce them from renewable feedstocks. The catalytic hydrogenation of the cellulose-derived levulinic acid[205] to γ-valerolactone and the subsequent acid-supported ring opening to produce 4-pentenoic acid together with its isomers has been reported (Scheme 3.2).[206,207]



Scheme 3.1. Chemical structure of ω-unsaturated alkyl benzoxazines.



Scheme 3.2. Synthesis of 4-pentenoic acid from cellulose waste.



Scheme 3.3. Synthesis and chemical structure of ω-unsaturated phenols: a) THF/Py, 0ºC to 70ºC; b) KOH/EtOH, 80ºC; c) 1) K_2CO_3, DMAC, 80ºC, 2) DMSO, 110ºC.

In addition, hydroquinone can be produced from D-glucose derived quinic acid[208] and 4-hydroxybenzoic can be produced from lignocellullosic waste.[209]

The synthesis of ω-unsaturated alkyl benzoxazines was carried out in two steps. In the first step, four different phenols with aliphatic chains attached to the para position through ether or O-CO/CO-O ester linkages were prepared using hydroquinone or 4-hydroxybenzoic acid as aromatic building blocks (Scheme 3.3). 4-hydroxyphenyl-10-undecenoate (Ph1) and 4-hydroxyphenyl-4-pentonoate (Ph2) were synthesized by reaction of 10-undecenoyl chloride and 4-pentenoyl chloride with an excess of hydroquinone. 4-(10-Undecenyloxy) phenol (Ph3) and 10-undecenyl 4-hydroxylbenzoate (Ph4) were synthesized respectively following a modification of reported procedures.[210,211] In the case of the *p*-hydroxybenzoate ester, DMAC is described as reaction solvent but using DMSO resulted in a drastic reduction of by-products percentage. The structure of these phenol compounds was confirmed by ^{1}H- and ^{13}C-NMR analysis. As can be seen Figure 3.1, ^{1}H-NMR spectra of the synthesized phenols are consistent with the proposed structures. The typical resonance of –C**H**=CH$_2$ and –CH=C**H**$_2$ appeared between 5.8-5.7 ppm and 4.0-4.9 ppm, for Ph1, Ph3, and Ph4, respectively. In the case of Ph2 appeared between 5.9-5.8 ppm and 5.1-5.0 ppm, respectively. The resonance of –OH was mobile due to the NMR conditions.

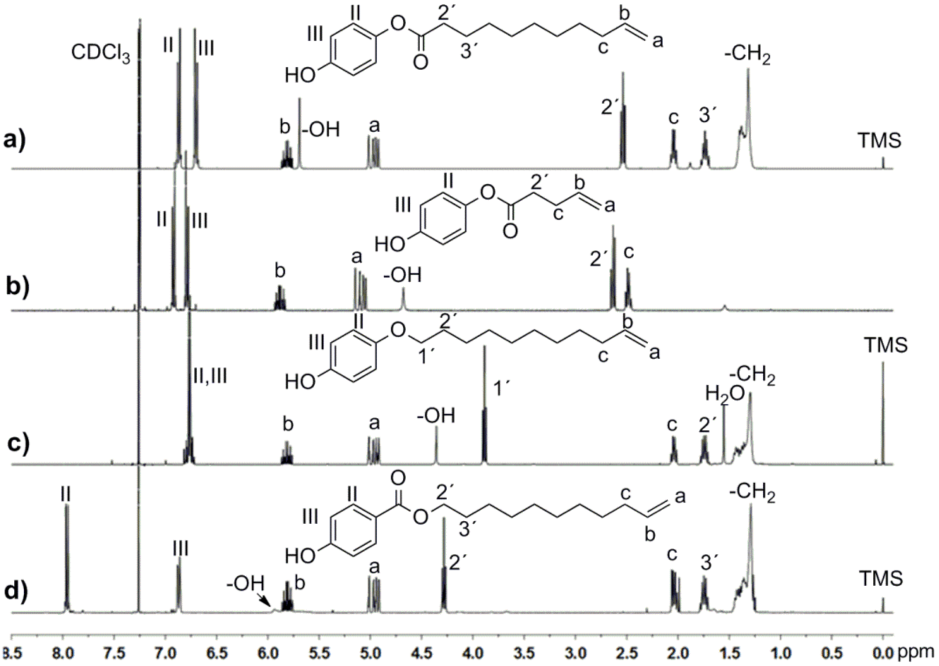
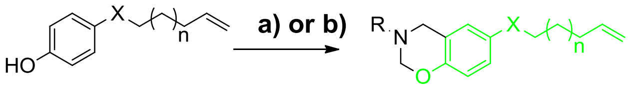


Figure 3.1. ^{1}H-NMR spectra of ω-unsaturated phenols; a) Ph1, b) Ph2, c) Ph3, and d) Ph4.

In the next step, the synthesized phenols were converted into the corresponding benzoxazine monomers (B1-5). Building the benzoxazine ring is generally simply accomplished by reaction of a phenol, formaldehyde solution and an amine. The main drawback of this basic procedure is the extensive formation of oligomers, which reduces the yield of benzoxazine and difficults the purification. This undesired side-reaction has been reported to be promoted by water, polar solvents, and high temperatures.[8,33,35] In practice, oligomer formation can be minimized by using paraformaldehyde instead of formaldehyde solution and a triazine derivative instead of the pure amine in bulk condutions or with the help of apolar solvents such as toluene.[8,30] Synthesis of N-phenyl benzoxazines B1, B2, B4, and B5 was carried out using 1,3,5-triphenylhexahydro-1,3,5-triazine and paraformaldehyde in toluene (method a in Scheme 3.4).



	X	n	R
B1	: OOC	6	Ph
B2	: OOC	0	Ph
B3	: OOC	6	n-Pr
B4	: O	7	Ph
B5	: COO	6	Ph

Scheme 3.4. General synthesis of ω-unsaturated benzoxazine monomers: a) 1,3,5-triphenylhexahydro-1,3,5-triazine, paraformaldehyde, toluene, 90ºC (B1, B2, B4, and B5); b) n-propylamine, paraformaldehyde, bulk 80ºC (B3).

The nature of the substituted attached to nitrogen also plays an important role on the curing behavior of the benzoxazine ring[46,63] giving materials with Mannich-bridges of different thermal stability.[47,212] Thus, the n-propyl benzoxazine B3 was considered for comparative purpose. In the case of B3, n-propylamine and paraformaldehyde in bulk was used (method b in Scheme 3.4) since aliphatic triazines are not easy accessible.

Following these procedures, monomers B1 to B5 were prepared in 60 to 80% yield as low melting point solids (B1, B2 and B4) or oils (B3 and B5). The structure of these compounds was confirmed by ^{1}H- and ^{13}C-NMR analysis. As can be seen in Figure 3.2a the typical characteristic resonances of -Ph-CH_2-N- and –O-CH_2-N- appeared at 5.3 and 4.6 ppm for B1,B2, B4, and B5, and 4.8 and 3.9 ppm in the case of B3, confirming the presence of cyclic benzoxazine structure. The same trends are observed in the ^{13}C-NMR spectra (Figure 3.2b), where the characteristic resonance of –O-CH_2-N- and -Ph-CH_2-N- appeared at 79.7 and 50.5 ppm for B1,B2, B4, and B5, and 82.7 and 50.3 ppm in the case of B3.

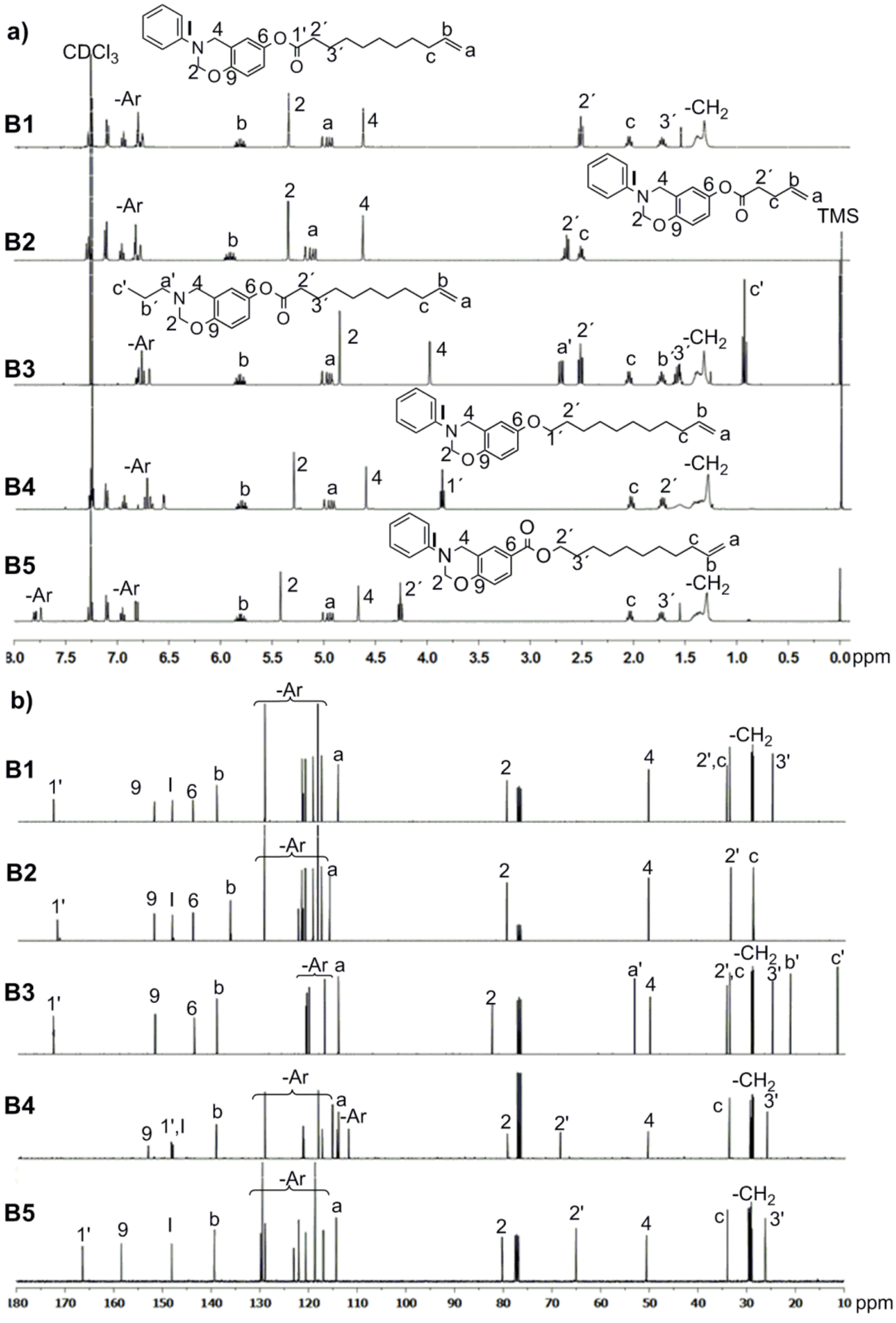
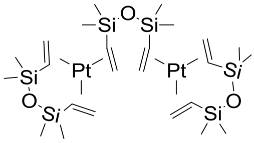


Figure 3.2. a) ^{1}H- and b)^{13}C-NMR spectra of ω-unsaturated benzoxazine monomers.

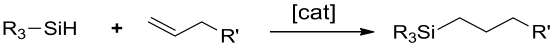
3.1.2 α,ω-*bis*-Benzoxazine Synthesis via Hydrosilylation

Hydrosilylation of olefins, the addition of a silicon-hydride bond across a carbon-carbon double bond, is among the most important and widely used methods for the production of industrially important organosilicon compounds.[213-216] Olefin hydrosilylation was discovered in 1947 by Sommer et al.[217] as a radical-mediated reaction of trichlorosilane and 1-octene in the presence of peroxide with low selectivity. Even, Si-H addition to double bonds is catalyzed by a variety of transition metal complexes[218] the discovery in 1955 of hexachloroplatinic acid ($H_2PtCl_6.6H_2O$ in isopropanol, Speier's catalyst) led this transformation to be widely adopted and applied in the silicone chemistry.[219,220] Later, Karstedt[221] developed platinum(0) complexes containing vinyl-siloxane ligands which showed better solubility and higher catalytic activity than Speier's catalyst.[222-224] Pt-based catalysts have good tolerance to functional groups and high selectivity in the addition of hydrosilanes to carbon-carbon double bonds. Thus, commercially available Karstedt's catalyst [Pt_2(*sym*-tetramethyldivinyldisiloxane)$_3$] (Scheme 3.5) and Speier's catalyst are the most commonly used catalysts for the hydrosilylation processes and.

It is well documented[213,219,220] that the hydrosilylation of 1-alkenes is catalyzed by transition metals and proceeds with anti-Markovnikov selectivity (β–addition), leading to 1-silylalkenes (Scheme 3.6).



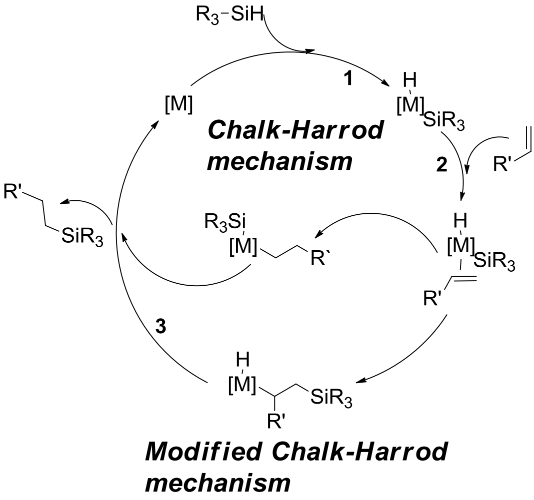
Scheme 3.5. Formula of Karstedt's catalyst.



Scheme 3.6. Transition metal catalyzed hydrosilylation of 1-alkene.

Several mechanisms have been proposed for the platinum-catalyzed homogenous hydrosilylation reaction. The most commonly cited mechanism was developed by Chalk and Harrod in 1965.[225] The Chalk-Harrod mechanism, as it is shown in Scheme 3.7, consists of three important elementary steps: 1) oxidative addition of Si-H to the metal alkene complex, 2) migratory insertion of coordinated alkene into the M-H bond, and 3) reductive elimination of Si-C product and regeneration of metal alkene complex. However, this mechanism could not explain the induction period or the formation of vinylsilanes.

Thus, another mechanism called the modified Chalk-Harrod mechanism was proposed (Scheme 3.7).[226] This mechanism describes the migratory olefin insertion into the M-Si bond rather than into the M-H bond followed by the C-H reductive elimination. In addition, Lewis et al.[227,228] proposed an alternative mechanism based on colloid formation in the initial step which explains the induction period.

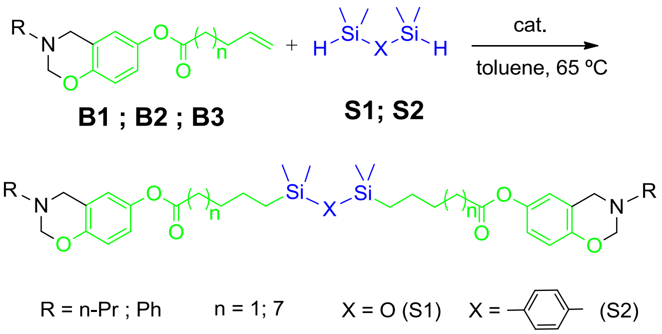


Scheme 3.7. Chalk-Harrod and modified Chalk-Harrod mechanism of transition metal catalyzed hydrosilylation of alkenes.

Hydrosilylation of double bonds is a well established methodology that allows efficiently coupling different reactive moieties in very high conversions and usually under mild conditions.[229] Hydrosilylation has already been applied to unsaturated fatty acids[230-237] and has been used to prepare main chain flexible polybenzoxazines as described previously.[115,116,238]

In this work, α,ω-*bis*-benzoxazines (BS) synthesis was carried out via hydrosilylation of 6-(ω-alkenoyloxy)benzoxazines (B1-3) with two difunctional silanes having different Si-H reactivity: 1,1,3,3-tetramethyldisiloxane (S1) and 1,4-phenylene-bis-dimethylsilane (S2) (Scheme 3.8).

In order to find the appropriate experimental conditions for the hydrosilylation of the benzoxazine substrates, several experiments using Karstedt's catalyst at different catalyst loadings and temperatures were carried out. In all cases a Si-H/CH_2=CH- stoichiometric ratio was used and the progress of the reaction was monitored by ^{1}H-NMR after 24h (Table 3.1).



Scheme 3.8. Hydrosilylation of the 6-(ω-alkenoyloxy)benzoxazines with disilanes S1 and S2.

Table 3.1 Hydrosilylation of benzoxazines B1, B2, and B3 with disilanes S1 and S2 after 24h under different conditions.

Entry	Monomer/ silane	Cat (%)[a]	T (°C)	Si-C (%)[b]	CH_2=CH (%)[c]	CH=CH (%)[d]
1[e]	B1/S1	0.04	25	29.3	70.5	--
2	B1/S1	0.04	25	76.5	23.5	--
3	B1/S1	0.04	65	96.5	3.5	< 1
4	B2/S1	0.04	25	69.2	30.8	--
5	B2/S1	0.04	65	97.3	2.7	< 1
6	B3/S1	0.04	25	0.5	99.5	--
7	B3/S1	0.04	65	33.6	53.0	13.4
8	B3/S1	0.09	65	46.5	21.8	31.7
9	B3/S1	0.15	65	90.2	2.2	7.6
10	B3/S1	0.04	90	52.2	17.1	25.7
11	B1/S2	0.04	25	89.3	9.7	< 1
12	B1/S2	0.04	65	98.0	< 1	1.8
13	B2/S2	0.04	25	85.6	14.4	< 1
14	B2/S2	0.04	65	98.0	< 1	2.0
15	B3/S2	0.04	65	49.1	17.2	33.7
16	B3/S2	0.15	65	91.2	1.6	7.2

[a] Molar percentage of platinum. [b] Determined by ^{1}H-NMR from the signal at 0.5 ppm (C**H**$_2$-Si). [c] Percentage of remaining starting double bond determined by ^{1}H-NMR from the signal at 4.9 ppm (B1 and B3) and 5.1 ppm (B2) (-CH=C**H**$_2$). [d] Percentage of double bond isomerization determined by ^{1}H-NMR from the signal at 5.4 ppm (-C**H**=C**H**). [e] Experiment using Speier's catalyst in THF.

Preliminary experiments using Speier's catalyst showed low activity towards our substrates as exemplified in Table 3.1 entry 1. Water in catalyst was found to have a negative effect by reacting in some extent with the benzoxazine ring. This behavior was even more significant when isopropyl alcohol (IPA) instead of THF was used as catalyst solvent. ^{1}H-NMR spectrum of the reaction product after 24h shows a decrease in the intensity of the double bonds signals and the appearance of new signals at 4.4, 4.2 and 3.8 ppm, which can be related with ring opening products. Benzoxazine ring opening by water or alcohols has been reported in the literature.[51] According to these results the rest of the study was carried out using Karstedt's catalyst.

As general trend in Table 3.1, monomers B1 and B2 show a similar reactivity whereas B3 is much less reactive. For monomers B1 and B2 at room temperature, incomplete hydrosilylation was observed after 24h (Entries 2, 4, 11, and 13) but higher conversions were reached for S2. This seems to indicate that S2 has higher reactivity when compared with S1 which is in the reverse order expected attending electronic effects.[233,239] Results in Table 3.1 indicate that hydrosilylation is clearly improved by temperature, thus at 65ºC (Entries 3, 5, 12, and 14) almost complete double bond consumption is reached. Under the conditions studied no significant double bond isomerisation was observed for monomers B1 and B2. Olefin isomerisation is a competitive reaction that generally occurs when less reactive silanes i.e. trialkylsilanes and less active catalysts were used.[239-241] Using the same catalyst conversion (0.04%), monomer B3 did not react at 25ºC (Entry 6), and only partial hydrosilylation (33.6% and 49.1%) was reached after 24h at 65ºC (Entries 7 and 15). In this case, it is worth to note that significant amounts of double bond isomerisation products were observed. Increasing temperature to 90ºC (Entry 10) does not improve the Si-H addition but significantly increases the amount of isomerised products. On the contrary, increasing the catalyst loading showed a beneficial effect in the reaction. At 65ºC, using 0.09% of platinum (Entry 8) an increase in both the hydrosilylation products was observed but about 22% of B3 still remain unreacted. With 0.15% of platinum (Entries 9 and 16) the hydrosilylation proceeds fast enough to produce the desired addition products in good yield minimizing the isomerisation products that remain below 8% in both cases. B3 lower reactivity has to be related with the aliphatic nature of the benzoxazine nitrogen substituent. Platinum catalyst can tolerate a wide range of functional groups but inhibition can occur in presence of groups with strong coordinating character.[242] Amines are among the compounds that have been described to coordinate with the active platinum centers thus poisoning the catalyst or reducing its activity.[243,244] In our case, monomers have two different tertiary amine groups: B1 and B2 are derived from an aromatic amine, whereas B3 is derived from n-propylamine and so, strong coordination with the catalyst active sites and reduction of their activity can be expected for the latter.

For curing experiments and material characterization the synthesis was scaled up to 10 mmol using selected conditions according to Table 3.1: Karstedt's catalyst; [CH_2=CH-] = 1M in toluene; stoichiometric Si-H/CH_2=CH ratio; 65ºC and 24h. Catalyst loading was adjusted according to relative monomer reactivity: 0.04% for B1 and B2 and 0.15% for B3. In this way α,ω-*bis*-benzoxazines B1S1, B1S2, B2S1, B2S2, B3S1, and B3S2 were purified by column chromatography to remove the Pt catalyst and obtained in good yields (77 to 90%) as pale yellow solids (B1S1, B1S2) or oils (B2S1, B2S2, B3S1, and B3S2). All monomers present excellent solubility in common solvents. Structure and absence of noticeable amounts of by-products were confirmed by ^{1}H-NMR, ^{13}C-NMR, and FTIR-ATR analysis. ^{1}H-NMR spectra of corresponding dimers (B1S2, B2S2, and B3S1) with all assignments are shown in Figure 3.3.

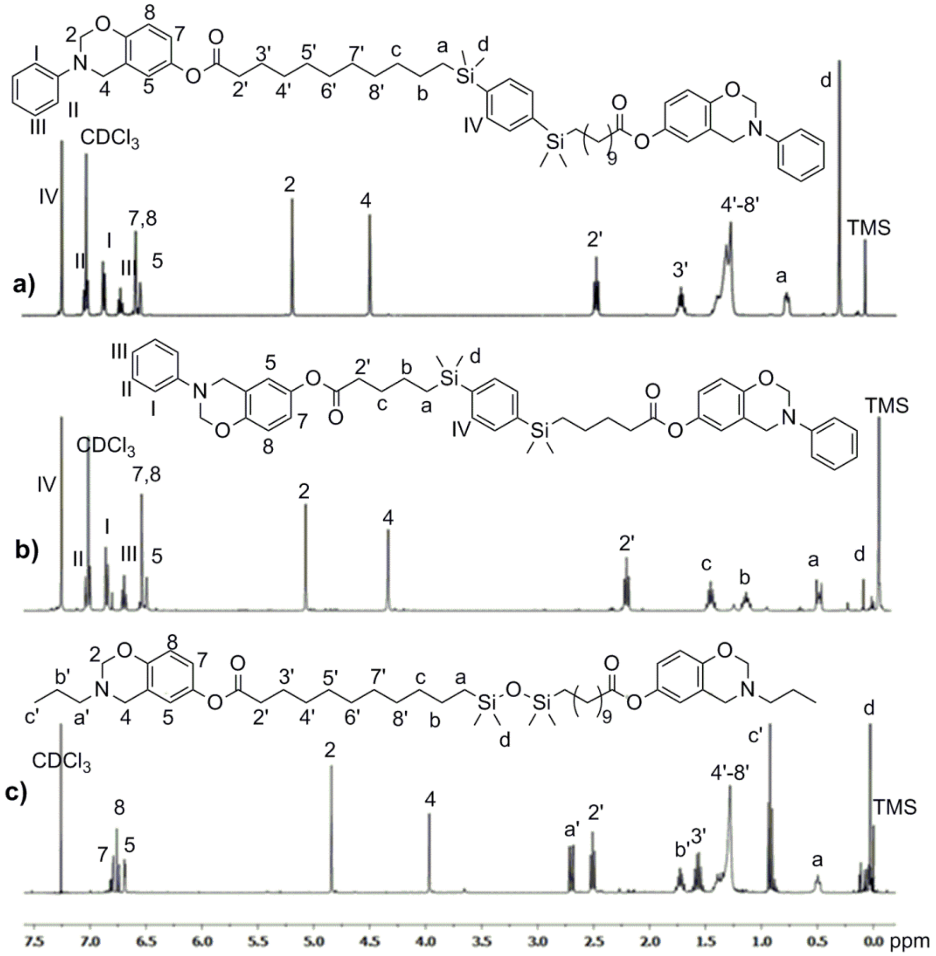
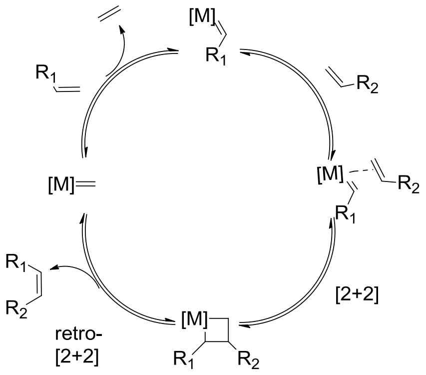


Figure 3.3. ^{1}H-NMR spectra of dimers: a) B1S2, b) B2S2, and c) B3S1.

