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