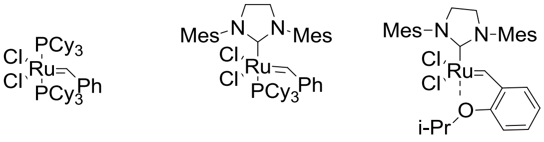
3.1.3 α,ω-*bis*-Benzoxazine Synthesis via Metathesis

Over the past decade, olefin metathesis has become a powerful synthetic tool in organic chemistry and polymer science as a versatile C-C bond forming reaction.[245-249] The importance of this reaction was recognized in 2005 with the Nobel Prize to Y. Chauvin, R. H. Grubbs, and R. R. Schrock.[250] In 1964, Banks and Bailey[251] performed the first investigation on olefin metathesis. However, it was not until 1967 that Calderon and co-workers[252,253] recognized that both ROP of unsaturated alicyclic compounds and the disproportionation of acyclic olefins were the same reaction and coined the term "olefin metathesis." ('Metathesis' from the Greek means 'changing of position'). Few years later, in 1971 Chauvin and Hérisson[254] proposed the commonly accepted mechanism of olefin metathesis. According to this mechanism the [2+2] cycloaddition reaction between an olefin and a transition metal alkylidene complex leads to form an intermediate metallacyclobutane. This intermediate then leads to a new olefin and a metallic alkylidene that have been exchanged carbons (Scheme 3.9).

After Chauvin[254] proposed the metathesis mechanism, the development of rational catalyst design became accelerated. In 1990 Schrock[255,256] introduced a well-defined, molybdenum-based catalyst. Mo-based catalysts are generally considered more reactive but also highly sensitive to air, moisture, and are less tolerant towards polar functional groups.[257,258] These drawbacks limit their applications. On the other hand, ruthenium-based catalysts exhibit quite good reactivity in a variety of metathesis processes under mild conditions and notable high tolerance to water, air, and various functional groups.[259,260]



Scheme 3.9. Olefin metathesis mechanism proposed by Chauvin and Hérisson.[254]

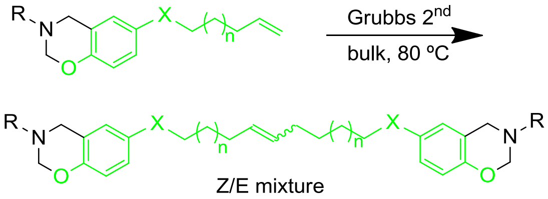


G1st **G2nd** **H-G2nd**

Scheme 3.10. Ru-based metathesis catalysts: Grubss 1st generation (G1st), Grubbs 2nd generation (G2nd), and Hoveyda-Grubbs 2nd generation (H-G2nd).

In the early of 1990s, Grubbs synthesized the first well-defined ruthenium based catalyst; Grubbs 1st generation (G1st).[261,262] This catalyst is based on a ruthenium atom surrounded by five ligands; two neutral electron-donating entities (e.g. trialkylphosphines, N-heterocyclic carbenes), two mono-anionic groups (e.g. halides), and one alkylidine group (e.g. unsubstituted and substituted methylidenes). G1st catalyst consists of tricyclohexyl phosphines as ligands. Although G1st catalyst is less active than the Schrock molybdenum-based catalyst, exhibits much higher functional group tolerance. Many groups have focused on developing catalytic activity, thermal stability and functional group tolerance.[263] Addressing these aims, 2nd generation catalyst systems have been developed by Grubbs and Hoveyda groups.[264-266] Thus, the substitution of one of the trialkyl phosphine ligands by an N-heterocyclic carbene (NHC) lead to the 2nd generation catalysts (Sceheme 3.10).

Olefin metathesis research in the last years has produced beneficial recognition of its potential applications.[267-269] Metathesis reactions have been shown to be an efficient and powerful tool for the synthesis of a wide variety of monomers and polymers.[245,270] The development of new highly active and robust metathesis catalysts[271,272] allows dimerizing or polymerizing unsaturated substrates in the presence of several functional groups as long as the terminal olefins are far enough apart from them. Thus, olefin metathesis exploits the synthetic potential of oleochemicals by using the intrinsic double



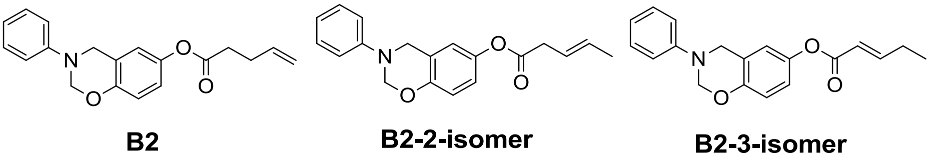
	X	n	R
MB1 :	OOC	6	Ph
MB2 :	OOC	0	Ph
MB3 :	OOC	6	n-Pr
MB4 :	O	7	Ph
MB5 :	COO	7	Ph

Scheme 3.11. Synthesis of the α,ω-*bis*-benzoxazine monomers.

bond functionality of fatty acids and their derivatives[191-194,273] but to our best knowledge they have not been used in the field of benzoxazines with exception of the polymerization of a norbornene monomer bearing thermally curable benzoxazine group *via* ring opening metathesis polymerization (ROMP) in the presence of G1st generation catalyst.[274]

In this work, α,ω-*bis*-benzoxazine monomers (MB) were preapared *via* self-metathesis (SM) of 6-(ω-alkenoyloxy)benzoxazines (B1-5) under bulk conditions at 80ºC in the presence of G1st, G2nd or H-G2nd (Scheme 3.11). To choose the appropriate catalyst and conditions for each unsaturated substrate, first several experiments varying the type, amount of catalyst, reaction time, and temperature were carried out.

As standard conditions 5% catalysis loading in bulk and 80ºC under vacuum (2 mmHg) were selected according to the reported literature.[191,192] G2nd and H-G2nd were tested because preliminary runs using G1st gave poor SM conversions. Reactions were monitored by ^{1}H-NMR spectroscopy measuring the amount of SM, non reacted or isomerised products. The percentage of SM product was determined from the intensity of the (C**H**=C**H**) signal at 5.5 ppm whereas the percentage of remaining starting product was determined from the intensity of the (CH=C**H**$_2$) signal at 4.9 ppm (B1, B3, B4, and B5) and 5.1 ppm (B2) (CH=C**H**$_2$). In the case of B2 extensive isomerisation of the starting product was observed (*vide infra*). In this case, the percentage of 3- and 2-pentenoate isomers were determined from the signals of the C**H**=C**H** groups at 6.1 ppm (3-isomer) and 5.7 ppm (2-isomer), respectively (Scheme 3.12, Figure 3.4)



Scheme 3.12. Chemical structure of B2 monobenzoxazine and its 3- and 2-isomers.

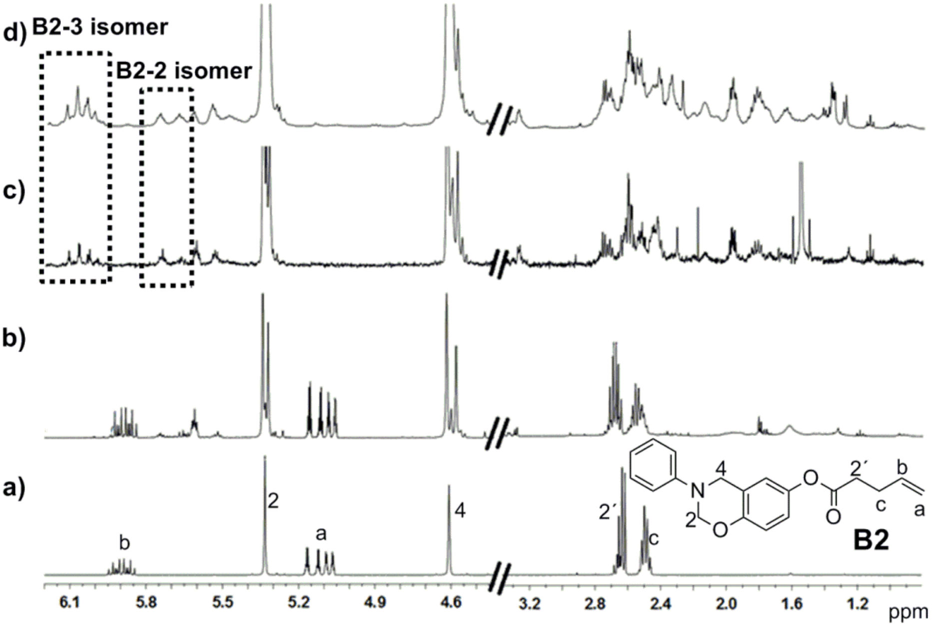


Figure 3.4. ^{1}H-NMR spectra of a) B2 benzoxazine monomer, b) in the presence of 10% p-benzoquinone and 5% G2nd at 40ºC, c) in the presence of 5% H-G2nd at 80ºC, and d) in the presence of 5% G2nd at 80ºC.

The experimental conditions tested and the obtained results are collected in Table 3.2.

Table 3.2. Metathesis of benzoxazines B1 to B5 under different conditions.

Entry	Monomer	Cat[a]	T (°C)/ t(h)	CH=CH (%)[b]	CH=CH$_2$ (%)[c]	2/3-CH=CH (%)[d]
1	B1	G2nd	80/8	96.0	4.0	--
2	B1	G2nd	80/24	99.5	<1	--
3	B1	H-G2nd	80/8	83.5	16.5	-
4	B1	H-G2nd	80/24	96.5	3.5	--
5	B2	G2nd	80/8	17.0	<1	35.5/47.5
6	B2	G2nd	80/24	14.4	<1	38.2/45.4
7	B2	G2nd	60/24	13.0	<1	39.5/47.5
8	B2	G2nd [f]	40/8	14.7	<1	35.0/50.3
9	B2[e]	G2nd	40/24	4.1	70.0	14.7/11.1
10	B2	H-G2nd	80/8	13.8	<1	46.9/37.6
11	B2	H-G2nd	80/24	15.5	< 1	45.8/38.2
12	B2	H-G2nd	60/24	10.3	<1	47.0/42.7
13	B2[e]	H-G2nd	40/24	8.10	80.8	0/11.1
14	B3	G2nd	80/8	96.8	3.2	--
15	B3	G2nd	80/24	99.8	<1	--
16	B3	H-G2nd	80/8	85.4	14.6	--
17	B3	H-G2nd	80/24	96.9	3.1	--
18	B4	G2nd	80/24	99.5	<1	--
19	B5	G2nd	80/24	99.8	<1	--

[a] Unless specified, 5% of catalyst was used. [b] Metathesis product by ^{1}H-NMR spectroscopy.[c] Starting product by ^{1}H-NMR spectroscopy. [d] Percentage of 3- and 2-pentenoate isomers of B2 determined by ^{1}H-NMR spectroscopy. [e] In presence of 10% *p*-benzoquinone. [f] 2% of catalyst was used.

In the case of B1 (Entries 1 to 4), good SM results were obtained with both catalyst but 24h were required for disappearance of the starting product, which was almost complete in the case of G2nd catalyst (Entry 2). Results for B2 were much more disappointing for both G2nd and H-G2nd catalyst. Even when the starting product was consumed in only 8h (Entries 5 and 10) the yield of SM product was very low and do not increase significantly with time (Entries 6 and 11). Detailed analysis of the crude reaction mixture revealed the extensive formation of 3- and 2-pentenoate isomers (>80%) (Scheme 3.12). Olefin isomerisation promoted by metathesis catalysts have been described for some specific substrates.[275] It seems to be related with the formation of metal hydride species by catalyst decomposition,[267] which in turn, is promoted by high temperatures, high catalyst loadings, and long reaction times. However, reducing reaction time, temperature, and catalyst loading (Entries 7, 8, and 12) gave no positive effect. Olefin isomerisation has also been described to be inhibited by certain additives. We carried out SM experiments in presence of 10% benzoquinone[276] (Entries 9 and 13) with no significant isomerisation inhibition but a reduction in the catalytic activity (Figure 3.4). It seems that under the studied conditions isomerisation of pentenoyl residues proceeds in a faster way than SM so; the synthesis of MB2 was dropped off.

SM of B3 (Entries 14 to 17) followed similar trends than the observed for B1, again 5% of G2nd catalyst after 24h at 80ºC leads to the best results. Thus, the same conditions were used to test SM of B4 (Entry 18) and B5 (Entry 19) with similar satisfactory results. In this way, the synthesis of the α,ω-*bis*-benzoxazine monomers MB1, MB3, MB4, and MB5 were finally scaled up using the above conditions and the resulting crude products purified by column chromatography to remove the Ru catalyst. Structure of monomers was confirmed by ^{1}H-NMR, ^{13}C-NMR and FTIR-ATR spectroscopy. The representative ^{1}H-NMR spectra of B5 and B4 (Figure 3.5) show the characteristic benzoxazine signals and the absence of signals attributable to ring opening products. All metathesis products are also characterized by two close triplets at c.a 5.4 ppm in some cases partially overlapped with the N-CH_2-O benzoxazine signal. These signals differ intensity and can be attributed to the E and Z isomers of the central double bond. The relative E/Z ratio resulting from the SM process could be estimated from 77:23 for MB5 to 81:19 for MB1 confirming that the metathesis process gives mostly the E isomer.[277]

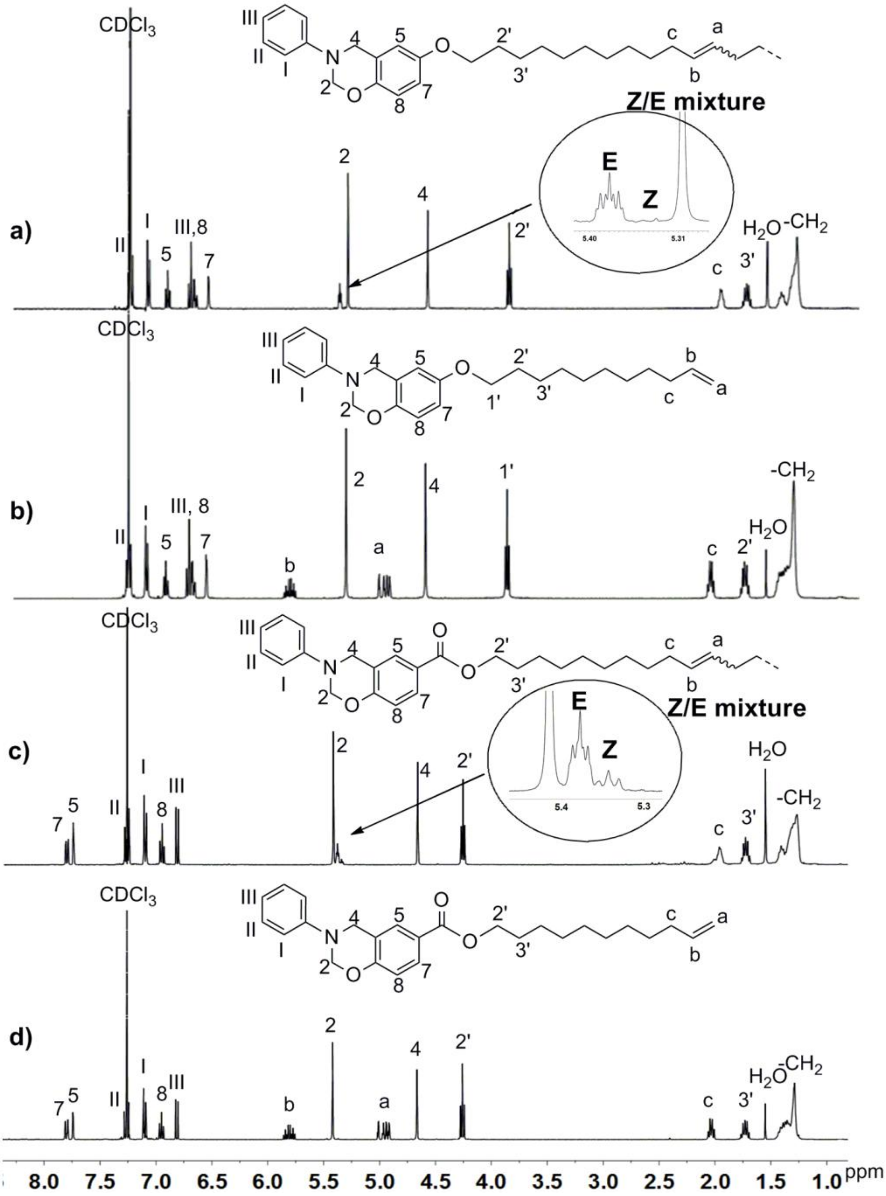


Figure 3.5. Representative ^{1}H-NMR spectra of a) MB4, b) B4, c) MB5, and d) B5. Region between 5.5 and 5.3 ppm has been expanded.

3.1.4 Curing of α,ω-*bis*-Benzoxazine Monomers

Before preparing thermoset materials, the thermal properties and curing behavior of the α,ω-*bis*-benzoxazines were analyzed by DSC and TGA and compared with their monofunctional benzoxazine precursors (Table 3.3).

Table 3.3. DSC and TGA characterization of mono and difunctional benzoxazine monomers.

	DSC			TGA		
Monomer	Tm (°C)[a]	T_o (°C)[b]	T_{max} (°C)[b]	$T_{5\%}$ (°C)[c]	T_{m1}/ T_{m2} (°C)[d]	T_{m1} (%)[e]
B1	52	259	271	268	273/451	6
B1S1	42	253	266	265	267/453	3
B1S2	82	254	266	267	266/452	5
MB1	62	256	266	266	261/450	4
B2	43	270	278	251	272/420	9
B2S1	-18	265	270	262	267/436	6
B2S2	0	252	263	275	263/432	3
B3	22	246	253	246	289/435	27
B3S1	-44	238	250	260	245/435	3
B3S2	-20	236	249	262	240/452	3
MB3	9	229	243	261	237/432	3
B4	50	262	274	253	268/456	12
MB4	122	258	268	247	251/445	6
B5	-52	253	263	251	258/456	7
MB5	-30	254	261	326	243/455	1

[a] Maximum temperature of the melting endotherm. [b] Onset (T_0) and maximum (T_{max}) temperatures of the curing exothermic peak. [c] Temperature of 5% weight loss. [d] Temperature of the maximum decomposition rate for the first (T_{m1}) and second (T_{m2}) stages. [e] Weight loss at the temperature of the maximum decomposition rate for the first (T_{m1}) stages.

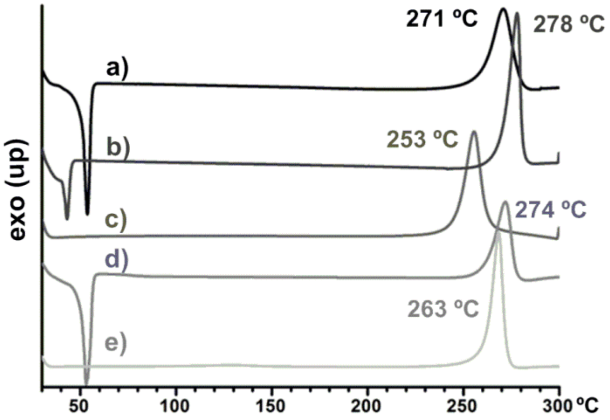


Figure 3.6. DSC thermograms of monofunctional benzoxazine monomers a) B1, b) B2, c) B3, d) B4, and e) B5.

As can be seen in Table 3.3 and Figure 3.6-8, ω-unsaturated monofunctional benzoxazine monomers exhibit melting endotherms between -52 and 52ºC and α,ω–*bis*-benzoxazine monomers present melting endotherms at temperatures between -30 and 122ºC. A significant influence of the monomer structure on melting temperatures is observed. With the exception of the relatively high melting point MB4, all *bis*-benzoxazine monomers have low melting points or are liquid at room temperature. This fact, together with their good solubility in common solvents such as DCM, THF, or acetone ensures an easy processability of these monomers.

Bis-benzoxazine derived from the aromatic silane (S2), as expected, present higher melting temperatures than their siloxane counterparts (S1). The length of the aliphatic spacer and the nature of the nitrogen substituent seem also to have a noticeable influence. In the case of B1, hydrosilylation gives solid products but in the case of B2, the resulting dimers are liquid. This probably can be related with the disturbing effect of the silane moiety which prevents short aliphatic chains to crystallize.

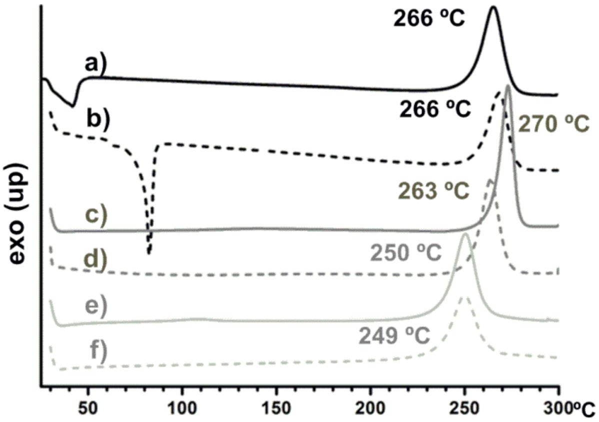


Figure 3.7. DSC thermograms of *bis*-functional benzoxazine dimers a) B1S1, b) B1S2, c) B2S1, d) B2S2, e) B3S1, and f) B3S2.

Substitution of the nitrogen phenyl group by the n-propyl group produces a decrease in the melting temperature of both, the monofunctional benzoxazine B3 and the resulting dimers B3S1 and B3S2.

In the case of the *bis*-benzoxazine obtained by metathesis reaction, N-n-propyl benzoxazine MB3 dimer has lower melting point than its N-phenyl counterpart MB1 due to its lower aromatic content. For N-phenylbenzoxazine series, B4 and MB4 have higher melting points than B5 and MB5 which are liquids at room temperatures. This can be related with their differences in structure flexibility which favors packing and crystallization. These monomers differ on the linking group between the benzoxazine ring and the aliphatic chain that change from a flexible ether linkage (Ar-O) to an increasing rigidity ester linkage (Ar-O-CO) and (Ar-CO-O).

In addition to melting endotherm, all benzoxazine monomers present a relatively sharp exothermic peak between 220 and 280ºC which is characteristic for the curing process of conventional non-activated

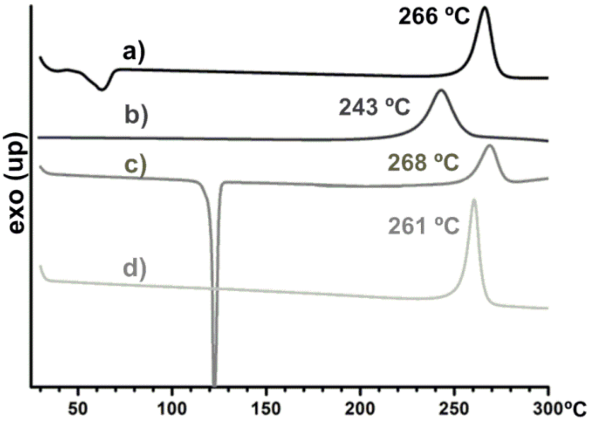


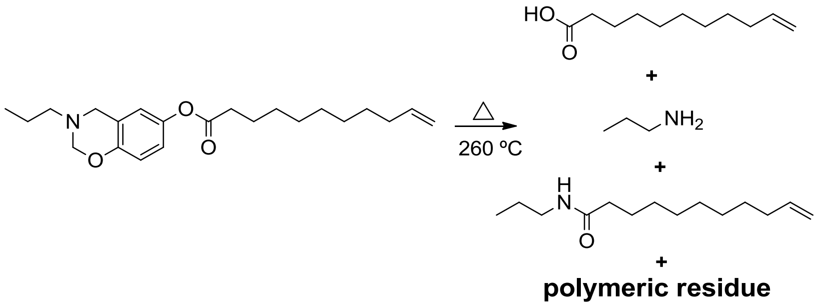
Figure 3.8. DSC thermograms of bi-functional benzoxazine dimers a) MB1, b) MB3, c) MB4, and d) MB5.

benzoxazines.[31] As expected, no significant differences were observed when monofunctional and difunctional benzoxazines were compared (Figure 3.6-8). Electronic influence of silicon moieties in *bis*-benzoxazines must be negligible as they are far away from the benzoxazine ring. Also, influence of the monomer structure on the curing temperatures seems to be less pronounced. It has been estabilished that electron withdrawing groups in position 6 activate the benzoxazine ring-opening,[31] conversely the maximum temperature of the curing exotherms follows the expected order MB4 (-O) > MB1 (-OOC-) > MB5 (-COO-) but in very close range of temperatures. Slightly lower curing temperatures were observed for B3 series monomers in agreement with higher reactivity of N-alkyl benzoxazines.

When thermal stability was analyzed by TGA, all benzoxazine monomers (B, BS, or MB type) presented two main degradation stages (Table 3.3). The first, at about 240-290ºC, occurs at the same temperature range than the exotermic peak observed by DSC and associated to the curing process. The second, much more prominent, is detected at 420-460ºC and can be associated to the complete degradation of the monomeric/oligomeric structure. According to the results, it is clear that thermal curing of most benzoxazine monomers overlaps in some extent with the first degradation stage. The weight loss at the temperature of the maximum degradation rate of the first stage is between 1 and 9% but significantly higher for the monofunctional precursors, especially in the case of B3 (27%) and B4 (12%). In the case of B3 and its difunctional benzoxazine derivatives, this early degradation seems to be inherent to the benzoxazine ring, thus it cannot be due to the silicon moieties or to remaining traces of platinum or ruthenium catalysts.

To gain more insight on the nature of the first degradation process, monobenzoxazines B1 and B3 were pyrolized at 260ºC and the volatile compounds analyzed by ^{1}H-NMR and GC-MS. In the case of B1, 10-undecenoic acid was detected as main product together with a small quantity of aniline. B3 also yielded to 10-undecenoic acid but much higher amounts of propylamine together with a small amount of the reaction product of both compounds, the N-propyl-10-undeceneamide (Scheme 3.13).

These results indicate that ester linkage is the weakest side in the structure and that aliphatic benzoxazine ring is rather unstable as reported in the literature.[47] In both cases ^{1}H-NMR analysis of the residue showed the disappearance of the methylene benzoxazine signals and the apparition of a broad signal at 3.9-3.4 ppm associated to Mannich bridges[39] formed in the



Scheme 3.13. Pyrolysis reaction of B3 monomer at 260ºC.

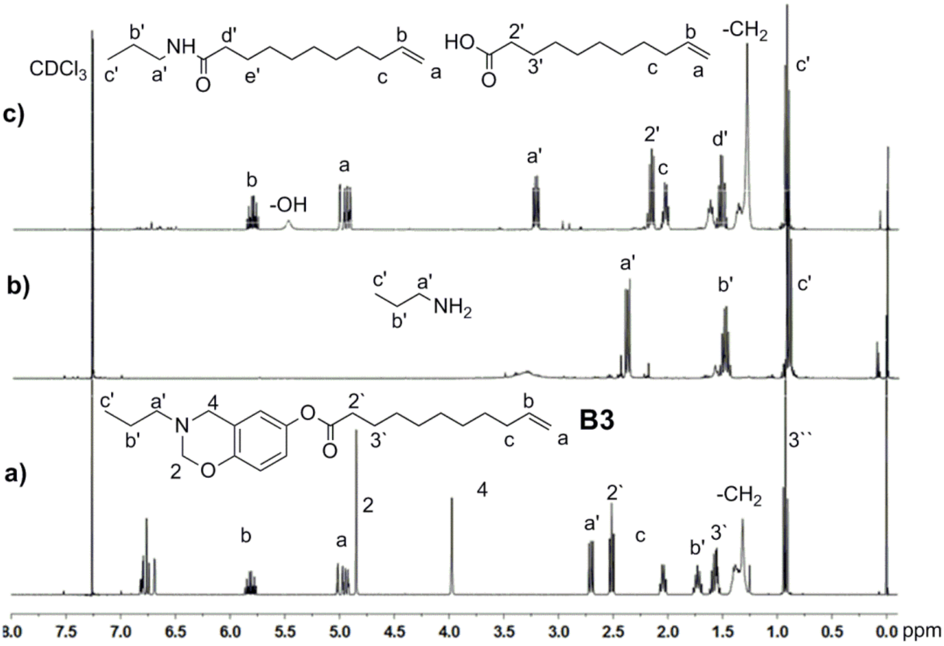


Figure 3.9. ^{1}H-NMR spectra of a) B3 benzoxazine monomer, b) 2nd fraction of pyrolysis reaction (150ºC), c) last fraction of pyrolysis reaction (210ºC).

ring opening. N,O-ketalic bridges[60] were not detected under the tested conditions (Figure 3.9).

To prevent degradation during curing, experiments at temperatures below the onset temperature of degradation by TGA were carried out. Thus, isothermal heating at different preset temperatures were monitored by DSC and FTIR-ATR. In Figure 3.10, results for B1S2 are collected as example. These experiments allow determining that progressive heating up to a maximum temperature of 180ºC (exception in the case of B3 series) affords the complete curing of all monomers as evidenced by the absence of any remaining curing exotherm in DSC traces after curing cycle (Figure 3.10a). Changes in FTIR-ATR spectra (Figure 3.10b) also confirm the complete ring opening of benzoxazine.[38,278] Bands at 1220 and 1029 cm^{-1} (asymmetric and symmetric stretching of C-O-C in oxazine ring) and 1174 and 876 cm^{-1}

(asymmetric and symmetric stretching of C-N-C in oxazine ring) completely disappear. Moreover the intense signals at 1600, 1498, 920, and 898 cm^{-1}, corresponding to C=C stretching and C-H bending of trisubstituted benzene rings, strongly decrease their intensity and new bands at 1657 and 1478 cm^{-1} corresponding to the stretching modes in tetrasubstituted benzene ring appear.

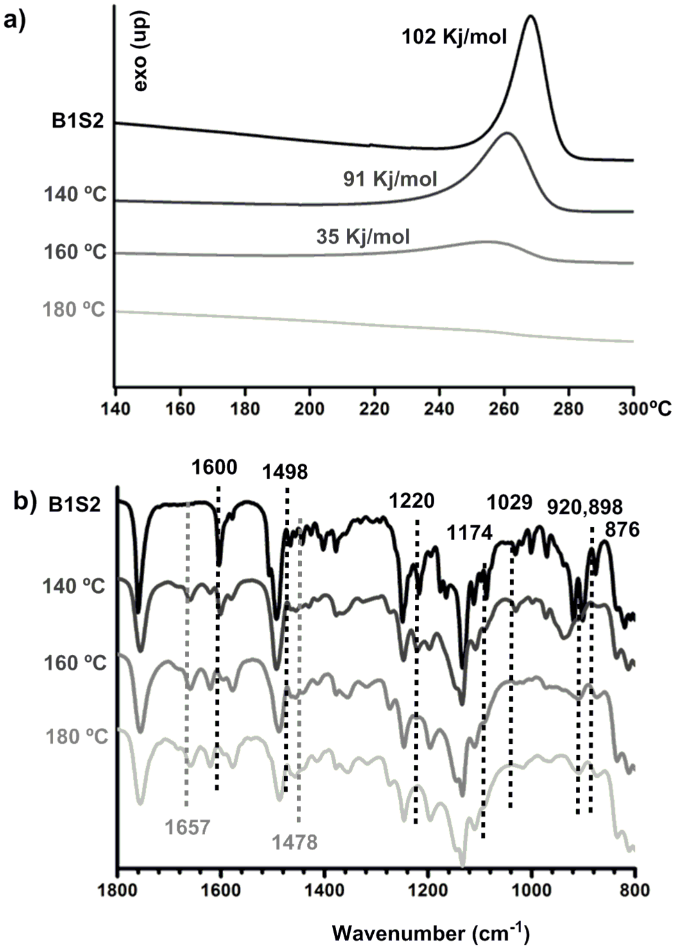


Figure 3.10. a) DSC thermograms of B1S2 and after consequently heating 2h at 140ºC, 4h at 160ºC, and 2h at 180ºC. b) FTIR-ATR spectra of B1S2 and the intermediate materials produced during the curing cyle. Blacklines in the spectra indicate bands that disappear or decrease. Gray lines indicate new bands.

Decreasing curing temperatures by using catalyst was also considered. Several acidic and Lewis acid catalysts have been reported to effectively activate the cationinc ring opening of the benzoxazine ring.[50,59,63] In recent works $BF_3.Et_2O$ has been evaluated as effective curing promoter.[51,153] So the curing behavior of some benzoxazine monomers in presence of 1, 2, and 3% (w/w) of $BF_3.Et_2O$ was compared by DSC. In Figure 3.11, reprensentative DSC plots obtained for B1S2 are shown. Results indicate that increasing amounts of $BF_3.Et_2O$ as catalyst lead to a progressive decrease of the maximum of the curing exotherm. In the case of B1S2 (Figure 3.11), temperature decreases from 267 to 234 ºC when a 3% (w/w) of catalyst is used. However, even the use of catalyst allows curing at temperatures lower than the ones of the beginning of monomer decomposition; the resulting materials show significantly poorer thermo-mechanical properties when compared with the non-catalyzed materials (*vide infra*). This behavior is probably because Lewis acids also can promote ester group hydrolysis and phenolysis. Given the structural similarity of all monomers, it is not expected to behave differently so, the use of $BF_3.Et_2O$ was not considered.

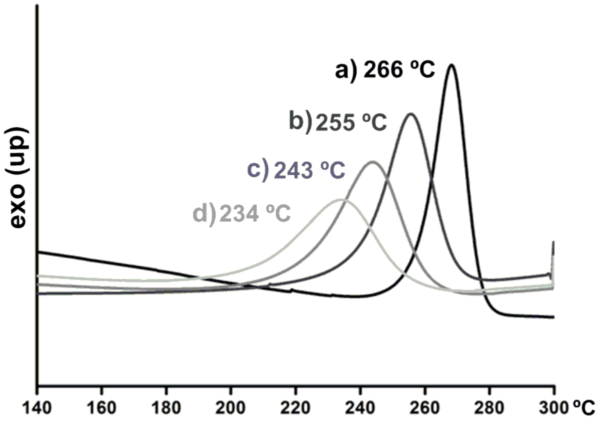


Figure 3.11. DSC thermograms of pristine B1S2 (a) and their mixtures with 1% (w/w) (b), 2% (w/w) (c), and 3% (w/w) (d) of $BF_3.EtO_2$ as catalyst.

According to the above studies, α,ω-*bis*-benzoxazine monomers were cured without catalyst in Teflon coated glass molds (25x10x0.49 mm) heating the samples from 120 to 180ºC at 0.1 ºC/min for N-Phenylbenzoxazine derivatives (B1S1, B1S2, B2S1, B2S2, MB1, MB4, and MB5) and from 140 to 200ºC at 0.1 ºC/min for N-n-propylbenzoxazine derivatives (B3S1, B3S2, and MB3) (curing cycle: 10h). After completion of the curing cycle, samples of the resulting brown transparent flexible plates where analyzed by DSC to discard any residual curing enthalpy.

Efficiency of curing conditions was also checked by measuring the percentage of crosslinked material after extraction with DCM. Results collected in Table 3.4, indicate an extensive crosslinking in the case of B1, B2, B4 and B5 derivatives but not for the B3 counterparts. The large amounts of soluble products, more than 30%, in PB3S1, PB3S2, and PMB3 seem to indicate that N-n-propylbenzoxazine curing proceeds in a less extensive way giving noticeable fractions of linear or branched products. These results could be related to the poor stability of the N- alkylbenzoxazine ring at relatively low temperatures. This lack of stability has been evidenced by pryrolisis experiments of B3 benzoxazine monomer. After the curing cycle, none of the PB3S1, PB3S2, and MB3 do not show any curing exotherm by DSC. Moreover, bands of the benzoxazine ring are absent in the FTIR-ATR spectrum which confirms that benzoxazine ring is consumed but most probably giving a mixture of branched and lineal structures. Release of n-propylamine during DSC and curing experiments stands for this behavior. In addition, decomposition processes seem not to play an important role in the formation of these soluble fractions since weight losses at 240 ºC by TGA are negligible in both cases (3%, Table 3.3).

Referring the catalyst effect, again a clear evidence of low crosslinking extends can be inferred from the amount of soluble fraction in Table 3.4 for the case of B1S2.Upon curing, monofunctional benzoxazine monomers B1, B2, B3, B4, and B5 let to brittle materials with poor mechanical properties. On the contrary, materials obtained from the hydrosilylation and metathesis monomers are flexible and have reasonably good mechanical properties.

Table 3.4. Insoluble fraction content and thermal and thermomechanical properties of the α,ω-*bis*-benzoxazine thermosets.

	DMTA			TGA		
Polymer	IF (%)[a]	E′ (MPa)[b]	Tan δ_{max} (ºC)	$T_{5\%}$ (ºC)	T_{max} (ºC)	$R_{800ºC}$ (%)
PB1S1	96.8	2020	92	302	447	29
PB1S2	94.5	2630	96	323	444	26
PB1S2[c]	86.5	1870	75	292	465	36
PMB1	95.4	2400	117	294	444	29
PB2S1	91.1	3080	101	280	434	41
PB2S2	92.8	4070	117	291	422	37
PB3S1	54.8	2080[d]	22	292	415	24
PB3S2	31.7	2990[d]	24	303	455	25
PMB3	66.6	---	71	294	440	25
PMB4	96.5	2000	107	291	448	22
PMB5	92.6	2300	119	315	457	19

[a] Percentage of insoluble material after extraction in DCM at 40ºC for 24h. [b] Determined at room temperature. [c] Sample cured in the presence of 3% (w/w) of $BF_3.Et_2O$. [d] Values determined at -30ºC.

Storage modulus ranging from 2000 to 4000 MPa are maintained for a wide temperature up to 50ºC for monomers obtained by hydrosilylation and 60ºC for monomers obtained by metathesis derived thermosets (Figure 3.12). The measured values are significantly lower when compared with the BPA benzoxazine-based materials (20.000 MPa) as expected their high aliphatic content and their lower crosslinking densities. This parameter can be roughly estimated from the plateau of the elastic modulus in the rubbery state.[279] This theory is strictly valid only for lightly crosslinked materials and therefore can be used only to make qualitative comparisons. Thus, values of storage modulus indicate that these materials have low crosslinking densities which were otherwise expected by their structure consisting of two benzoxazine rings separated by long aliphatic spacers.

Accordingly, materials derived from B2 (PB2S1 and PB2S2) with shorter aliphatic moieties, have the maximum elastic modulus values (Table 3.3 and Figure 3.12).

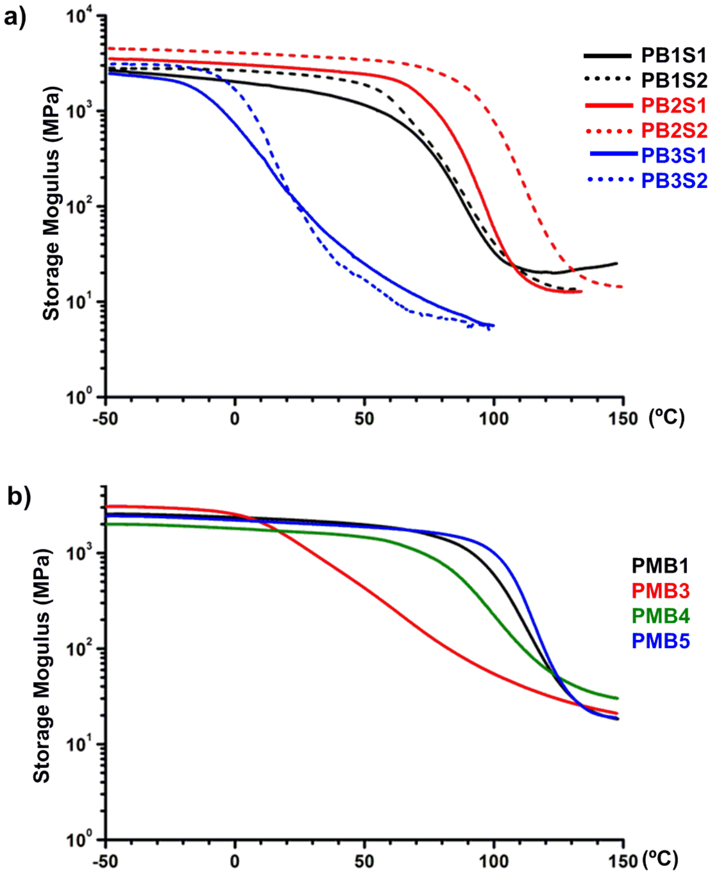


Figure 3.12. Storage modulus of thermosets a) PB1S1, PB1S2, PB2S1, PB2S2, PB3S1, and PB3S2; b) PMB1, PMB3, PMB4, and PMB5.

Moreover, thermosets derived from the aromatic silane S2, have higher elastic modulus values than the obtained from the more flexible aliphatic silane S1. B3 series (PB3S1, PB3S2, and PMB3) show a differentiated behavior with a storage modulus that starts decreasing at much lower temperatures than B1, B2, B4, and B5 series. In the case of PB3S1 and PB3S2, a progressive decrease of the loss modulus starts at much lower temperatures than PMB3. B1 series (PB1S1, PB1S2, and PMB1) show a similar behavior with the storage modulus where siloxane derived thermoset results relatively lower storage modulus than aromatic silane derived and metathesized derived thermosets.

Analysis of the height and width of the Tan δ peak (Table 3.4 and Figure 3.13) indicate than crosslinking densities increase in the order PMB4 > B1S1~B1S2 ~ MB1 > MB5 > B2S1 > B2S2. Moreover, PMB1 and PMB5 seem to have a more homogeneous network structure than PMB4; B2 derivatives gave materials with lower crosslinking density but higher homogenity than B1 derivatives. This trend could be related to differences in monomer flexibility during the curing process. B3 series (PB3S1, PB3S2, and PMB3) show again a different behaviour with a multimodal broad and asymmetric Tan δ peaks which are consistent with a poorly homogenous structure due to the presence of large amounts of non crosslinked material. T_gs, estimated as the maximum of the Tan δ peak (Table 3.4), are in the range of 92-119ºC for B1, B2, B4, and B5-based series and significantly lower T_g (22, 24, and 71ºC) for B3 based series which are affected by the plasticizing effect of the soluble fraction. Again, the shorter aliphatic spacer in B2 series gave materials with lower segmental mobility. Influence of the rigid aromatic silane coupling agent S2 on T_g values are detected only for B2 series. The long aliphatic spacers in B1 and B3 series likely attenuate the effect of the silane nature.

All monomers, except B3 series, were cured following the same curing cycle but not all benzoxazine rings have the same reactivity. It is well known that ring opening of benzoxazines is activated by the presence of electron withdrawing and specially affected by electrodonating groups.[31] Thus, benzoxazine reactivity is expected increase in the order MB5 (Bz-COO) > MB1

(Bz- OOC-) ≥ MB4 (Bz-O-). Moreover, it must be taken into account that whereas ester groups behave as rigid blocks, ether linkages are highly flexible and this could explain why PMB4 having a higher crosslinking density than PMB1 and PMB5 posses a lower T_g value.

Concerning the use of $BF_3.Et_2O$ as curing catalyst, the resulting materials show clearly poorer properties. In Table 3.4 the DMTA and TGA

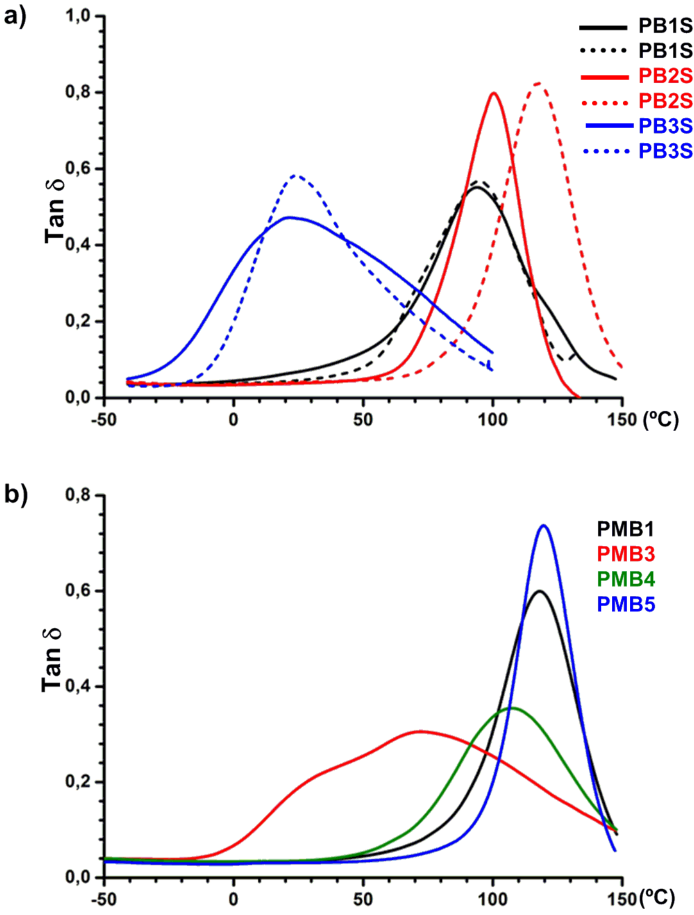


Figure 3.13. Tan δ of thermosets a) PB1S1, PB1S2, PB2S1, PB2S2, PB3S1, and PB3S2; b) PMB1, PMB3, PMB4, and PMB5.

characteristics of PB1S2 cured with 3% (w/w) of $BF_3.Et_2O$ have been included for comporative purpose. In all cases studied, thermosets obtained in presence of catalyst show lower elastic modulus, lower T_g values and Tan δ peaks than the non-catalyzed counterparts, which suggests lighter crosslinking densities.

Materials thermal stability under nitrogen atmosphere was studied by TGA (Figure 3.14). All systems present a 5% weight loss at temperatures comprised between 280 and 323ºC and a main degradation step with maximum weight loss rate at 415-465ºC. The presence of the aromatic silane coupling agent clearly increases thermal stability at low temperatures where PB1S2 thermoset possesses relatively the higher $T_{5\%}$, but also do not seem to influence the main decomposition step and the residue at high temperatures. On the other hand, the influence of the benzoxazine monomer structure in the thermal stability can be inferred except for PMB5 that seems to starts its degradation at slightly higher temperatures than its metathesized counterparts. Char residues for polybenzoxazines obtained by hydrosilylation at 800ºC under N_2 are comprised between 24 and 41% where are comprised between 19 and 29% for polybenzoxazines obtained by metathesis reaction which are lower than hydrosilylation counterparts. Obviously, the absence of silicon moieties is the responsible of the lower char residues.

The drawbacks of curing using $BF_3.Et_2O$ as catalyst can be also inferred from TGA data. For PB1S2 cured with 3% (w/w) of $BF_3.Et_2O$ (Table 3.4), decomposition starts clearly at lower temperatures. On the contrary, at high temperatures some beneficial effect on the char yield is observed. This behavior can be rationalized by the presence of remaining $BF_3.Et_2O$, which catalyzes ester bond cleaving at low temperatures but promotes additional crosslinking reactions at high temperatures.

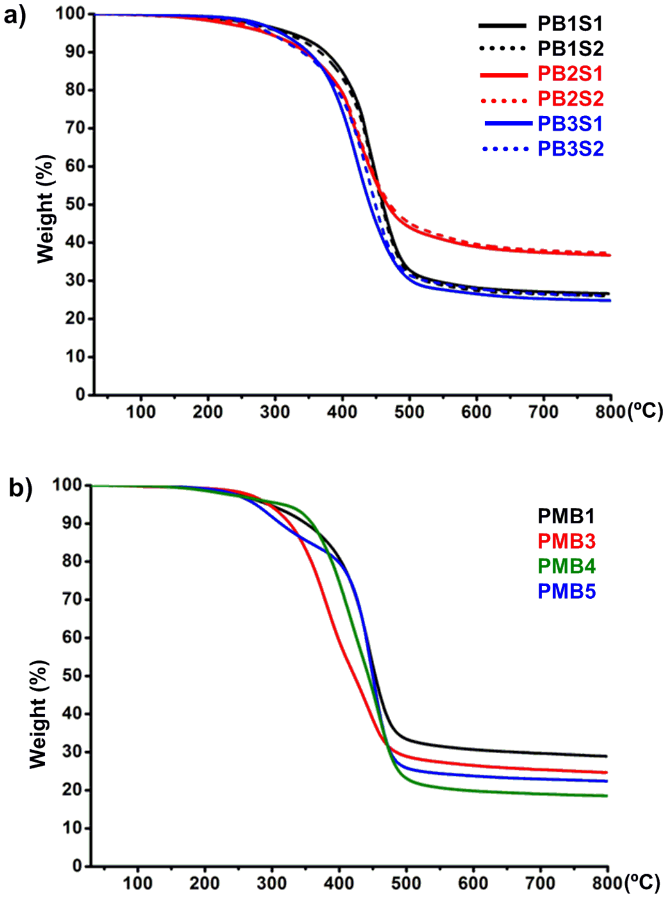


Figure 3.14. TGA thermograms of thermosets; a) BS and b) BM series.

DMTA was also used to characterize mechanical properties using flexural tests measurements at 35ºC. The resulting stress-strain curves (Figure 3.15) seem to correlate with segmental flexibility rather than the crosslinking density. Also, a significant influence of monomer structure in the final material properties has been observed. Whereas the low consistency of samples PB3S1 and PB3S2 prevent DMTA measurements, the rest of samples behave as tough to elastic materials. The length of the aliphatic chain and the nature of the coupling silane seem to determine the mechanical behavior. Thus, even with a lower crosslinking density, PB2S1 and PB2S2 behave as tougher materials than PB1S1 and PB1S2 due to the shorter aliphatic chain. Moreover, the presence of flexible siloxane moieties (PB1S1 and PB2S1) gives more elastic materials than their rigid aromatic silane counterparts (respectively PB1S2 and PB2S2).

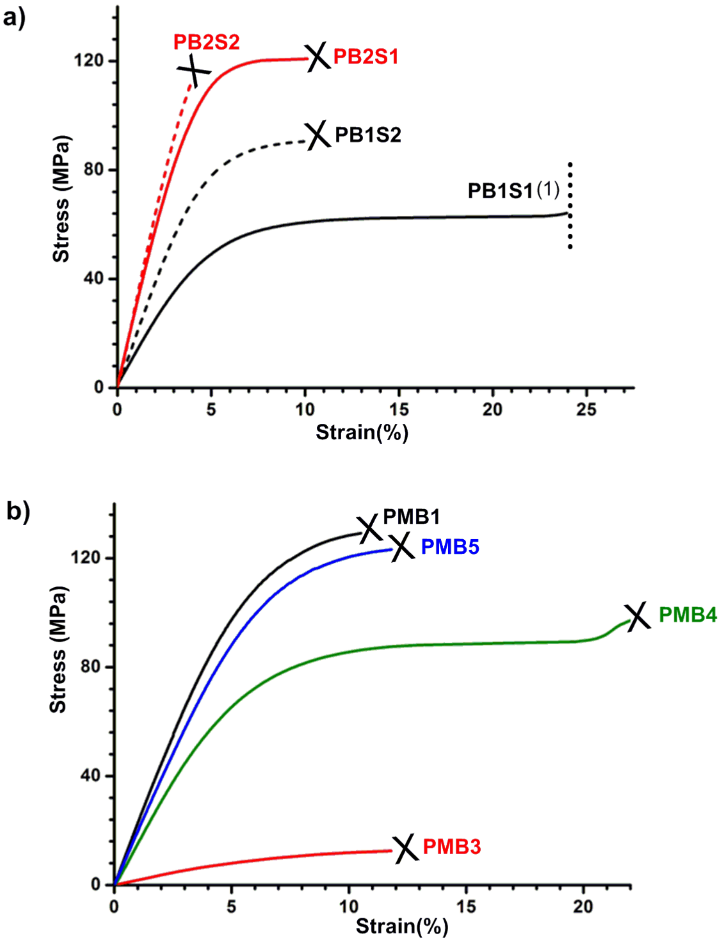


Figure 3.15. Bending measurements by DMTA of thermosets a) PB1S1, PB1S2, PB2S1, PB2S2, PB3S1, and PB3S2; b)PMB1, PMB3, PMB4, and PMB5. [1]Curve ends at the DMTA measurement limit (no sample break).

Also, the nature the linking group between the benzoxazine ring and the aliphatic chain that change from a flexible ether linkage (Ar-O) to an increasing rigidity ester linkage (Ar-O-CO) and (Ar-CO-O) influence the flexural properties of the cured films. Thus, systems containing relatively rigid ester groups (PMB1 and PMB5) behave as tougher materials than PMB4 which behave softer and more elastic. In addition, silane moiety (aromatic or siloxane) gives more elastic properties where the difference can be seen between PB1S1, PB1S2 and PMB1 materials. PB1S1 and PB1S2 are more elastic than PMB1. Finally, PMB3 shows very poor mechanical properties in accordance with its high content of soluble materials.

Surface properties are an important parameter which determines the range of applications of coating and film materials. To estimate this parameter, contact angle measurements were carried out in polybenzoxazine films using water (Figure 3.16 and Figure 3.17).

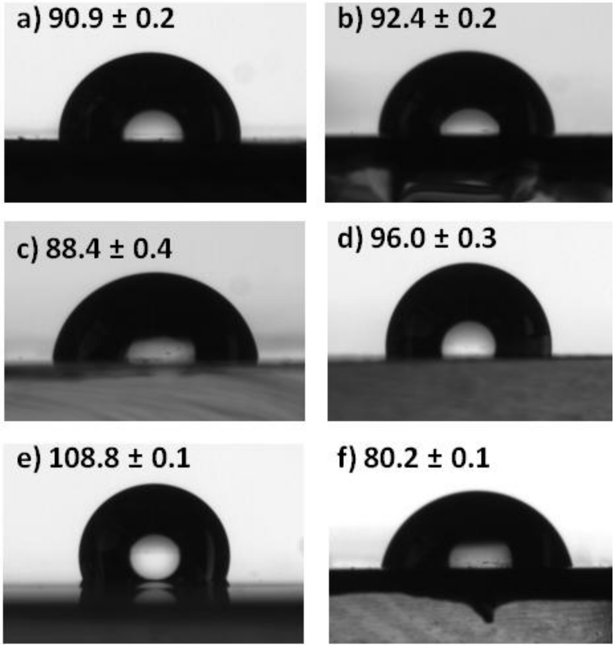


Figure 3.16. Contact angle measurement of film samples a) PB1S1, b) PB1S2, c) PB2S1, d) PB2S2, e) PB3S1, and f) PB3S2.

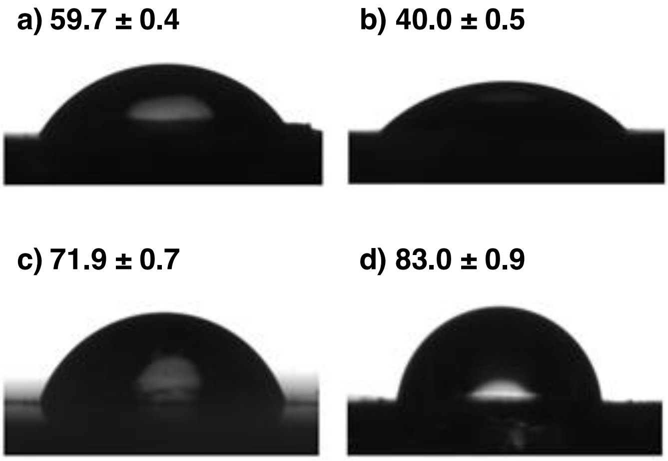


Figure 3.17. Contact angle measurement of film samples a) PMB1, b) PMB3, c) PMB4, and d) PMB5.

Surface polarity in polybenzoxazine materials depends on many factors such as surface roughness and structural factors. Structure dependence of surface properties can be understood as a balance between aliphatic content and type of functional groups which depends on the structure of the starting monomer, and the curing extent, which determines the amount of phenolic and Mannich bridges formed.[280,281] Polybenzoxazines are featured by strong intramolecular hydrogen bonding between phenolic hydroxyl and amino groups which tend to decrease the surface energy whereas intermolecular hydrogen bonding has the contrary effect.[280,281] Additionally, factors such as surface roughness and anisotropy have to be also taken into account.

Surface properties were analyzed by contact angle measurements at 25ºC depositing the deionized water on polymer films prepared by casting and curing the monomers over the glass slides. As can be seen in Figure 3.16, thermosetting materials prepared behave very different. When comparing B1 and B2 series, it is clear that the presence of a shorter aliphatic chain (PB2S1 and PB2S2) increase surface polarity due to its low aliphatic content. The silane nature also influences surface behavior, thus siloxane-based polymers (PB1S1 and PB2S1) present lower contact angles than the aromatic silane-based counterparts (PB1S2 and PB2S2).

B3 based series again show a different behavior that has to be related to the poor homogenity of these materials and its poor crosslinked structure that produces a high content of polar terminal groups. PB3S1 and PB3S2 behave respectively as the least and most polar material in absolute term. This fact is not easily predictable taking into account the structures of the starting monomers and could be related with an incomplete curing and the formation of different polymer structures as is apparent from DSC and DMTA results.

In PMB series, surface polarity increases in the order PMB1 > PMB4 > PMB5 (Figure 3.17). Differences in crosslinking density determine the amount of free phenolic groups available to form intra- and intermolecular hydrogen bonding. Moreover, water affinity should be affected by the electronic character of the groups linked to the aromatic ring. Strength of the phenolic hydrogen bonding should be weakened by the presence of electron withdrawing groups. This is consistent with the lower contact angle observed for PMB5 but it does not explain the order observed for PMB1 and PMB4. Additionally, polarity of the different ester and ether groups has to be considered. Thus, it must be concluded that the concurrence of many effects affecting surface polarity, prompts to predict the surface behavior accurately. The different hydrogen bonding capacity also is likely to affect the mechanical behavior observed by DMTA as properties of benzoxazine materials are strongly dependent of the intra- and intermolecular hydrogen bonding balance.[282]

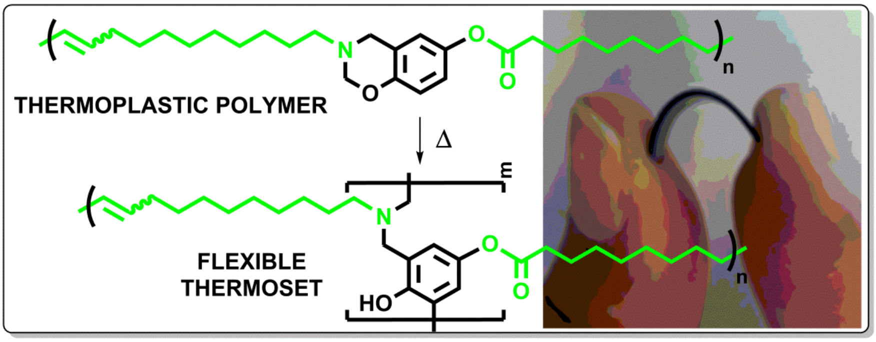
As final remark, thermosetting materials obtained using the hydrosilylation and metathesis approach offers a palette of material with different properties. Thus, it is well demonstrated that selecting the appropriate benzoxazine design, materials with different properties can be prepared.

3.1.5 Conclusion

Renewable unsaturated fatty acid derivatives have been used to prepare a set of *bis*-benzoxazine monomers with different aliphatic spacers *via* the self-metathesis or hydrosilylation of the fatty acid double bond moieties. Two different silane moieties were combined with different benzoxazine monomers which are lead to flexible and tough thermoset films. Moreover, metathesis reaction fails in the case of the derivative with the shorter aliphatic chain due to the extensive double bond isomerisation. For longer aliphatic chains, self-metathesis yields the desired dimers in excellent yields. These monomers are oils or easily processable solids which, on curing thermically, give polybenzoxazine films with different toughness, flexibility, and surface polarity degrees.

3.2 Integrating Plant Oils into Thermally Curable Main-Chain Benzoxazine Polymers via ADMET Polymerization

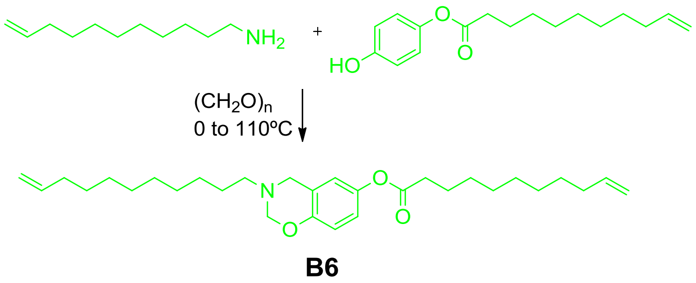
A novel biobased α,ω–diene (B6) bearing a thermally curable benzoxazine group is synthesized and polymerized *via* acyclic diene metathesis (ADMET) using Hoveyda-Grubbs second generation catalyst (H-G2nd). The benzoxazine-containing diene monomer was designed based on 10-undecenoic acid and 10-undecenyl amine as castor oil derived platform chemicals and hydroquinone. H-G2nd allowed the polymerization of B6 with no degradation of the heterocyclic ring structure. The M_n and crosslinker content was modulated by using a monofunctional comonomer (methyl10-undecenoate) to end-cap polymer chains. DSC was used to demonstrate that the obtained thermoplastic prepolymers are able to yield thermosets after thermally activated ring opening polymerization just simply by heating up to around 200ºC. Thermal and mechanical properties of the cured polybenzoxazines are also discussed.



3.2.1 α,ω-Diene Benzoxazine Synthesis

Inspired by the molecular structure of other biobased α,ω-diene monomers reported by Meier and others[283,284] a benzoxazine containing diene monomer (B6 Scheme 3.14) was designed based on castor oil derivatives and hydroquinone.[177] Combining the previously described ω-unsaturated alkyl phenol (Ph1) with 10-undecenyl amine and paraformaldehyde in a solventless fashion, B6 was synthesized. 10-Undecenyl amine was synthesized by converting 10-undecenyl alcohol into the corresponding azide and subsequent reduction with $LiAlH_4$.[285,286]

B6 structure was confirmed by NMR and FTIR-ATR spectroscopy. The ^1H-NMR spectrum shown in Figure 3.18a clearly confirmed the structure of B6. The typical characteristic resonances of –Ph-CH_2-N- and -O-CH_2-N- of the oxazine ring appeared at 3.96 and 4.83 ppm, confirming the presence of the cyclic benzoxazine structure. Moreover, no signals of starting materials or oligomerized products were observed after purification by column chromatography (Hexane: EtOAc, 10:1). ^{13}C-NMR spectra of B6 benzoxazine monomer is shown in Figure 3.18b and shows all the expected signals.



Scheme 3.14. Synthesis of α,ω-diene benzoxazine B6.

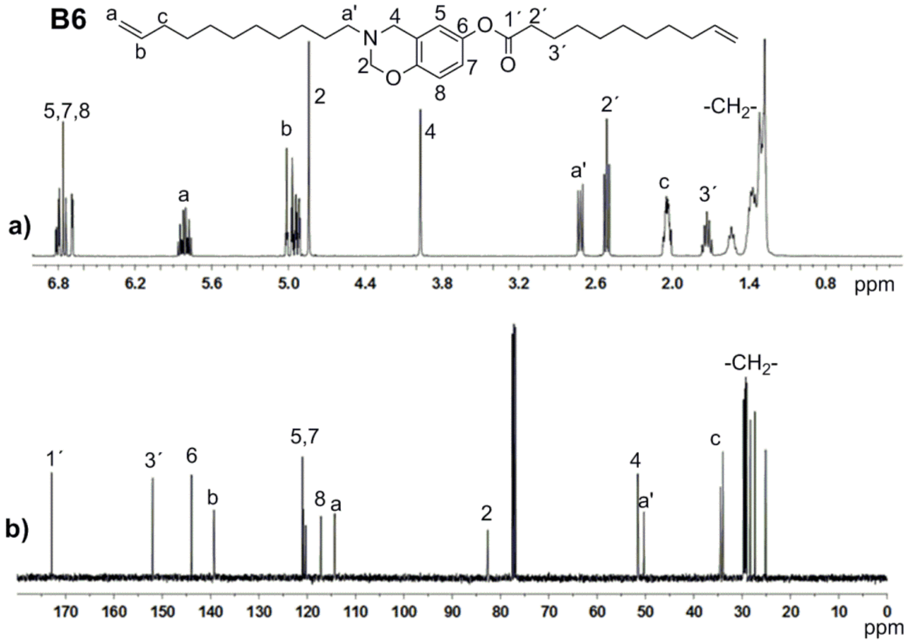
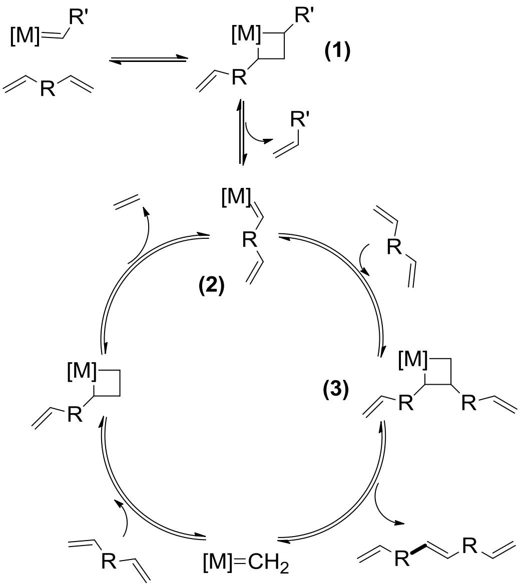


Figure 3.18. a) ^{1}H- and b) ^{13}C-NMR spectra of α,ω–diene B6 monomer.

3.2.2 ADMET Polymerization of α,ω-Diene Benzoxazine Monomer

Acyclic diene metathesis (ADMET) has recently been demonstrated to be an outstanding tool for the preparation of fatty acid-based polymers from α,ω-diene monomer.[287,288] ADMET polymerization is a step-growth polymerization driven by the release of ethylene leading to high molecular weight polymers from monomer, dimer, trimer or so on.[249,289,290] The ADMET polymerization cycle proceeds *via* the metal-carbene mechanism which was well established by Wagener et al.[291] (Scheme 3.15).

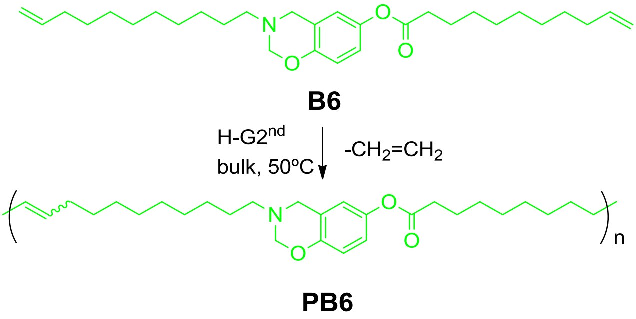
The [2+2] cycloaddition reaction between the olefin and metal methylidene carbine leads to form an intermediate metallacyclobutane (1). This intermediate then decomposes by a [2+2] cycloreversion, releasing ethylene and produces a α-substituted metal alkylidine (2). Subsequent reaction between the double bond of a diene results a α,β-substituted metallocylobutane (3), which subsequently leads to polymer formation and



Scheme 3.15. Generally accepted ADMET polymerization mechanism.

regenerates the metal methylidene carbine. The cycle proceeds with coordination of another diene or growing polymer, followed by productive cleavage and the evolution of the ethylene.

The polymerization of B6 was initially investigated using Grubbs 1st and 2ndgeneration catalysts (G1st and G2nd). Unfortunately, they gave very poor results. On the contarary H-G2nd gave better results probably because its notorious tolerance and activity in the presence of coordinative and non-coordinative heteroatoms.[284,292-294] ADMET reactions were run for 15h at 50ºC in absence of solvent and under vacuum to remove the released ethylene (Scheme 3.16, Table 3.5). A polymer (PB6) with low apparent molar mass of 3000 g mol^{-1} (SEC) together with poor monomer conversion was produced in the presence of 0.5% H-G2nd catalyst. Monomer conversion was determined by comparing the ^{1}H-NMR peak of the vinyl hydrogens before and after polymerization.



Scheme 3.16. ADMET polymerization of α,ω-diene benzoxazine monomer B6.

Table 3.5. Polymerization conditions and properties of main-chain benzoxazine polymers from B6.

Polymer	mol% H-G2nd [a]	mol% UDM[b]	mmol Bz/g polymer	M_n SEC	PDI	M_n NMR[e]	D_p
PB6-1	1	0	2.129[c]	10800	1.9	-	-
PB6-2	2	0	2.129[c]	11600	2.0	10500	22
PB6-3	5	0	2.129[c]	16300	2.4	-	-
PB6-4	2	5	2.099[d]	11500	1.9	9500	20
PB6-5	2	10	2.054[d]	6900	2.2	5500	12
PB6-6	2	25	1.971[d]	5600	1.9	2800	6

[a] 50ºC in bulk for 15h. [b] Methyl-10-undecenoate [c] Calculated from theoretical repeating unit. [d] Calculated from ^{1}H-NMR spectrum after precipitation. [e] Determined from ^{1}H-NMR end-group analysis.

Using higher amounts of catalyst, an obvious increase of the viscosity of the reaction mixture was noticed after 15h and almost quantitative monomer conversion was determined by ^{1}H-NMR spectroscopy. As can be seen in Table 3.5, polymers PB6-1 with M_n = 10800 g mol^{-1} (dispersity 1.9, monomer conversion >98%) and PB6-2 with 11600 g mol^{-1} (dispersity 2.0, monomer conversion >98%) were produced in the presence of 1 and 2 mol % catalyst, respectively. The ADMET polymerization in the presence of *p*-benzoquinone to reduce olefin isomerization[295] or in the presence of solvent (toluene) to homogenize the reaction mixture was also attempted but did not give better results. On the other hand, average molar masses of polymers obtained using 5 mol % at 50ºC and 2 mol % H-G2nd catalyst at 80ºC were slightly higher. However, the obtained polymers were not completely soluble in common organic solvents, suggesting that some kind of crosslinking reaction might have taken place. Consequently, we concluded that 2 mol% H-G2nd catalyst at 50ºC in bulk is the best suited for the polymerization of B6 and retained this condition for further polymerizations.

PB6 polymers containing thermally curable benzoxazine groups in the main-chain with apparent molar mass at around 10000 g mol^{-1} were isolated as dark green sticky solids. The polymerization was verified by the coalescence of two absorbance bands from the α-olefin gropus in B6 at 992 and 907 cm^{-1} into a single band at 969 cm^{-1} indicating a mostly trans 1,2-disubtituted olefin and a successful polymerization.[296] ^{1}H-NMR spectrum of representative main-chain benzoxazine-containing PB6-2 polymer is shown in Figure 3.19a. In comparison with the ^{1}H-NMR of the corresponding monomer shown in Figure 3.18a, a clean and complete transformation of the B6 monomer to unsaturated polymer is observed. The resonances from the terminal olefins of B6, at roughly 5.0 and 5.7 ppm, condense to a peak at 5.4 ppm in PB6-2, while the chemical shifts of the other peaks are maintained and slightly broadened. The same trends are observed in the ^{13}C-NMR spectra (Figure 3.19b), where the terminal olefin resonances at 139 and 114 ppm in B6 are condensed to an internal olefin peak in PB6-2 (two peaks due to cis/trans isomers). It is noteworthy to highlight that both ^{1}H- and ^{13}C-NMR analysis demonstrate that benzoxazine ring remains intact after ADMET polymerization.

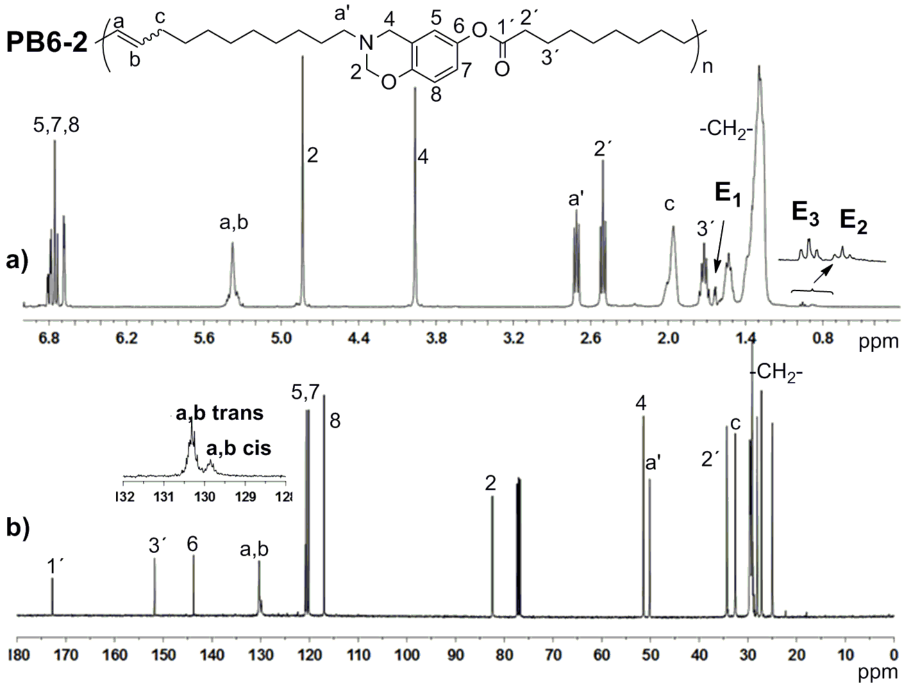


Figure 3.19. a) ^{1}H- and b) ^{13}C-NMR spectra of PB6-2 polymer.

Interestingly, three methyl end-groups signals at 1.60 ppm (E1,-CH_2=CH-CH_3), 0.88 ppm (E2, -CH_2=CH-CH_2-CH_3), and 0.96 ppm (E3, -CH_2=CH-$(CH_2)_n$-CH_3 with $n \geq 2$) which result from isomerization of terminal vinyl groups were observed in the ^{1}H-NMR spectrum. The degree of polymerization (DP) and the molecular weight (M_n) of B6 polymer obtained with no chain stopper (PB6-2) was calculated from the ratio of the ^{1}H-NMR proton signal intensities of the end groups (E_1-E_3) compared to the proton signal intensities of the methylene CH_2-N of the polymer chain (P) in the ^{1}H-NMR spectrum (Figure 3.20).

The DP was calculated according to: $DP = \dfrac{3x\int P}{\int E1 + \int E2 + \int E3}$

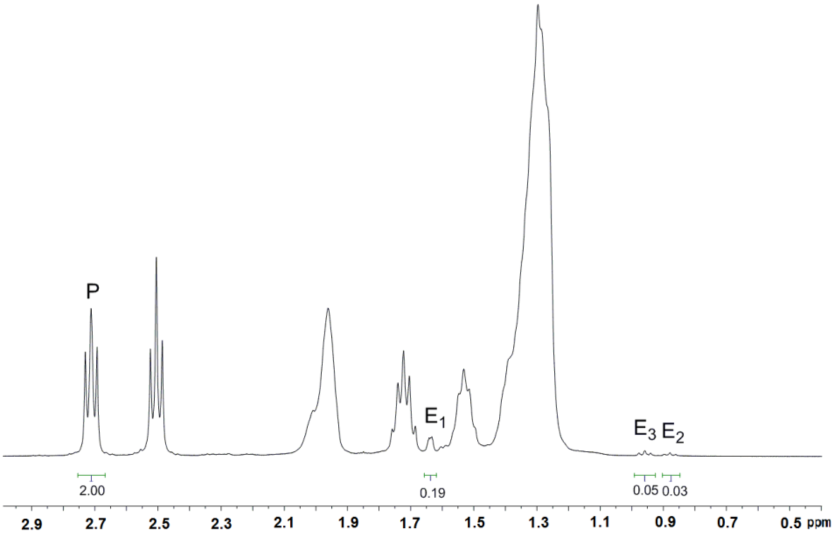


Figure 3.20. Molecular weight estimation for PB6-2 by ^{1}H-NMR spectroscopy.

From the integration of the end groups' signals, a molecular weight of 10500 g mol^{-1}, which is in good agreement with SEC data, was determined for PB6-2 polymer.

3.2.3 ADMET Polymerization of α,ω-Diene Benzoxazine Monomer in the Presence of Chain Stopper

Once demonstrated that ADMET polymerization of the benzoxazine-containing diene B6 can afford moderate molecular weight polymers containing thermally curable benzoxazine groups in the main chain, our interest was to modulate the molecular weight and benzoxazine crosslinker content of PB6 regarding their potential processability, film forming performance, as well as thermal and mechanical properties of the corresponding cured thermosets. Thus, B6 was polymerized in the presence of 5, 10, and 25 mol % of methyl10-undecenoate (UDM) as a chain stopper (Table 3.6, PB6-4, PB6-5, and PB6-6). As can be seen in Figure 3.21, when polymerization was carried out in the presence of UDM, a new methyl ester end-group signal E_4 at 3.6 ppm (-$COOCH_3$) appeared in the ^{1}H-NMR spectra of corresponding polymers. As expected, E_4 chain end resonance intensity increased as the chain stopper feed increased. Consequently, benzoxazine reactive groups' content decreased progressively. SEC analysis of PB6-4, PB6-5, and PB6-6 revealed a progressive shift of the SEC curves of the obtained polymers to lower molecular weight. Thus, apparent molecular weight decreased from 11500 Da for PB6-4 to 5600 Da for PB6-6. We determined the average DP (and corresponding M_n values) *via* ^{1}H-NMR analysis by comparing the integration of the CH_2-N protons of polymer chain with that E1-4 chain ends.

The DP was calculated according to: $\mathrm{DP} = \dfrac{3\mathrm{x}\int \mathrm{P}}{\int \mathrm{E1} + \int \mathrm{E2} + \int \mathrm{E3} + \int \mathrm{E4}}$

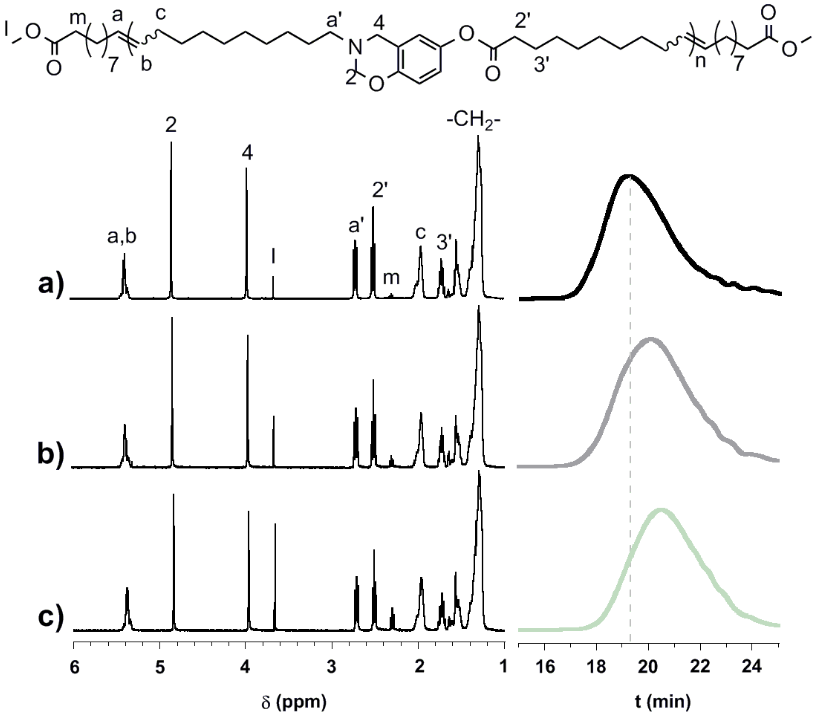


Figure 3.21. ^{1}H-NMR spectra in $CDCl_3$ and SEC curves of main-chain benzoxazine polymers a) PB6-4, b) PB6-5, and c) PB6-6 end-capped with methyl ester groups.

Table 3.6. Melt viscosity and thermal properties of main-chain benzoxazine polymers.

Polymer	$\lvert\eta^*\rvert^{80ºC}$ (Pa·s)	$\lvert\eta^*\rvert^{100ºC}$ (Pa·s)	T_g (ºC)	T_o (ºC)	T_{max} (ºC)	ΔH(J/g)
PB6-1	-	-	-	-	-	-
PB6-2	3480.3	998.6	-26	177	229	168
PB6-3	-	-	-	-	-	-
PB6-4	3581.0	1051.0	-28	177	230	163
PB6-5	294.7	144.9	-29	169	220	140
PB6-6	12.8	4.4	-33	158	216	132

PB6-4, PB6-5, and PB6-6 were isolated as dark green highly viscous oils and were found to be soluble in toluene, THF, and chloroform, indicating their good processing properties in solution processes. The melt viscosity and thermal properties of the resulting polymeric polybenzoxazine precursors were investigated (Table 3.6). The PB6-4, PB6-5, and PB6-6 viscosities were determined using a rheometer at 80 and 100ºC under oscillation frequency of 1 Hz. As expected, lower molecular weight as well as higher temperature leads to a decrease in the overall viscosity. Interestingly, moderate temperatures were enough to give a low enough melt viscosity to adequately process PB6-5 and 6 materials (i.e., impregnate fiber matrices) without the aid of solvent. On the other hand, the thermal properties were evaluated using the T_g observed by DSC.

The T_g of the lowest molecular weight polymer PB6-6 was around -33ºC. However, only a slight increase in T_g as a function of the molecular weight was observed. The thermal curing behaviors of resulting polymeric benzoxazine precursors were examined by DSC. It is well known that benzoxazines typically exhibit exothermic peaks at around 200-250ºC, which can be ascribed to ROP. PB6-4, PB6-5, and PB6-6 display exothermic behavior in the same high-temperature region. Figure 3.22 shows DSC thermograms in the region 60-280ºC, with the onset and peak temperatures of the crosslinking exotherms as well as exothermic energy indicated. As can be seen, a systematic increase on the onset and maximum temperatures as a function of the molecular weight was observed. We assumed that it was because the chain mobility of the polymer. It was also noteworthy that, the exothermic energy increased with an increase in the benzoxazine content from 132 to 163 J/g.

According to the DSC data and preliminary studies the curing of PB6-2, PB6-4, PB6-5, and PB6-6 polymers was carried out in a mold by heating samples at different temperatures and times (1h at 140ºC, 3h at 160ºC, 2h at 170ºC, 2h at 180ºC, and 1h at 200ºC). All cured materials were obtained as black films but only CPB6-5 and 6 successfully supported significant manual bending operation (Figure 3.23).

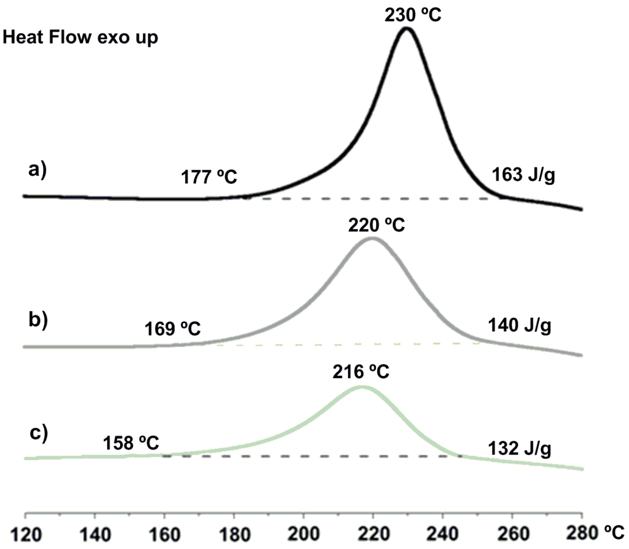


Figure 3.22. DSC thermograms of main-chain benzoxazine polymers a) PB6-4, b) PB6-5, and c) PB6-6.

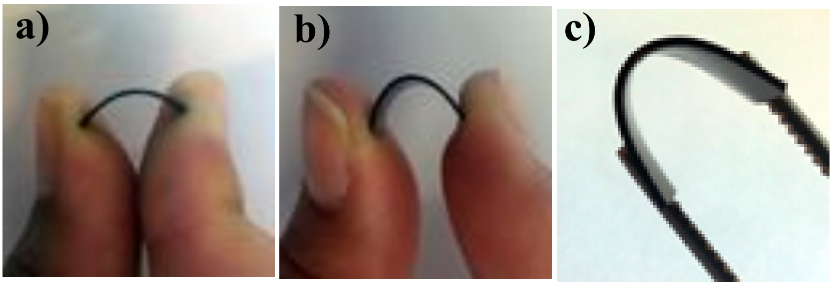


Figure 3.23. Photographs of the bending for cured polybenzoxazines a) CPB6-4, b) CPB6-5, and c) CPB6-6.

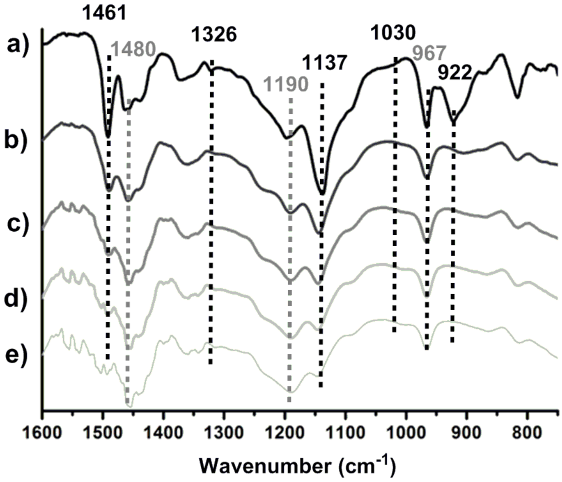


Figure 3.24. FTIR-ATR monitoring of PB6-5 crosslinking curing cycle; a) at room temperature, b)1h at 160ºC, c) 1h at 170ºC, d) 1h at 180ºC, and e) 30 min. at 200ºC.

The curing completeness was supported by DSC and FTIR-ATR spectroscopy. DSC thermograms of polybenzoxazines CPB6-4, CPB6-5, and CPB6-6 show the absence of any residual exotherm after the above described curing cycle, indicating complete ring-opening of benzoxazine groups. Additionally, FTIR-ATR analysis of the cured films supported a complete reaction. As can be seen in Figure 3.24, the characteristic absorption bands attributed to the oxazine structure at 922 cm^{-1} (C-H of benzene ring), 1030 cm^{-1} (C-O-C), and 1326 cm^{-1} (-CH_2-) gradually decreased after each curing stage and disappeared after the 200ºC cure step. Meanwhile, the very strong band assigned to the asymmetric stretching mode of C-N-C shifted from 1137 to around 1190 cm^{-1}. Additionally, the characteristic absorption band of tri-substituted benzoxazine ring around 1490 cm^{-1} completely disappear, whereas a new band ascribed to tetra-substituted aromatic ring (1480 cm^{-1}) appeared. It is important to point out that the absorption band at 967 cm^{-1} corresponding to the out-of-plane C-H band of 1,2-disubstituted olefin remains intact after the reaction, suggesting that all carbon-carbon double bonds do not react and increase the crosslinking density.

The crosslinking extent was qualitatively investigated by extracting the soluble fraction of cured samples. As can be seen in Table 3.7, the soluble fractions increase as the molecular weight and benzoxazine content of the parent polymeric precursor decrease due to the decreasing number of crosslink points available in the linear polymer. The viscoelastic, mechanical, and thermal properties of CPB6 polymers were investigated using DMTA, flexural test, and TGA and the result are summarized in Table 3.7.

Table 3.7. Thermal and mechanical properties of cured polybenzoxazines.

		DMTA				TGA		
Cured Polymer	SF[a] (%)	T_g (ºC)	Storage modulus[b] (MPa)	Ultimate bending stress (MPa)	Bending strain at break (%)	$T_{5\%}$ (ºC)	T_{max} (ºC)	$R_{800ºC}$ (%)
CPB6-4	2	87	1706	59	13	317	443	27
CPB6-5	4	68	1319	24	30	310	448	23
CPB6-6	13	54	817	18	36	308	448	20

[a] Percentage of soluble fraction after extraction in DCM at 40ºC for 24h. [b] Measured at 25ºC.

Several important mechanical parameters can be derived from the DTMA data. The storage modulus of a solid sample at room temperature provides a measure of the material stiffness under deformation. As can be seen in Figure 3.25a, DMTA data correlate with flexural tests results. The storage modulus increases as the molecular weight and benzoxazine content of the parent linear polymer increase.

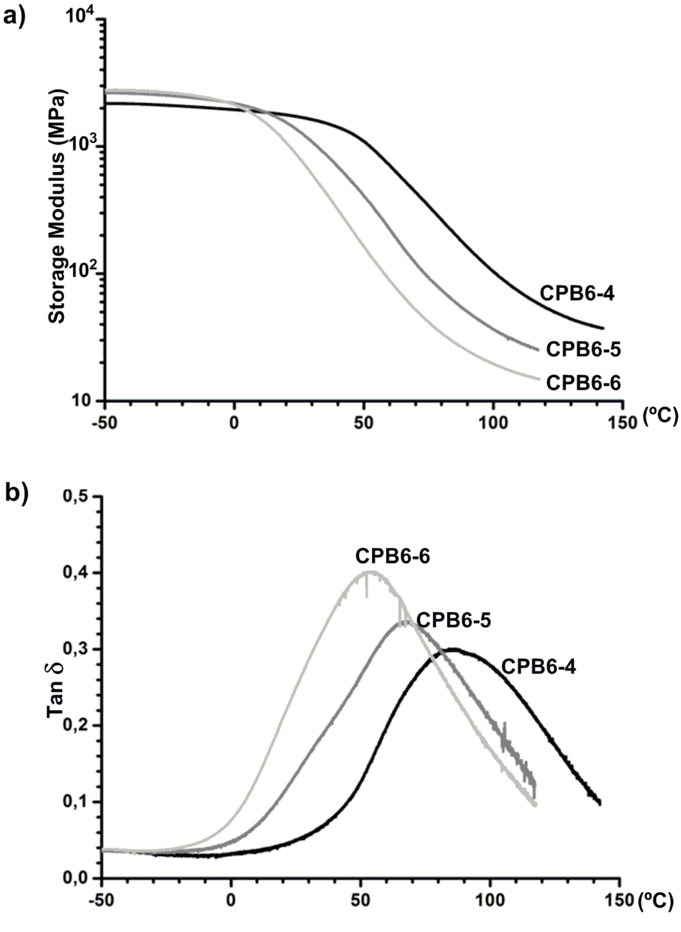


Figure 3.25. a) The storage modulus and b) Tan δ as a function of the temperature of cured polybenzoxazine CPB6-4, CPB6-5, and CPB6-6.

DMTA also allows the determination of the T_g of the crosslinked materials. The α-relaxation peak of the Tan δ is associated with the T_g and corresponds to the transition midpoint of the log of the storage modulus curve. The T_g value drops from sample CPB6-4 to sample 5 and 6 as consequence of the lower molecular weights and benzoxazine contents of PB6-5 and 6 with respect to 4. One can also analyze the Tan δ peak to provide a qualitative insight into the network structure. As can be seen in Figure 3.25b, the height of the Tan δ peak, which is associated with the crosslinking density decreases as the crosslinker content increase. Because Tan δ is the ratio of viscous components to elastic components, one can assume that the decreasing height is associated with lower segmental mobility and fewer relaxation species and is therefore indicative of a higher degree of crosslinking for these polymers. As can be seen in Figure 3.26a, also, ultimate bending stress increases as the molecular weight and benzoxazine content of the parent linear polymer increase. Otherwise, the bending strain at break decreases as the crosslinking degree increases, due to the enhanced brittleness.

Regarding the thermal stability properties evaluated by TGA analysis under nitrogen atmosphere, the 5% weight loss is the highest (317ºC) for the highest crosslinked polybenzoxazine CPB6-4 whereas, the lowest correspounds to the lowest crosslinked system CPB6-6 (Figure 3.26b). The same trend was observed for char yield at 800ºC. All polybenzoxazines showed one main weight loss degradation step around 445ºC, which can be related with the breaking of Mannich bridge, and degradation of aliphatic polymer chain occurring simultaneously.

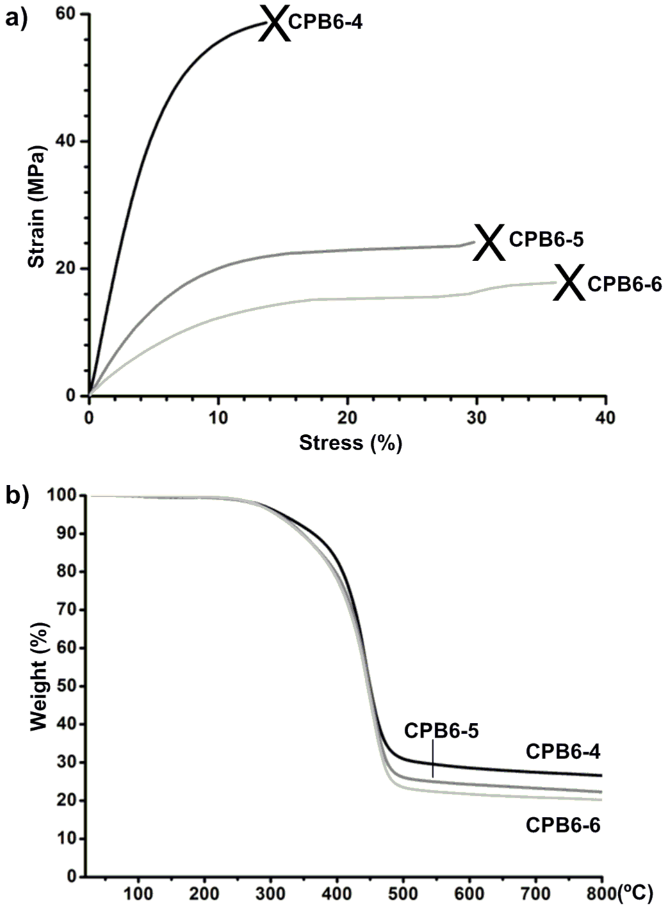


Figure 3.26. a) Bending measurements and b) TGA analysis of cured polybenzoxazines CPB6-4, CPB6-5, and CPB6-6.

3.2.4 Conclusion

Reported for the first time, ADMET polymerization was applied to a α,ω-diene bearing a thermally curable benzoxazine group. The benzoxazine-containing diene monomer was designed based on 10-undecenoic acid and 10-undecenyl amine as castor oil derived platform chemicals and hydroquinone. H-G2nd catalyst afforded quite high molecular weight polymers with no degradation of the heterocyclic ring structure. Using methyl 10-undecenoate as a chain stopper, thermally curable polymeric polybenzoxazine precursors with molecular weight ranging from 5600 to 11600 g mol^{-1} were obtained. The benzoxazine groups have been shown to readily undergo thermal ring-opening reaction in the absence of added catalyst to form crosslinked polymer networks. The viscoelastic, mechanical and thermal properties of the cured polybenzoxazines were dominated by the molecular weight and crosslinker content of the parent thermoplastic polymer. The results presented within this contribution envision that plant oils and fatty acids derived therefrom can be used to reduce polybenzoxazine chemistry reliance on petroleum as well as impart unprecedented properties to these phenolic-like materials.

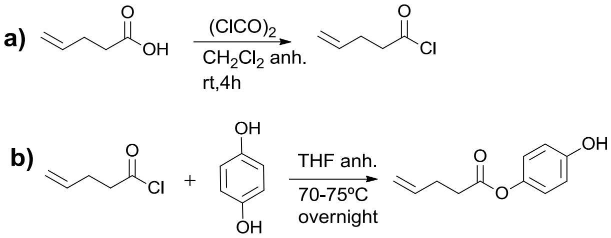
Experimental Part

4.1 Materials

The following chemicals were obtained from the sources indicated and used as received: hydroquinone (Aldrich), 4-toluenosulfonyl chloride (Fluka), p-benzoquinone (Aldrich), 10-undecenoyl chloride (Aldrich), 4-pentenoyl chloride (Aldrich), 4-hydroxybenzoic acid (Aldrich), 10-unden-1-ol (Aldrich), bromo-1-undecene (Aldrich), 10-undecenoic acid (Aldrich), aniline (Aldrich), n-propylamine (Merck), 1,1,3,3-tetramethyldisiloxane (S1), 1,4-*bis*(dimethylsilyl)-benzene (S2), Hexachloroplatinic acid hexahydrate Pt 38-40% (Speier's catalyst), [Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex] solution in xylene Pt 2% (Karstedt catalyst) (Aldrich), Grubbs 1st generation, Grubbs 2nd generation and Hoveyda-Drubbs 2nd generation (Aldrich), lithium aluminum hydride (Aldrich), tetraethylammonium iodide (Aldrich), paraformaldehyde (Scharlau), pyridine (Scharlau), vinyl ether (Aldrich), sodium hydroxide (Scharlau), anhydrous magnesium sulfate (Scharlau), potassium carbonate (Scharalau), and sodium azide (Scharlau). Toluene, ethanol, ethyl acetate were used as received. N-hexane was distillated. Diethylether was dried over benzophenone-sodium and used freshly destilated. Tetrahydrofuran (THF) was dried over benzophenone-sodium and used freshly destilled. Dimethylsufoxide (DMSO) was dried over CaH_2 and distilled under reduced pressure; dichloromethane (DCM) was dried, over phosphorous pentoxide and used freshly destillated. THF for SEC analysis was high performance liquid chromatograpghy grade (HPLC) (VWR).

4.2 Synthesis of Phenol Derivatives

4.2.1 Synthesis of 4-Hydroxyphenyl-4-Pentenoate



a) A solution of 4-pentenoic acid (10 g, 10.2 mL, 0.10 mol) in dry DCM (50 mL) was stirred under argon at room temperature and oxalyl chloride (14.3 g, 9.51 mL, 0.11 mol) added dropwise over 15 min. The solution was stirred at room temperature for 4h. The reaction mixture was concentrated in vacuo.[297] Yield: 80%.

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 2.61 (t, 2H, C**H**$_2$), 3.15 (t, 2H, C**H**$_2$), 5.12 (m, 2H, C=C**H**$_2$), 5.94 (m, 1H, C=C**H**).

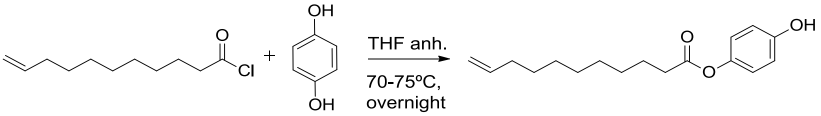
b) In a 250-mL round-bottomed flask, (27.5 g, 0.25 mol) of hydroquinone in 150 mL dry THF and 4 mL of pyridine were introduced and cooled to 0-5°C. (5.9 g, 0.05 mol) of 4-pentenoyl chloride in 10 mL of dry THF were added dropwise to the cold solution under vigorous stirring. When the addition was complete, the mixture was heated to reflux overnight and poured onto water-ice. The crude product was collected by filtration and recrystallized twice from heptane to give a white crystalline solid. Yield: 60%, mp. 68-70°C.

FTIR (cm^{-1}): 3446 (OH), 1737 (C=O), 1641 (C=C).

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 6.94-6.78 (dd, 4H, Ar-**H**), 5.94-5.84 (m, 1H, $CH=CH_2$), 5.15-5.05 (dd, 2H, $CH=C\mathbf{H}_2$), 4.68 (s, 1H, -O**H**), 2.62 (t, 2H, $C\mathbf{H}_2COO$), 2.49 (m, 2H, $C\mathbf{H}_2CH=CH_2$).

^{13}C NMR ($CDCl_3$, δ ppm): 173.0 (**C**OO-), 153.6 (**C**-OH), 144.0 (**C**-OOC), 139.3 ($\mathbf{C}H=CH_2$), 122.5 (**C**H meta to OH), 116.2 (**C**H ortho to OH), 116.1 ($CH=\mathbf{C}H_2$), 33.7 ($\mathbf{C}H_2CH=CH_2$), 29.0 ($OOC\mathbf{C}H_2CH_2$).

4.2.2 Synthesis of 4-Hydroxyphenyl-10-Undecenoate



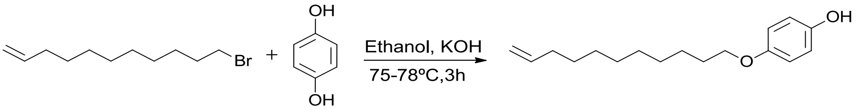
The synthesis was carried out following the same procedure as for 4-hydroxyphenyl-4-pentenoate but starting from (27.5 g. 0.25 mol) of hydroquinone in 150 mL dry THF, 4 mL of pyridine and (10.2 g, 0.05 mol) of 10-undecenoyl chloride in 10 mL of dry THF. The crude product was recrystallized twice from heptane giving a white crystalline solid.[298] Yield: 68%, mp. 66-68°C.

FTIR (cm^{-1}): 3452 (OH), 1737 (C=O), 1641 (C=C).

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 6.89-6.68 (dd, 4H, Ar-**H**), 5.86-5.76 (m, 1H, $C\mathbf{H}=CH_2$), 5.69 (s, 1H, O**H**), 5.02-4.91 (dd, 2H, $CH=C\mathbf{H}_2$), 2.53 (t, 2H, $C\mathbf{H}_2COO$), 2.02 (m, 2H, $C\mathbf{H}_2CH=CH_2$), 1.74 (m, 2H, $C\mathbf{H}_2CH_2COO$), 1.41-1.31 (m, 10H, $(C\mathbf{H}_2)_n$).

^{13}C NMR ($CDCl_3$, δ ppm): 173.8 (**C**OO), 153.6 (**C**OH), 144.0 (**C**OOC), 139.3 ($\mathbf{C}H=CH_2$), 122.4 (**C**H meta to OH), 116.2 (**C**H ortho to OH), 114.3 ($CH=\mathbf{C}H_2$), 34.5 ($\mathbf{C}H_2CH=CH_2$), 33.9 ($\mathbf{C}H_2COO$), 29.4-29.0 ($(\mathbf{C}H_2)_5$), 25.1 ($OOCCH_2\mathbf{C}H_2$).

4.2.3 Synthesis of 4-(10-Undecenyloxy)phenol



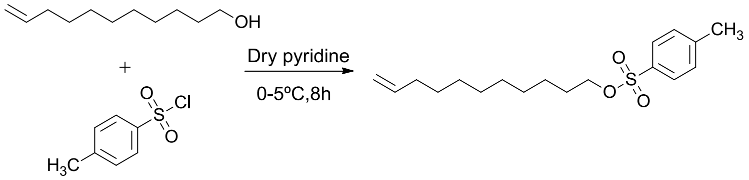
Hydroquinone (13.9 g, 0.12 mol) and 11-bromo-1-undecene 10.0 g (0.04 mol) were dissolved in 60 mL ethanol under a nitrogen atmosphere. The solution was heated under reflux and a solution of potassium hydroxide (2.5 g, 0.04 mol) in water 8 mL was added dropwise during 1h. The resulting suspension was heated for 3h and poured onto 500 mL of ice/water and extracted with diethylether (3 x 40 mL). The combined organic layers were dried with anhydrous $MgSO_4$ and concentrated under reduced pressure to give oil that solidifies upon cooling. The product was purified by recrystallyzing twice in hexane to give a white crystalline solid. Yield 53%.[210] Mp. 59-61ºC.

FTIR (cm^{-1}): 3423 (OH), 1642 (C=C), 1234 (C-O).

^1H NMR ($CDCl_3$,TMS, δ ppm): 6.81-6.72 (m, 4H, Ar-**H**), 5.87-5.76 (m, 1H, C**H**=CH_2), 5.01-4.91 (dd, 2H, CH=CH_2), 4.35 (s, 1H, O**H**), 3.88 (t, 2H, CH_2O), 2.04 (m, 2H, CH_2CH=CH_2), 1.74 (m, 2H, C$H_2$$CH_2$O), 1.46-1.29 (m, 12H, (CH_2)$_6$).

^{13}C NMR ($CDCl_3$, δ ppm): 153.5 (**C**-OH), 149.4 (**C**H-O), 139.4 (**C**H=CH_2), 116.1 (**C**H meta to OH), 115.5 (**C**H ortho to OH), 114.2 (CH=**C**H_2), 68.8 (**C**H_2-O), 33.9 (**C**H_2CH=CH_2), 29.6-29.0 ((**C**H_2)$_6$), 26.2 (OCH_2**C**H_2).

4.2.4 Synthesis of 10-Undecenyl *p*-Toluenesulfate



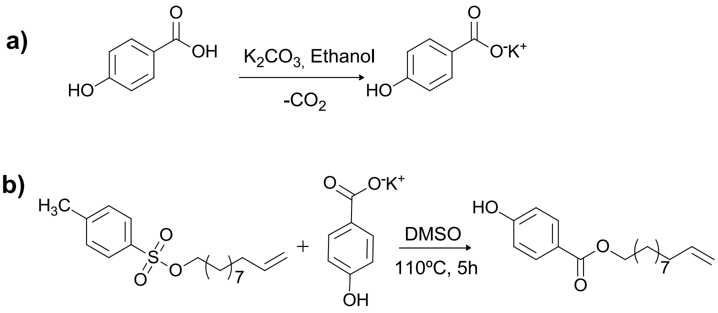
10-Undecenol (107.7 g, 0.63 mol) and 200 mL anhydrous pyridine were placed in a 500-mL round-bottom flask. A solution of *p*-toluenesulfonyl chloride (126.2 g, 0.66 mol) in 200 mL anhydrous pyridine was added dropwise at 0-5ºC and the reaction mixture was stirred for 8h. The solution was poured into ice/water (1 L), stirred for 2h and then extracted with diethylether (Et_2O) (3x200 mL). The combined organic layers were washed with 25% HCl (4x250 mL), H_2O (2x500 mL), diluted $NaHCO_3$ (2x500 mL), H_2O (2x500 mL) and dried with $MgSO_4$. After removal of the drying agent by filtration and the solvent under reduced pressure, the raw product was used in the next step without further purification.[299] Yield: 95%.

FTIR (ν cm^{-1}): 2924-2854 (C-H), 1640 (C=C), 1359 (S=O stretching).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 7.79-7.77 (d, 2H, Ar-**H**), 7.35-7.33 (d, 2H, Ar-**H**), 5.83-5.76 (m, 1H, C**H**=CH_2), 5.01-4.91 (dd, 2H, CH=C**H**$_2$), 4.01 (t, 2H, OC**H**$_2$), 2,44 (s, 3H, C**H**$_3$), 2.05-2.00 (m, 2H, C**H**$_2$CH=CH_2), 1.64-1.60 (m, 2H, OCH_2C**H**$_2$), 1.35-1.21 (m, 12H, (C**H**$_2$)$_6$).

^{13}C NMR ($CDCl_3$, δ ppm): 144.6 (**C**S), 138.9 (**C**CH_3), 133.1 (**C**H=CH_2), 129.7 (**C**H meta to S), 127.7 (**C**H orto to S), 114.1 (CH=**C**H$_2$), 70.6 (**C**H$_2$S), 33.7 (**C**H$_2$CH=CH_2), 29.2-28.7 ((**C**H$_2$)$_6$), 25.2 (OCH_2CH_2**C**H$_2$), 21.5 (**C**H$_3$).

4.2.5 Synthesis of 10-Undecenyl 4-Hydroxybenzoate



a) Potassium 4-hydroxybenzoate was prepared as follows: a mixture of 4-hydroxybenzoic acid (4.2 g, 0.03 mol) and K_2CO_3 (2.1 g, 0.015 mol) in ethanol (30 mL) was heated under reflux until CO_2 formation stopped (5h). Ethanol was removed under reduced pressure and the resulting salt dried in an oven at 100ºC for 48h.

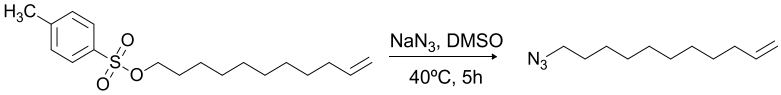
b) Over a solution of potassium 4-hydroxybenzoate (5.3 g, 0.03 mol) in 30 mL DMSO, 10-undecenyl 4-toluenesulfate (10.0 g, 0.03 mol) in 10 mL in DMSO was added. The mixture was heated at 120ºC for 3h, poured onto ice/water and extracted with Et_2O (3x100 mL). The combined organic layers were washed with cold 5% $NaHCO_3$, with water and finally dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product purified by column chromatography (hexane/ethylacetate=10/1) to give a pale yellow oil.[211] Yield: 67%

FTIR (cm^{-1}): 3338 (OH), 1679 (C=O), 1641 (C=C).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 7.95 (d, 2H, Ar-**H**), 6.85 (d, 2H, Ar-**H**), 5.96 (s, 1H, O**H**), 5.87-5.76 (m, 1H, C**H**=CH_2), 5.01-4.91 (dd, 2H, CH=C**H**$_2$), 4.28 (t, 2H, C**H**$_2$OOC), 2.04 (m, 2H, C**H**$_2$CH=CH_2), 1.74 (m, 2H, CH_2C**H**$_2$OOC), 1.46-1.28 (m, 12H, $(CH_2)_6$).

^{13}C NMR ($CDCl_3$, δ ppm): 167.6 (**C**OO), 160.9 (**C**OH), 139.3 (**C**H=CH_2), 132.0 (**C**H meta to OH), 122.2 (**C**HCOO), 115.5 (**C**H ortho to OH), 114.2 (CH=**C**H_2), 65.4 (**C**H_2COO), 33.9 (**C**H_2CH=CH_2), 29.6-28.8 ((**C**H_2)$_6$), 26.1 (OOCCH_2**C**H_2).

4.2.6 Synthesis of 10-Undecenyl Azide



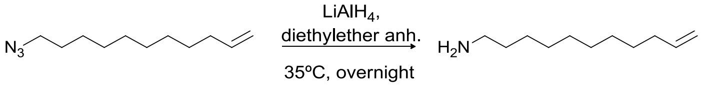
10-Undecenyl *p*-toluenesulfonate (127.7 g, 0.38 mol) was dissolved in DMSO in a 500-mL round-bottom flask. To the stirred solution, sodium azide (63.2 g, 0.97 mol) and tetraethylammonium iodide (0.2 g, 0.007 mol) were added and the reaction mixture was allowed to stir under argon for 5h at 40ºC. The solution was poured into ice/water (1 L), stirred for 2h and then extracted with Et_2O (3x200 mL). The combined organic layers were washed with 5% HCl (4x250 mL), H_2O (2x500 mL), diluted $NaHCO_3$ (2x500 mL), H_2O (2x500 mL) and dried with $MgSO_4$. After removal the drying agent by filtration and the solvent under reduced pressure, the raw product was used in the next step without further purification. Yield: 93%.

FTIR (ν cm^{-1}): 2925-2854 (C-H, stretching), 2091 (N=N=N, stretching), 1640 (C=C).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 5.84-5.77 (m, 1H, C**H**=CH_2), 5.01-4.91 (dd, 2H, CH=C**H**$_2$), 3.25 (t, 2H, C**H**$_2N_3$), 2.05-2.01 (m, 2H, C**H**$_2$CH=CH_2), 1.61-1.57 (m, 2H, C**H**$_2$CH_2N_3), 1.37-1.25 (m, 12H, (C**H**$_2$)$_6$).

^{13}C NMR ($CDCl_3$, δ ppm): 139.2 (**C**H=CH_2), 114.2 (CH=**C**H_2), 51.5 (**C**H_2N_3), 33.9 (**C**H_2CH=CH_2), 29.5-28.9 ((**C**H_2)$_6$), 26.8 (**C**H_2CH_2CH_2N_3).

4.2.7 Synthesis of 10-Undecenyl Amine



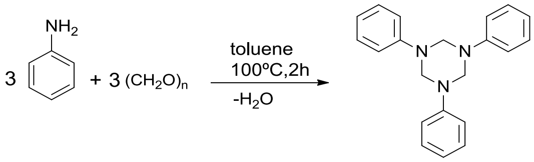
In a 1 L round-bottom flask, lithium aluminum hydride (7.7 g, 0.20 mol) was suspended in 770 mL anhydrous diethylether. Then, 10-undecenyl azide (15.3 g, 0.78 mol) was added dropwise and the reaction mixture stirred overnight. The reaction was quenched by drop-by-drop addition of 40 mL water. The organic layer was filtered and 10-undecenyl amine was used without any purification.[300] Yield: 94%.

FTIR (ν cm^{-1}): 3400-3300 and 3330-3250 (N-H, stretching), 2925-2854 (C-H, stretching), 1640 (C=C).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 5.86-5.75 (m, 1H, C**H**=CH_2), 5.01-4.89 (dd, 2H, CH=C**H**$_2$), 2.67 (t, 2H, C**H**$_2$$NH_2$), 2.06-2.00 (m, 2H, C**H**$_2$CH=CH_2), 1.44-1.27 (m, 12H, (C**H**$_2$)$_6$), 1.16 (s, 2H, N**H**$_2$).

^{13}C NMR ($CDCl_3$, δ ppm): 139.2 (**C**H=CH_2), 114.2 (CH=**C**H$_2$), 42.0 (**C**H$_2$$NH_2$), 33.9 (**C**H$_2$CH=$CH_2$), 29.5-28.9 ((**C**H$_2$)$_6$), 26.7 (**C**H$_2$$CH_2$$CH_2$$NH_2$).

4.2.8 Synthesis of 1,3,5-Triphenylhexahydro-1,3,5-Triazine



According to reported procedures;[301,302] (93 g, 1 mol) aniline was added to 1 mol of paraformaldehyde in a 250-mL two-necked round-bottomed flask with magnetic stirring. The mixture was heated up to 100°C and 75 mL of toluene was added under continuous stirring for 2 h. The mixture was then cooled, filtered, and washed several times with small amounts of cold toluene. The product was dried at 60°C. Yield: 77%.

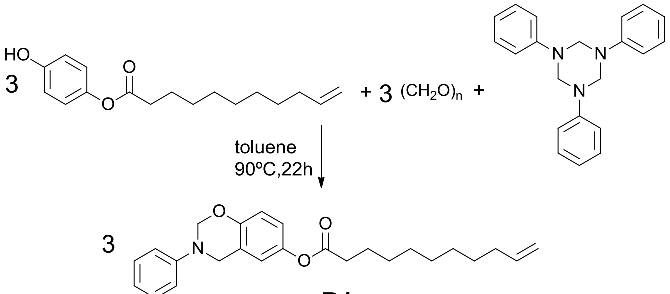
FT-IR (cm^{-1}): 1599, 1499, 755 and 692 (monosubstituted benzene), 1163, 1203 and 1336 cm−1 (C-N-C).

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 7,24-6,85 (m, 15H, Ar-**H**), 4.88 (s, 6H, C**H**$_2$-N).

^{13}C NMR ($CDCl_3$, δ ppm): 150 (N-Ar), 130 (**C**H meta to N), 122 (**C**H para to N), 118 (**C**H orta to N), 68 (**C**H$_2$-N).

4.3 Synthesis of Benzoxazine Monomers

4.3.1 Synthesis of 3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl-10-undecenoate (B1)



B1

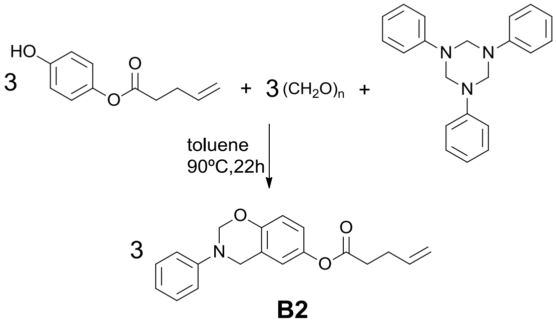
1,3,5-triphenylhexahydro-1,3,5-triazine (3.8 g, 0.012 mol), paraformaldehyde (1.1 g, 0.031 mol), and 30 mL toluene were placed into a 250 mL two-necked round bottomed flask and the mixture stirred at 0 °C for 15 min. 4-hydroxyphenyl-10-undecenoate (10.0 g, 0.036 mol) was added portionwise with stirring at 0°C during 30 min. The temperature was raised gradually up to 90°C and kept stirring for 22h. After cooling to room temperature, toluene was evaporated under reduced pressure and the residue dissolved in Et_2O (400 mL), washed several times with aqueous 2M NaOH (500 mL) with H_2O (500 mL) and dried with anhydrous $MgSO_4$. After concentration the resulting yellow solid was purified by recrystallization in hexane to give pale yellow crystals. Yield: 82%, mp. 50-52°C.

FTIR (cm^{-1}): 1751 (C=O), 1642 (C=C), 1029 (C-O-C), 1166 (C-N-C), 942 (N-CH2-O Bz ring).

^1H NMR ($CDCl_3$, TMS, δ ppm): 7.28-6.76 (m, 8H, Ar-**H**), 5.86-5.76 (m, 1H, C**H**=CH_2), 5.34 (s, 2H, NC$\mathbf{H_2}$O), 5.01-4.91 (m, 2H, CH=C$\mathbf{H_2}$), 4.61 (s, 2H, N**C**H_2Ar), 2.51 (t, 2H, CH_2COO), 2.05 (m, 2H, C**H**$_2$CH=CH_2), 1.72 (m, 2H, -C**H**$_2$CH_2COO), 1.39-1.29 (m,10H (C**H**$_2$)$_5$).

^{13}C NMR (CDCl$_3$, δ ppm): 172.8 (**C**OO), 152.1 (**C**-O), 148.4 (**C**-N), 144.2 (**C**-OOC), 139.3 (**C**H=CH_2), 129.4 (**C**H meta to N), 121.8-117.8 (6 Ar**C**), 114.3 (CH=**C**H$_2$), 79.7 (N**C**H$_2$O), 50.5 (N**C**H$_2$Ar), 34.4 (**C**H$_2$COO), 33.9 (**C**H$_2$CH=CH_2), 29.4-29.0 ((**C**H$_2$)$_5$), 25.1 (**C**H$_2$CHCOO).

4.3.2 Synthesis of 3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl-4-pentenoate (B2)



B2

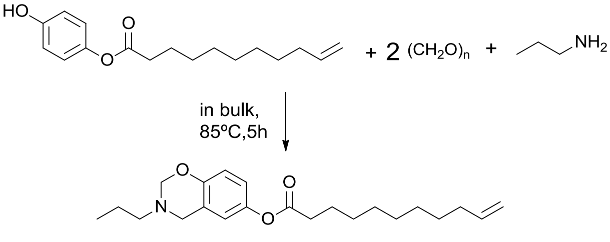
The synthesis was carried out following the same procedure as for B1 starting from 1,3,5-triphenylhexahydro-1,3,5-triazine (5.7 g, 0.018 mol), paraformaldehyde (1.7 g, 0.056 mol) in 45 mL toluene and 4-hydroxyphenyl-4-pentenoate (10.0 g, 0.056 mol). The resulting yellow solid was purified by recrystallization in hexane to yield pale yellow solid. Yield: 76 % mp. 41-43°C.

FTIR (cm^{-1}): 1747 (C=O), 1641 (C=C), 1224 (C-O-C), 1136 (C-N-C), 933 (N-CH_2-O Bz ring).

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 7.28-6.75 (m, 8H, Ar-**H**), 5.91-5.85 (m, 1H, C**H**=CH_2), 5.34 (s, 2H, NC**H**$_2$O), 5.15-5.05 (dd, 2H, CH=C**H**$_2$), 4.61 (s, 2H, NC**H**$_2$C), 2.65 (m, 2H, C**H**$_2$COO), 2.50 (m, 2H, C**H**$_2$CH=CH_2).

^{13}C NMR ($CDCl_3$, δ ppm): 172.1 (**C**OO-), 152.0 (**C**-O), 148.4 (**C**-N), 144.0 (**C**-OOC), 136.5 (**C**H=CH_2), 129.5-117.8 (8 Ar**C**), 116.1 (CH=**C**H$_2$), 79.6 (N**C**H$_2$O), 50.5 (N**C**H$_2$Ar), 33.7 (**C**H$_2$COO), 29.0 (**C**H$_2$CH=CH_2).

4.3.3 Synthesis of 3-Propyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl-10-undecenoate (B3)



B3

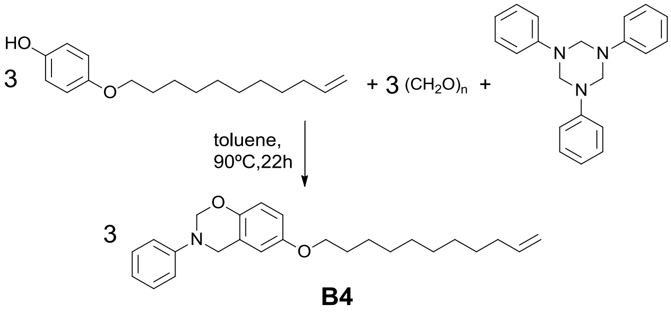
In a 100 mL round bottomed flask with paraformaldehyde (6.6 g, 0.22 mol), n-propylamine (6.5 g, 0.11 mol) was added dropwise during 15 min at 0ºC. The mixture was stirred 15 min and 4-hydroxyphenyl-10-undecenoate (20.0 g, 0.07 mol) was added portionwise with stirring at 0°C during 30 min. The temperature was raised gradually up to 85ºC and the mixture kept stirring for 5 h. After cooling to room temperature, the mixture was dissolved in Et_2O (400 mL), washed several times with aqueous 2M NaOH (500 mL) and H_2O (500 mL) and dried with anhydrous $MgSO_4$. After concentrating, the resulting red oil was purified by column chromatography (hexane/ethylacetate=10/1) to give a pale yellow oil. Yield: 67%

FTIR (cm^{-1}): 1755, (C=O), 1640 (C=C), 1176 (C-N-C), 1025 (C-O-C), 977 (N-CH_2-O Bz ring).

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 6.81-6.68 (m, 3H, Ar-**H**), 5.84-5.76 (m, 1H, C**H**=CH_2), 5.01-4.91 (m, 2H, CH=C**H**$_2$), 4.84 (s, 2H, NC**H**$_2$O), 3.97 (s, 2H, NC**H**$_2$Ar), 2.69 (t, 2H, NC**H**$_2CH_2CH_3$), 2.51 (t, 2H, CH_2C**H**$_2$COO), 2.03 (m, 2H, C**H**$_2$CH=CH_2), 1.72 (m, 2H, OOCCH_2C**H**$_2$), 1.55 (m, 2H, CH_2C**H**$_2CH_3$), 1.39-1.25 (m, 10H, (C**H**$_2$)$_5$), 0.92 (t, 3H, CH_2CH_2C**H**$_3$).

^{13}C NMR ($CDCl_3$, δ ppm): 172.9 (CH_2**C**OO), 151.9 (**C**-O), 143.9 (**C**-OOC), 139.3 (**C**H=CH_2), 121.0-120.3 (2 **C**H ortho to OOC and **C** meta to OOC), 117.1 (**C**H ortho to O-CH_2), 114.3 (CH=**C**H$_2$), 82.7 (N**C**H$_2$O), 53.5 (N**C**H$_2CH_2CH_3$), 50.3 (N**C**H$_2$Ar), 34.5 (**C**H$_2$COO), 33.9 (**C**H$_2$CH=CH_2), 29.4-29.0 ((**C**H$_2$)$_4$), 25.1 (**C**H$_2CH_2$COO), 21.4 (NCH_2**C**H$_2CH_3$), 11.8 (NCH_2CH_2**C**H$_3$).

4.3.4 Synthesis of 3-Phenyl-6-(undec-10-en-1-yloxy)-3,4-dihydro-2H-benzo[e][1,3]oxazine (B4)



1,3,5-Triphenylhexahydro-1,3,5-triazine, (6.3 g, 0.02 mol), paraformaldehyde (1.8 g, 0.06 mol) and 50 mL toluene were placed into a 250 mL two-necked round bottomed flask and the mixture stirred at 0ºC for 15 min. 4-(10-undecenyloxy)phenol (16.0 g, 0.06 mol) was added portionwise with stirring at 0ºC during 30 min. The temperature was raised gradually up to 90ºC and kept stirring for 22h. After cooling to room temperature, toluene was evaporated under reduced pressure and the residue dissolved in Et_2O

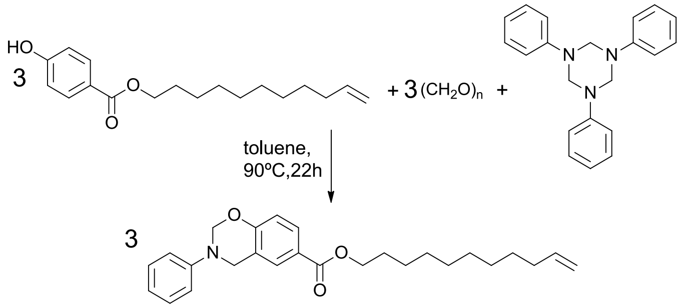
(400 mL), washed several times with aqueous 2M NaOH (500 mL) and H_2O(500 mL) and dried with anhydrous $MgSO_4$. After concentration the resulting orange solid was purified by column chromatography (hexane/ethyl acetate=10/1) to give a pale yellow solid. Yield: 67%, mp. 47-50ºC.

FTIR (ν cm^{-1}): 1641 (C=C), 1168 (C-N-C), 1224 (C-O), 1033 (C-O-C), 944 ($N\text{-}CH_2\text{-}O$ Bz ring).

^1H NMR ($CDCl_3$,TMS, δ ppm): 7.28-6.56 (m, 8H, Ar-**H**), 5.86-5.76 (m, 1H, $C\mathbf{H}=CH_2$), 5.30 (s, 2H, NCH_2O), 5.02-4.91 (dd, 2H, $CH=C\mathbf{H}_2$), 4.59 (s, 2H, $N\mathbf{CH}_2Ar$), 3.86 (m, 2H, $C\mathbf{H}_2CO$), 2.04 (m, 2H, $C\mathbf{H}_2CH=CH_2$), 1.73 (m, 2H, $C\mathbf{H}_2CH_2CO$), 1.43-1.29 (m, 10H $(C\mathbf{H}_2)_5$).

^{13}C NMR ($CDCl_3$, δ ppm): 153.4 (**C**-O), 148.6, (**C**-O-(CH2)n), 148.3 (**C**-N), 139.4 ($\mathbf{C}H=CH_2$), 129.4 (**C**H meta to N), 121.5 (**C**H para to N), 121.5-112.2 (6 Ar**C**), 114.3 ($CH=\mathbf{C}H_2$), 79.6 ($N\mathbf{C}H_2O$), 68.7 ($\mathbf{C}H_2O$), 50.7 ($N\mathbf{C}H_2Ar$), 34.0 ($\mathbf{C}H_2CH=CH_2$), 29.7-29.1 ($(\mathbf{C}H_2)_6$), 26.2 ($\mathbf{C}H_2CH_2CO$).

4.3.5 Synthesis of Undec-10-en-1-yl 3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylate (B5)



B5

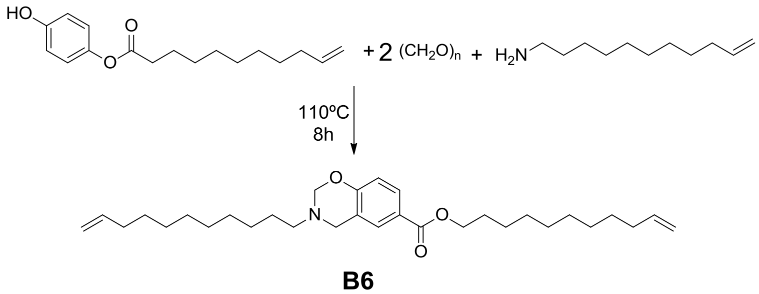
The synthesis was carried out following the same procedure as for B4 starting from 1,3,5-triphenylhexahydro-1,3,5-triazine (6.3 g, 0.02 mol), paraformaldehyde (1.8 g, 0.06 mol) in 50 mL toluene and 10-undecenyl 4-hydroxybenzoate (17.4 g, 0.06 mol). The resulting solid was purified by column chromatography (hexane/ethylacetate=10/1) to give a pale yellow liquid. Yield: 65%.

FTIR (ν cm^{-1}): 1709 (C=O), 1641 (C=C), 1159 (C-N-C), 1027 (C-O-C), 936 ($N-CH_2-O$ Bz ring).

^1H NMR ($CDCl_3$,TMS, δ ppm): 7.28-6.76 (m, 8H, Ar-**H**), 5.87-5.75 (m, 1H, C**H**=CH_2), 5.41 (s, 2H, $NC\mathbf{H}_2O$), 5.01-4.90 (dd, 2H, CH=$C\mathbf{H}_2$), 4.66 (s, 2H, $NC\mathbf{H}_2Ar$), 4.22 (m, 2H, $C\mathbf{H}_2COO$), 2.04 (m, 2H, $C\mathbf{H}_2CH=CH_2$), 1.73 (m, 2H, $C\mathbf{H}_2CH_2COO$), 1.43-1.25 (m, 10H $(C\mathbf{H}_2)_5$).

^{13}C NMR ($CDCl_3$, δ ppm): 166.5 ($\mathbf{C}OOCH_2$), 158.4 (**C**-O), 148.1 (**C**-N), 139.3 (**C**H=CH_2), 129.5 (**C**H meta to N), 129.8-114.3 (6 Ar**C**), 118.7 (**C**H orto to N), 114.3 (CH=$\mathbf{C}H_2$), 80.3 ($N\mathbf{C}H_2O$), 65.0 ($\mathbf{C}H_2COO$), 50.6 ($N\mathbf{C}H_2Ar$), 33.9 ($\mathbf{C}H_2CH=CH_2$), 29.6-28.9 ($(\mathbf{C}H_2)_6$), 26.2 ($\mathbf{C}H_2CHCOO$).

4.3.6 Synthesis of 3-(Undec-10-en-1-yl)-3,4-dihydro-2H-benzo[e] [1,3] oxazin-6-yl undec-10-enoate (B6)



B6

10-Undecenyl amine (6.6 g, 0.04 mol) and paraformaldehyde (4.8 g, 0.16 mol) were placed into 100 mL two-necked round-bottom flask and stirred at 0ºC for 15 min. 4-Hydroxyphenyl-10-undecenoate (7.4 g, 0.02 mol) was added portionwise with stirring at 0ºC during 30 min. The temperature was raised gradually up to 110ºC and kept stirring for 8h. After cooling to room temperature, the residue was dissolved in Et_2O (400 mL), washed several times with aqueous 2N NaOH (500 mL), H_2O (500 mL), and dried with $MgSO_4$. After concentration, the resulting product was purified by column chromatography (hexane/ethylacetate=10/1) to give a yellowish solid. Yield: 56%, mp. 24-26ºC.

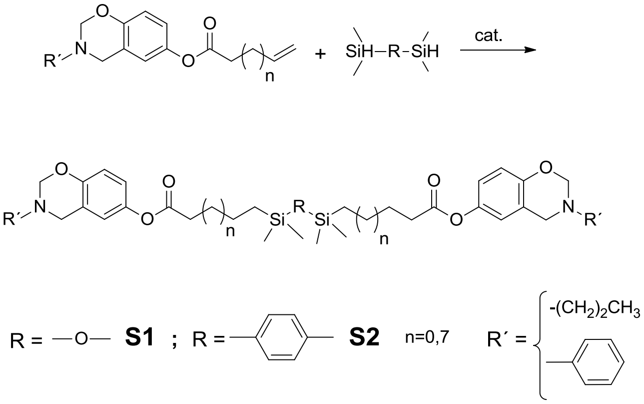
FTIR (ν cm^{-1}): 1757 (C=O), 1640 (C=C), 1180 (C-N-C), 1021 (C-O-C), 992 (=C-H), 976 (N-CH2-O), 907 (=C-H).

^{1}H NMR ($CDCl_3$,TMS, δ ppm):): 6.81-6.68 (m, 3H, Ar-**H**), 5.86-5.76 (m, 2H, C**H**=CH_2), 5.02-4.90 (dd, 4H, CH=C$\mathbf{H_2}$), 4.83 (s, 2H, NC$\mathbf{H_2}$O), 3.96 (s, 2H, NC$\mathbf{H_2}$Ar), 2.71 (t, 2H, C$\mathbf{H_2}$N), 2.51 (t, 2H, C$\mathbf{H_2}$COO), 2,06-2,01 (m, 4H, C$\mathbf{H_2}$CH=CH_2), 1.76-1.68 (m, 2H, C$\mathbf{H_2}$$CH_2$N), 1.55-1.51 (m, 2H, C$\mathbf{H_2}$$CH_2$COO), 1.38-1.27 (m, 22H, (C$\mathbf{H_2}$)$_{11}$).

^{13}C NMR ($CDCl_3$, δ ppm): 172.8 (**C**OO), 151.9 (**C**Ar-O), 143.9 (CAr-OO**C**), 139.3-139.2 (**C**H=CH_2), 120.9-120.3 (2 **C**H ortho to OOC and **C** meta to OOC), 117.1 (**C**H ortho to OCH_2), 114.3-114.2 (CH=**C**H_2), 82.6 (N**C**H_2O), 51.5 (N**C**H_2Ar), 50.2 (CH_2**C**H_2N), 34.4 (**C**H_2COO), 33.9 (**C**H_2CH=CH_2), 29.6-29.0 (10C, (**C**H_2)$_{10}$), 28.2 (**C**$H_2$$CH_2$N), 27.3 (**C**$H_2$$CH_2$$CH_2$N), 25.1 (**C**$H_2$$CH_2$COO).

4.4 Synthesis of Benzoxazine Dimers

4.4.1 General Procedure for the Hydrosilylation with 1,1,3,3-Tetramethyldisiloxane (S1) or 1,4-bis-(Dimethylsilyl)benzene (S2)

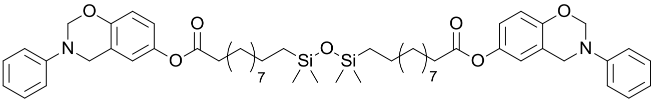


Hydrosilylations were carried out in toluene under argon atmosphere using Speier's (H_2PtCl_6) or Karstedt's [Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex] catalysts with Pt/C=C molar ratios between 0.04 to 0.15 at different temperatures (25, 65 and 90ºC).

For hydrosilylation studies, about 1 mmol of B1, B2 or B3 were dissolved in toluene (1 mL) and the stoichiometric amount of S1 or S2 was added. The resulting ≈1M mixture was stirred at room temperature for 5 min and then the required amount of catalyst was added dropwise with stirring (in the case of the Speier's catalyst a 10% (w/v) solution in THF or IPA was used). Temperature was kept at 25°C or raised gradually to 65 or 90°C. Reactions were monitored by ^{1}H-NMR and stopped when the double bond signals completely disappear or when their intensity remains constant. Toluene was evaporated under reduced pressure and the catalyst removed by means of a silica gel short path using hexane/ethylacetate as eluent. After solvent evaporation the product was dried under vacuum at room temperature for 24h.

Monomer synthesis for curing studies was carried out in 10 mmol scale using toluene (10 mL) and Karstedt's catalyst in 0.04% Pt/C=C molar ratio for B1 and B2 and 0.15 % Pt/C=C molar ratio for B3 at 65°C for 24h.

4.4.1.1 *Bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-11,11'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)diundecanoate (B1S1)*



B1S1

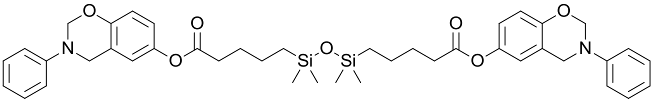
Yellow solid. Yield: 90%, mp. 40-42°C.

FTIR (cm^{-1}): 1749 (C=O), 1251 ($Si-CH_3$), 1161 (C-N-C), 1108 (Si-O-Si), 1033 (C-O-C), 938 ($N-CH_2-O$ Bz ring), 835 ($Si-CH_3$).

^1H NMR ($CDCl_3$, TMS, δ ppm): 7.29-6.77 (16H, Ar-**H**), 5.34 (s, 4H, $NC\mathbf{H}_2O$), 4.61 (s, 4H, $NC\mathbf{H}_2C$), 2.52 (t, 4H, $CH_2C\mathbf{H}_2COO$), 1.74 (m, 4H, $C\mathbf{H}_2CH_2COO$), 1.40-1,30 (m, 28H, $(C\mathbf{H}_2)_7$), 0.53 (t, 4H, $C\mathbf{H}_2Si$), 0.08 (s, 12H, $SiC\mathbf{H}_3$).

^{13}C NMR ($CDCl_3$, δ ppm): 172.8 (**C**OO), 152.1 (**C**-O), 148.4 (**C**-N), 144.2 (**C**-OOC), 129.4-117.8 (6 Ar**C**H and 1 Ar**C**), 79.7 ($N\mathbf{C}H_2O$), 50.6 (NCH_2Ar), 34.5 ($\mathbf{C}H_2COO$), 33.6 ($SiCH_2CH_2\mathbf{C}H_2$), 29.7-29.3 ($(\mathbf{C}H_2)_5$), 25.1 ($\mathbf{C}H_2CH_2COO$), 23.5 ($SiCH_2\mathbf{C}H_2CH_2$), 18.6 ($\mathbf{C}H_2Si$-), 0.5 ($Si\mathbf{C}H_3$).

4.4.1.2 *Bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dipentanoate (B2S1)*



B2S1

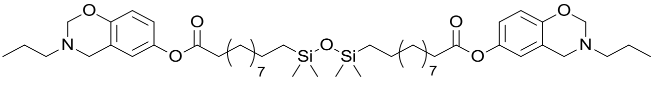
Pale yellow oil. Yield: 90%.

FTIR (cm^{-1}): 1753 (C=O), 1250 (Si-CH_3), 1137 (C-N-C), 1105 (Si-O-Si), 1030 (C-O-C), 928 (N-CH_2-O Bz ring), 839 (Si-CH_3).

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 7.28-6.74 (m, 16H, Ar-**H**), 5.33 (s, 4H, $NC\mathbf{H}_2O$), 4.60 (s, 4H, $NC\mathbf{H}_2C$), 2.52 (t, 4H, $CH_2C\mathbf{H}_2COO$), 1.74 (m, 4H, $C\mathbf{H}_2CH_2COO$), 1.42 (m, 4H, $C\mathbf{H}_2CH_2Si$), 0.56 (t, 4H, $C\mathbf{H}_2Si$), 0.07 (s, 12H, $SiC\mathbf{H}_3$).

^{13}C NMR ($CDCl_3$, δ ppm): 172.8 (**C**OO), 152.1 (**C**-O), 148.4 (**C**-N), 144.3 (**C**-OOC), 129.5-117.8 (6 Ar**C**H and 1 Ar**C**), 79.7 ($N\mathbf{C}H_2O$), 50.6 ($N\mathbf{C}H_2Ar$), 34.2 ($\mathbf{C}H_2COO$), 28.7 ($\mathbf{C}H_2CH_2COO$), 23.1 ($\mathbf{C}H_2CH_2Si$), 18.3 ($\mathbf{C}H_2Si$-), 0.6 ($Si\mathbf{C}H_3$).

4.4.1.3 *Bis(3-propyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-11,11′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)diundecanoate (B3S1)*



B3S1

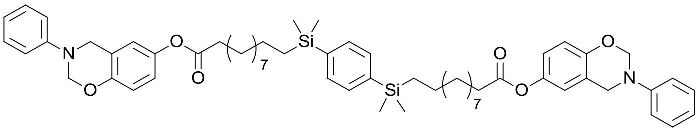
Pale yellow oil. Yield: 82%.

FTIR (cm^{-1}): 1756 (C=O), 1251 (Si-CH$_3$), 1176 (C-N-C), 1106 (Si-O-Si), 1045 (C-O-C), 929 (N-CH$_2$-O Bz ring), 838 (Si-CH$_3$).

^{1}H NMR (CDCl$_3$, TMS, δ ppm): 6.81-6.68 (m, 6H, Ar-**H**), 4.84 (s, 4H, NC**H**$_2$O), 3.96 (s, 4H, NC**H**$_2$Ar), 2.69 (t, 4H, NC**H**$_2$CH$_2$CH$_3$), 2.50 (t, 4H, CH$_2$C**H**$_2$COO), 1.72 (m, 4H, C**H**$_2$CH$_2$COO), 1.57 (m, 4H, NCH$_2$C**H**$_2$CH$_3$), 1.39-1.28 (m, 28H, (C**H**$_2$)$_7$), 0.92 (t, 6H, NCH$_2$CH$_2$C**H**$_3$), 0.5 (m, 4H, C**H**$_2$Si), 0.05 (s, 12H, SiC**H**$_3$).

^{13}C NMR (CDCl$_3$, δ ppm): 172.8 (**C**OO), 151.9 (**C**-O), 143.9 (**C**-OOC), 120.9-117.1 (3 Ar**C**H and 1 Ar**C**), 82.7 (N**C**H$_2$O), 53.4 (N**C**H$_2$CH$_2$CH$_3$), 50.2 (N**C**H$_2$Ar), 34.5 (**C**H$_2$COO), 33.5 (SiCH$_2$CH$_2$**C**H$_2$), 29.6-29.2 (SiCH$_2$**C**H$_2$CH$_2$ and (**C**H$_2$)$_5$), 25.1 (**C**H$_2$CH$_2$COO), 23.4 (SiCH$_2$**C**H$_2$CH$_2$), 21.4 (NCH$_2$**C**H$_2$CH$_3$), 18.5 (Si**C**H$_2$), 11.7 (NCH$_2$CH$_2$**C**H$_3$), 0.5 (Si**C**H$_3$).

4.4.1.4 *Bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-11,11′-(1,4-phenylenebis(dimethylsilanediyl)diundecanoate (B1S2)*



B1S2

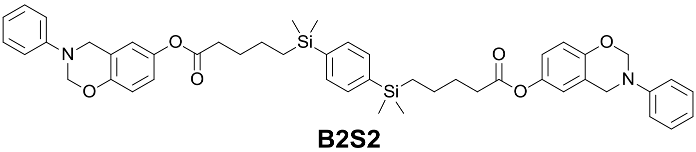
Pale yellow solid. Yield: 85%, mp. 80-82°C.

FTIR (cm^{-1}): 1760 (C=O), 1249 (Si-CH$_3$), 1165 (C-N-C), 1133 (Si-Ar-Si), 1031 (C-O-C), 918 (N-CH$_2$-O Bz ring), 835 (Si-CH$_3$).

^{1}H NMR (CDCl$_3$, TMS, δ ppm): 7.49 (s, 4H, ArC**H**-Si), 7.28-6.75 (m, 16H, Ar-**H**), 5.34 (s, 4H, NC**H**$_2$O), 4.61 (s, 4H, NC**H**$_2$C), 2.50 (t, 4H, CH$_2$C**H**$_2$COO), 1.72 (m, 4H, C**H**$_2$CH$_2$COO), 1.54-1.25 (m, 28H, (C**H**$_2$)$_7$), 0.74 (t, 4H, Si-CH$_2$C**H**$_2$), 0.24 (s, 12H, Si-C**H**$_3$).

^{13}C NMR (CDCl$_3$, δ ppm): 172.9 (**C**OO), 152.1 (**C**-O), 148.4 (**C**-N), 144.2 (**C**-OOC), 140.3 (Ar**C**-Si), 132.9 (Ar**C**H-Si), 129.4-117.8 (6 Ar**C**H and 1 Ar**C**), 79.7 (N**C**H$_2$O), 50.6 (N**C**H$_2$Ar), 34.5 (CH$_2$**C**H$_2$COO), 33.8 (**C**H$_2$CH$_2$CH$_2$Si), 29.7-29.2 ((**C**H$_2$)$_5$), 25.1 (**C**H$_2$CH$_2$COO), 24.0 (CH$_2$**C**H$_2$CH$_2$Si), 15.8 (CH$_2$CH$_2$**C**H$_2$Si), -2.8 (Si**C**H$_3$).

4.4.1.5 *Bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-5,5′-(1,4-phenylenebis(dimethylsilanediyl)dipentanoate (B2S2)*



B2S2

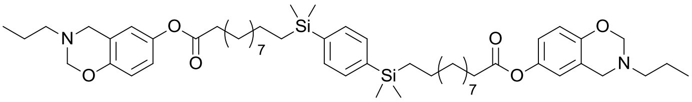
Pale yellow oil. Yield: 80%.

FTIR (cm^{-1}): 1752 (C=O), 1248 (Si-CH$_3$), 1160 (C-N-C), 1134 (Si-Ar-Si), 1030 (C-O-C), 929 (N-CH$_2$-O Bz ring), 832 (Si-CH$_3$).

^{1}H NMR (CDCl$_3$, TMS, δ ppm): 7.49 (s, 4H, ArC**H**-Si), 7.28-6.74 (m, 16H, Ar-C**H**), 5.34 (s, 4H, NC**H**$_2$O), 4.62 (s, 4H, NC**H**$_2$Ar), 2.50 (t, 4H, CH$_2$C**H**$_2$COO), 1.75 (m, 4H, C**H**$_2$CH$_2$COO), 1.44 (m, 4H, CH$_2$C**H**$_2$Si), 0.81 (m, 4H, C**H**$_2$CH$_2$Si), 0.27 (s, 12H, Si-C**H**$_3$).

^{13}C NMR (CDCl$_3$, δ ppm): 172.8 (**C**OO), 152.1 (**C**-O), 148.4 (**C**-N), 144.2 (**C**-OOC), 140.0 (Ar**C**-Si), 133.0 (Ar**C**H-Si), 129.4-117.8 (6 Ar**C**H and 1 Ar**C**), 79.7 (N**C**H$_2$O), 50.6 (N**C**H$_2$Ar), 34.1 (**C**H$_2$COO), 28.8 (**C**H$_2$CH$_2$CH$_2$Si), 23.7 (CH$_2$**C**H$_2$CH$_2$Si), 15.5 (CH$_2$CH$_2$**C**H$_2$Si), -2.9 (Si**C**H$_3$).

4.4.1.6 *Bis(3-propyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-11,11'-(1,4-phenylenebis(dimethylsilanediyl)diundecanoate (B3S2)*



B3S2

Pale yellow oil. Yield: 77%.

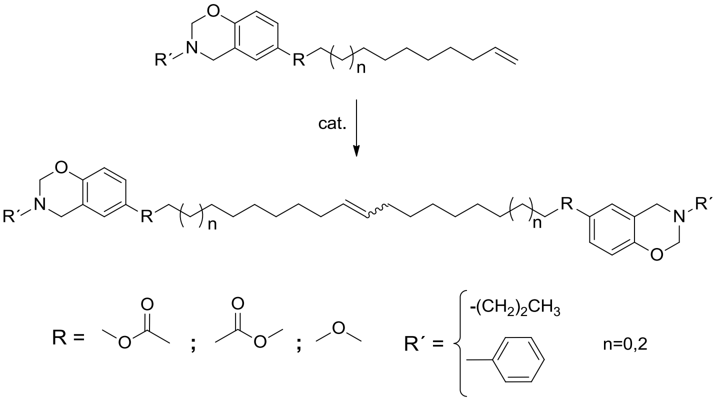
FTIR (cm^{-1}): 1756 (C=O), 1247 (Si-CH$_3$), 1176 (C-N-C), 1134 (Si-Ar-Si), 977 (N-CH2-O Bz ring), 837 (Si-CH$_3$).

^{1}H NMR (CDCl$_3$, TMS, δ ppm): 7.49 (s, 4H ArC**H**-Si), 6.82-6.69 (m, 6H, ArC**H**), 4.84 (s, 4H, NC**H**$_2$O), 3.97 (s, 4H, NC**H**$_2$C), 2.70 (t, 4H, CH$_3$CH$_2$C**H**$_2$N), 2.51 (t, 4H, CH$_2$C**H**$_2$COO), 1.72 (m, 4H, C**H**$_2$CH$_2$COO), 1.58 (m, 4H, CH$_3$CH$_2$CH$_2$N), 1.40-1.26 (m, 28H, (CH$_2$)$_n$), 0.92 (t, 6H, CH$_3$C**H**$_2$CH$_2$N), 0.74 (m, 4H, SiCH$_2$C**H**$_2$), 0.25 (t, 12H, Si-C**H**$_3$)

^{13}C NMR (CDCl$_3$, δ ppm): 172.9 (**C**OO), 151.9 (**C**-O), 143.9 (**C**-OOC), 140.3 (Ar**C**-Si), 132.9 (Ar**C**H-Si), 120.9-117.1 (3 Ar**C**H and 1 ArC), 82.6 (N**C**H$_2$O), 53.4 (N**C**H$_2$CH$_2$CH$_3$), 50.2 (N**C**H$_2$Ar), 34.5 (CH$_2$**C**H$_2$COO), 33.6 (**C**H$_2$CH$_2$CH$_2$Si) 29.7-29.4 ((**C**H$_2$)$_7$), 25.1 (**C**H$_2$CH$_2$COO), 24.0 (SiCH$_2$**C**H$_2$CH$_2$),

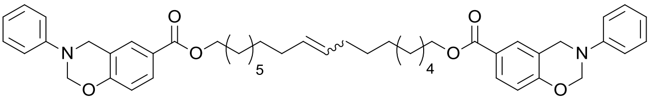
21.4 (NCH$_2$**C**H$_2$CH$_3$), 15.8 (Si**C**H$_2$), 11.8 (NCH$_2$CH$_2$**C**H$_3$), -2.8 (-Si**C**H$_3$).

4.4.2 General Procedure for Metathesis Dimerization



Metathesis reactions were carried out with 2% or 5% of G1st, G2nd, or H-G2nd catalysts. Reactions were carried out without solvent and under vacuum (2 mm Hg). (Experiments using p-benzoquinone as additive were also carried out). Under argon about 0.2g (0.5x10^{-3} mol) of B1, B2, B3, B4 or B5, the appropriate amount of catalyst and 1mL of DCM were put into a 10ml shlenck flask and the mixture was homogenized by stirring at room temperature for 20 min. After evaporating DCM under argon, the temperature was raised up to 40, 60 or 80ºC and maintained with magnetic stirring for 8 or 24h. The reaction progress was monitored by ^{1}H-NMR spectroscopy. The final reaction product was chromatographied using silica gel (hexane/ethylacetate, 10:1) to remove Ru byproducts and isolated by solvent evaporation under vacuum. Synthesis of MB1, MB3, MB4 and MB5 *bis*-benzoxazines was scaled up to 5 mmol scale using 5% G2nd catalyst at 80ºC for 24h.

4.4.2.1 *(Z/E)-bis(3-phenyl-3,4-dihydro-2H-benzo[e] [1,3]oxazin-6-yl) icos-10-enedioate (MB1)*



MB1

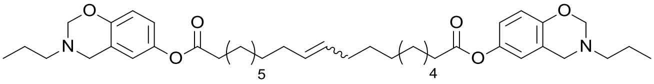
Light yellow solid. Yield: 70% mp. 59-62ºC

FTIR (ν cm^{-1}):1749 (C=O), 1250 (C-O-C), 1157 (C-N-C), 1033 (C-O-C), 953 (N-CH_2-Ar Bz ring), 938 (CH=CH).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 7.28-6.75 (m, 16H, Ar-**H**), 5.39-5.37 (m, 2H, C**H**=C**H**), 5.33 (s, 4H, NC**H**$_2$O), 4.61 (s, 4H, NC**H**$_2$Ar), 2.50 (t, 4H, CH_2C**H**$_2$COO), 1.97 (m, 4H, C**H**$_2$CH=CH), 1.72 (m, 4H, C**H**$_2$$CH_2$COO), 1.40-1.26 (m, 20H (C**H**$_2$)$_5$).

^{13}C NMR ($CDCl_3$, δ ppm): 172.8 (**C**OO), 152.1 (**C**-O), 148.4 (**C**-N), 144.2 (**C**-OOC), 129.4 (**C**H=**C**H), 121.0-118.5 (5 **C**H 1 **C**Ar), 117.8 (**C**H orto to C-O), 79.7 (N**C**H$_2$O), 50.6 (N**C**H$_2$Ar), 34.5 (**C**H$_2$$CH_2$COO), 32.7 (**C**H$_2$CH=CH), 29.8-29.2 ((**C**H$_2$)$_5$), 25.1 (**C**H$_2$$CH_2$COO).

4.4.2.2 *(Z/E)-bis(3-propyl-3,4-dihydro-2H-benzo[e] [1,3]oxazin-6-yl)eicos-10-enedioate (MB3)*



MB3

Light yellow syrup. Yield: 68%.

FTIR (ν cm^{-1}): 1754 (C=O), 1214 (C-O-C), 1175-1135 (C-N-C), 1085 (C-O-C), 975 ($N-CH_2-O$ Bz ring), 928 (CH=CH).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 6.81-6.68 (m, 6H, Ar-**H**), 5.39-5.37 (m, 2H, -C**H**=C**H**-), 4.84 (s, 4H, $NC\mathbf{H}_2O$), 3.96 (s, 4H, $NC\mathbf{H}_2C$), 2.69 (t, 4H, -$NC\mathbf{H}_2CH_2CH_3$), 2.50 (t, 4H, $CH_2C\mathbf{H}_2COO$), 1.97 (m, 4H, $C\mathbf{H}_2CH=CH$), 1.72 (m, 4H, $OOCCH_2C\mathbf{H}_2$), 1.56 (m, 4H, $NCH_2C\mathbf{H}_2CH_3$), 1.39-1.29 (m, 20H, $(C\mathbf{H}_2)_5$), 0.92 (t, 6H, $NCH_2CH_2C\mathbf{H}_3$).

^{13}C NMR ($CDCl_3$, δ ppm): 172.9 (**C**OO), 152.0 (**C**-O), 143.9 (**C**OOC), 130.5 (**C**H=**C**H), 121.0-120.3 (3**C** Ar), 117.1 (**C**H orto to C-O), 82.7 ($N\mathbf{C}H_2O$), 53.5 ($N\mathbf{C}H_2CH_2CH_3$), 50.3 ($N\mathbf{C}H_2Ar$), 34.5 ($\mathbf{C}H_2COO$), 32.7 ($NCH\mathbf{C}H_2CH_3$), 29.7-29.4 ($(\mathbf{C}H_2)_5$), 25.1 ($\mathbf{C}H_2CH_2COO$), 21.4 ($NCH_2\mathbf{C}H_2CH_3$), 11.8 ($NCH_2CH_2\mathbf{C}H_3$).

4.4.2.3 *(Z/E)-1,20-bis((3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin -6-yl) oxy)icos-10-ene (MB4)*

MB4

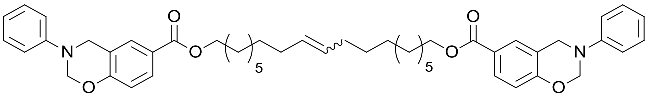
Light yellowish solid. Yield: 74% mp. 115-118ºC.

FTIR (ν cm^{-1}): (C=O), (C-O-C), (C-N-C), (C-O-C), ($N-CH_2-Ar$ Bz ring), (CH=CH).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 7.27-6.55 (m, 16H, Ar-**H**), 5.38-5.36 (m, 2H, C**H**=C**H**), 5.30 (s, 4H, $NC\mathbf{H}_2O$), 4.58 (s, 4H, $NC\mathbf{H}_2C$), 3.85 (m, 4H, $C\mathbf{H}_2CO$), 1.96 (m, 4H, $C\mathbf{H}_2CH=CH$), 1.72 (m, 4H, $CH_2C\mathbf{H}_2CO$), 1.41-1.24 (m, 20H, -$((C\mathbf{H}_2)_5)$).

^{13}C NMR (CDCl$_3$, δ ppm): 153.3 (**C**-O), 148.6 (**C**-0-(CH$_2$)n), 148.3 (**C**-N), 130.5 (**C**H=**C**H), 129.4 (**C**H meta to N), 121.5 (**C**H para to N),121.4-112.3 (12 Ar**C**), 79.6 (N**C**H$_2$O), 68.7 (**C**H$_2$O), 50.7 (N**C**H$_2$Ar), 32.7 (**C**H$_2$CH=CH), 29.8-29.3 ((**C**H$_2$)$_5$), 26.2 (**C**H$_2$CH$_2$CO).

4.4.2.4 *(Z/E)-icos-8-ene-1,20-diyl bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylate) (MB5)*



MB5

Light yellow oil. Yield: 68%.

FTIR (ν cm^{-1}): (C=O), (C-O-C), (C-N-C), (C-O-C), (N-CH$_2$-Ar Bz ring), (CH=CH).

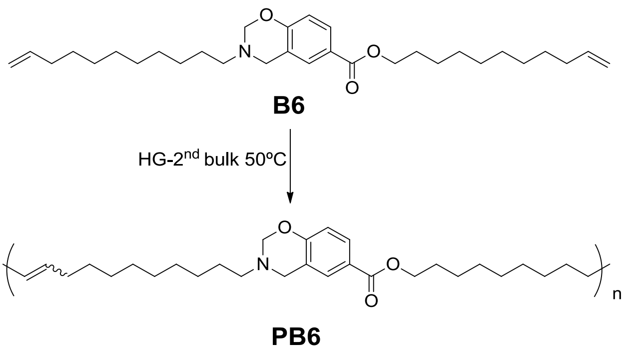
^{1}H NMR (CDCl$_3$,TMS, δ ppm): 7.84-6.82 (m, 16H, Ar-**H**), 5.41 (s, 4H, NC**H**$_2$O), 5.42-5.37 (m, 2H, C**H**=C**H**), 4.66 (s, 4H, NC**H**$_2$Ar), 4.29 (m, 4H, C**H**$_2$COO), 2.04 (m, 4H, C**H**$_2$CH=CH), 1.76 (m, 4H, C**H**$_2$CH$_2$COO), 1.44-1.30 (m,20H (C**H**$_2$)$_{10}$).

^{13}C NMR (CDCl$_3$, δ ppm): 166.4 (**C**OOCH$_2$), 158.4 (**C**-O), 148.1 (**C**-N), 129.8 (**C**H=**C**H), 129.5 (**C**H meta to N), 129.8-116.9 (6 Ar**C**), 118.6 (**C**H orto to N), 80.2 (N**C**H$_2$O), 65.0 (**C**H$_2$COO), 50.5 (N**C**H$_2$Ar), 32.7 (**C**H$_2$CH=CH), 29.8-28.8 ((**C**H$_2$)$_6$), 26.1 (**C**H$_2$CHCOO).

4.5 General Procedure for the ADMET Polymerization

The metathesis reactions were carried out with G1st, G2nd or H-G2nd catalysts. All metathesis reactions were carried out under vacuum in bulk. Benzoxazine monomer and catalyst were transferred into a dry 5 mL flask equipped with stir bar under argon atmosphere. If required, the respective amount of end-capper (methyl 10-undecenoate) was added. A small amount of anhydrous DCM was used to homogenize the reaction mixture at room temperature for 20 min. Full vacuum (0.01 mmHg) was placed and temperature was gradually increased up to desired temperature (50 or 80ºC). After 15h, the reaction was quenched by opening the flask and adding THF and vinyl ether (500-fold excess to the catalyst). The polymer was purified by precipitation of the polymer solution in THF into cold methanol. The polymer was then filtered and dried in an oven at 40ºC for 24h.

4.5.1 ADMET Polymerization of B6



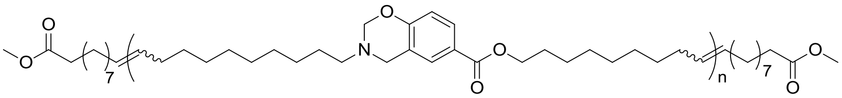
Dark green oil. Yield: 68%.

FTIR (ν cm^{-1}): 1755 (C=O), 1201 (C-N-C), 1030 (C-O-C), 967 (=C-H trans).

^{1}H NMR ($CDCl_3$,TMS, δ ppm): 6.81-6.68 (m, 3H, Ar-**H**), 5.41-5.34 (m, 2H, C**H**=C**H**), 4.83 (s, 2H, NC**H**$_2$O), 3.96 (s, 2H, NC**H**$_2$Ar), 2.71 (t, 2H, NC**H**$_2$CH$_2$), 2.50 (t, 2H, $\mathrm{C\mathbf{H}_2COO}$), 2.00-1.95 (m, 4H, $\mathrm{C\mathbf{H}_2CH{=}CH}$), 1.75-1.64 (m, 2H, $\mathrm{NCH_2C\mathbf{H}_2}$), 1.54-1.49 (m, 2H, $\mathrm{C\mathbf{H}_2CH_2COO}$), 1.38-1.26 (m, 22H, $\mathrm{(C\mathbf{H}_2)_{11}}$).

^{13}C NMR ($\mathrm{CDCl_3}$, δ ppm): 172.9 (**C**OO), 151.9 (**C**-O), 143.9 (**C**-OOC), 130.4 (**C**H=CH trans), 130.0 (**C**H=**C**H cis), 120.9-120.3 (2 **C**H ortho to OOC and **C** meta to OOC), 117.1 (**C**H ortho to O-$\mathrm{CH_2}$), 82.6 ($\mathrm{N\mathbf{C}H_2O}$), 51.6 ($\mathrm{N\mathbf{C}H_2Ar}$), 50.3 ($\mathrm{N\mathbf{C}H_2CH_2}$), 34.4 ($\mathrm{\mathbf{C}H_2COO}$), 32.7 ($\mathrm{\mathbf{C}H_2CH{=}CH}$), 30.4-29.1 (10C, $\mathrm{(\mathbf{C}H_2)_{10}}$), 28.2 ($\mathrm{\mathbf{C}H_2CH_2N}$), 27.3 ($\mathrm{\mathbf{C}H_2CH_2CH_2N}$), 25.1 ($\mathrm{\mathbf{C}H_2CH_2COO}$).

4.5.2 ADMET Polymerization of B6 in the Presence of 5%, 10% and 25% mol of Methyl 10-Undecenoate (UDM) as End-capper



FTIR (ν $\mathrm{cm^{-1}}$): 1756 (C=O), 1196 (C-N-C), 1030 (C-O-C), 967 (=C-H trans).

^{1}H NMR ($\mathrm{CDCl_3}$,TMS, δ ppm): 6.81-6.68 (m, 3H, Ar-**H**), 5.40-5.34 (m, 2H, C**H**=C**H**), 4.83 (s, 2H, $\mathrm{NC\mathbf{H}_2O}$), 3.96 (s, 2H, $\mathrm{NC\mathbf{H}_2Ar}$), 3.66 (s, 6H, $\mathrm{OC\mathbf{H}_3}$), 2.71 (t, 2H, $\mathrm{NC\mathbf{H}_2CH_2}$), 2.50 (t, 2H, $\mathrm{C\mathbf{H}_2COO}$), 2.29 (t, 4H, $\mathrm{C\mathbf{H}_2COOCH_3}$), 2.00-1.95 (m, 4H, $\mathrm{C\mathbf{H}_2CH{=}CH}$), 1.75-1.68 (m, 2H, $\mathrm{C\mathbf{H}_2CH_2N}$), 1.55-1.51 (m, 2H, $\mathrm{C\mathbf{H}_2CH_2COO}$), 1.29-1.28 (m, 50H $\mathrm{(C\mathbf{H}_2)_{25}}$).

^{13}C NMR ($\mathrm{CDCl_3}$, δ ppm): 172.9 (**C**OO), 151.9 (**C**-O), 143.9 (**C**-OOC), 130.4 (**C**H=CH trans), 130.0 (**C**H=**C**H cis), 120.9-120.3 (2 **C**H ortho to OOC and **C** meta to OOC), 117.1 (**C**H ortho to O-$\mathrm{CH_2}$), 82.6 ($\mathrm{N\mathbf{C}H_2O}$), 51.6 ($\mathrm{N\mathbf{C}H_2Ar}$), 50.3 ($\mathrm{N\mathbf{C}H_2CH_2}$), 34.4 ($\mathrm{\mathbf{C}H_2COO}$), 32.7 ($\mathrm{\mathbf{C}H_2CH{=}CH}$), 30.4-29.1 (10C, $\mathrm{(\mathbf{C}H_2)_{10}}$), 28.2 ($\mathrm{\mathbf{C}H_2CH_2N}$), 27.3 ($\mathrm{\mathbf{C}H_2CH_2CH_2N}$), 25.1 ($\mathrm{\mathbf{C}H_2CH_2COO}$).

4.6 Curing

4.6.1 Benzoxazine Dimers

Curing was performed between two teflon coated glass slides using a 0.49 mm Teflon mold spacer with a 25x10 mm^2 rectangular hollow. Samples were degassed by preheating at 110°C for 1h and cured following a preset temperature cycle: N-Phenylbenzoxazine derivatives (B1S1, B1S2, B2S1, B2S2, MB1, MB4, and MB5) were cured heating the sample from 120ºC to 180ºC at 0.1 °C/min. N-Propyl benzoxazine derivatives (B3S1, B3S2, and MB3) were cured heating the sample from 140°C to 200°C at 0.1 °C /min. B1S2 samples with catalyst were prepared adding 1%, 2% or 3% (w/w) of $BF_3.Et_2O$ to a DCM solution of the monomer (20% w/v) and evaporated to dryness prior to the degassing step. Curing was carried out heating the samples from 120ºC to 180ºC at 0.1 °C/min. The resulting polybenzoxazine themossets were labeled as PB1S1, PB1S2, PB2S1, PB2S2, PB3S1, PB3S2, PMB1, PMB3, PMB4 and PMB5. Percentage of insoluble fraction was determined by extraction in boiling dichloromethane for 24h and weighting the insoluble part.

4.6.2 Benzoxazine Polymers

Polybenzoxazine synthesis was performed between two Teflon coated glass slides using a 0.49 mm Teflon mold spacer with a 25.00x10.00 mm^2 rectangular hollow. Samples were degassed by preheating at 110ºC for 1h and cured following a preset temperature cycle: 140ºC 1h, 160ºC 3h, 170ºC 2h, 180ºC 2h, 200ºC 1h. All cured polybenzoxazines were subjected to soxhlet extraction with previously distilled DCM to determine their soluble fractions. The insoluble part was dried at 70ºC and weighted. The soluble fraction (SF) was defined as follows:

$$SF (\%) = ((Wi - Wd)/Wi) \times 100$$

Where Wd is the weight of dried sample after extraction and Wi is the initial weight of the sample.

4.7 Instrumentation and Characterization

4.7.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra were recorded on Varian VNMRS400. The samples were dissolved in deuterated chloroform, and ^{1}H-NMR and ^{13}C-NMR spectra were obtained at room temperature with tetramethylsilane (TMS) as an internal standard. ^{1}H NMR spectra for semiquantitative measurements were recorded using D1=15 s and 32 transients.

4.7.2 Infrared Spectroscopy (FTIR)

The FTIR spectra were recorded on a JASCO 680 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance and transmittance modes. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac. Teknokroma) was used to determine FTIR spectra.

4.7.3 Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system equipped with an Agilent 1100 series refractive-index detector. THF was used as an eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained with polystyrene (PS) standards. Agilent PLgel 3μm, 5 μm, and 20 μm MIXED-E types columns were used.

4.7.4 Rheological Measurements

Rheological measurements were carried out in the parallel plate mode (geometry of 25 mm) with an ARG2 rheometer (TA Instruments, UK, equipped with a Peltier system). Sine wave oscillation method frequency experiments were performed to measure apparent viscosities at different frequencies (from 10 to 0.1 Hz) and two temperatures (80 and 100ºC).

4.7.5 Differential Scanning Calorimetry (DSC)

Calorimetric studies were carried out on a Mettler DSC821e and DSC822e thermal analyzers using N_2 as a purge gas (100 ml/min). 6-12 mg samples were used for DSC analysis. T_g values were obtained from the second heating curves.

4.7.6 Thermal Gravimetric Analysis (TGA)

Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N^2 as a purge gas in the 30-800 ºC temperature range at scan rates of 10 ºC/min.

4.7.7 Thermal Degradation Study

Degradation studies were carried out on a Carbolite TZF 12/38/400 oven connected to a condenser cooled by liquid nitrogen. The analysis of the resulting product was carried out by ^{1}H-NMR and GC.

4.7.8 Gas Chromotography

Gas chromatography (GC) analysis was carried out with an Agilent 7820A GC system series equipped with FID dedector. DCM was ised as an eluent.

4.7.9 Dynamomechanical Thermal Analysis (DMTA)

Dynamomechanical properties were measured using a dynamic mechanical thermal analysis (DMTA) apparatus (TA Q800). Specimens (7.00 x 3.20 x 0.49 mm^3) were tested in a three point bending configuration. The thermal transitions were studied in the -50-160ºC range at a heating rate of 3 ºC/min and at a fixed frequency of 1 Hz.

Flexural measurements were carried out using a DMTA apparatus (TA Q800) in a 3-point bending configuration applying a ramp of 3 N/min at 35ºC. The support span was set at 5 mm.

4.7.10 Contact Angle Measurement

Contact angle measurements were determined at 25ºC using deionized water on polymer surfaces prepared by casting and curing monomers over glass slides. The water drop method (3μL) was used on an OCA 15EC contact angle setup (Neutek Instruments).

General Conclusions

General Conclusions

- 10-Undecenoic acid as a castor oil derivative has been incorporated into monofunctional, difunctional and main chain polymeric polybenzoxazine precursors.

- Hydrosilylation, self-metathesis, and acyclic diene metathesis polymerization have been proved to be efficient tools for coupling unsaturated fatty acid-containing benzoxazines in an effective way under mild conditions.

- The introduction of aliphatic blocks into the benzoxazine monomers structure decreases their melting point.

- Structural differences on polybenzoxazine precursors core do not significantly influence their ring opening thermal polymerization behavior.

- N-Phenyl based mono- and difunctional monomers lead to materials with higher crosslinking density, T_gs, and thermal stability than the N-n-propyl counterparts.

- Surface properties of the materials are difficult to be tuned due to the concurrence of multiple variables.

- The introduction of aliphatic blocks into monomeric and polymeric polybenzoxazine precursors allowed the preparation of inherently tough and flexible materials.

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Appendices

APPENDIX A LIST OF PUBLICATIONS

1. Gerard Lligadas, Alev Tuzun, Juan C. Ronda, Marina Galià, Virginia Cádiz, "Polybenzoxazines: new players in the bio-based polymer arena" Polym. Chem., 2014, 5, 6636-6644.

2. Alev Tuzun, Gerard Lligadas, Juan C. Ronda, Marina Galià, Virginia Cádiz, "Integrating plant oils into thermally curable main-chain benzoxazine polymers via ADMET polymerization" in press, doi:10.1016/j.eurpolymj.2014.12.023

3. Alev Tuzun, Gerard Lligadas, Juan C. Ronda, Marina Galià, Virginia Cádiz, "Fatty acid-derived benzoxazines. Part I: synthesis, polymerization and properties of ɑ,ω-bis-benzoxazine monomers obtained by hydrosilylation." Submitted.

4. Alev Tuzun, Gerard Lligadas, Juan C. Ronda, Marina Galià, Virginia Cádiz, "Fatty acids-derived benzoxazines. Part II: synthesis polymerization and properties of α,ω-bis-benzoxazine monomers obtained by self metathesis." Submitted.

APPENDIX B MEETING CONTRIBUTIONS AND STAGES

Meeting contributions

1. **Authors**: Alev Tuzun, Gerard Lligadas, Joan C. Ronda, Marina Galià, Virginia Cádiz
   Title: Polybenzoxazine Prepolymers from Renewable Fatty Acid Derivatives
   Type: Poster
   Congress: European Polymer Congress 2011
   Place of meeting: Granada ,Spain **Date of meeting:** June 2011

2. **Authors:** Alev Tuzun, Gerard Lligadas, Joan C. Ronda, Marina Galià, Virginia Cádiz
   Title: Fatty acid-derived α,ω-bis-benzoxazine monomers. Polymerization and polymer properties
   Type: Poster
   Congress: XIII Meeting of the Group of Polymers on the Spanish Royal Chemistry and Royal Physics Societies.
   Place of meeting: Girona, Spain **Date of meeting:** September 2014

3. **Authors:** Alev Tuzun, Gerard Lligadas, Joan C. Ronda, Marina Galià, Virginia Cádiz
   Title: Fatty Acid Derived Thermally Curable Main-chain Benzoxazine Prepolymers via Acyclic Diene Metathesis Polymerization
   Type: Poster
   Congress: XIII Meeting of the Group of Polymers on the Spanish Royal Chemistry and Royal Physics Societies.
   Place of meeting: Girona, Spain **Date of meeting:** September 2014

Stay abroad

Organization: Université de Mons- MATERIA NOVA

Department: Laboratory of Polymeric and Composite Materials (SPMC)

City: Mons **Country**: Belgium

Length: 3.5 months **Year**: 06-09/2014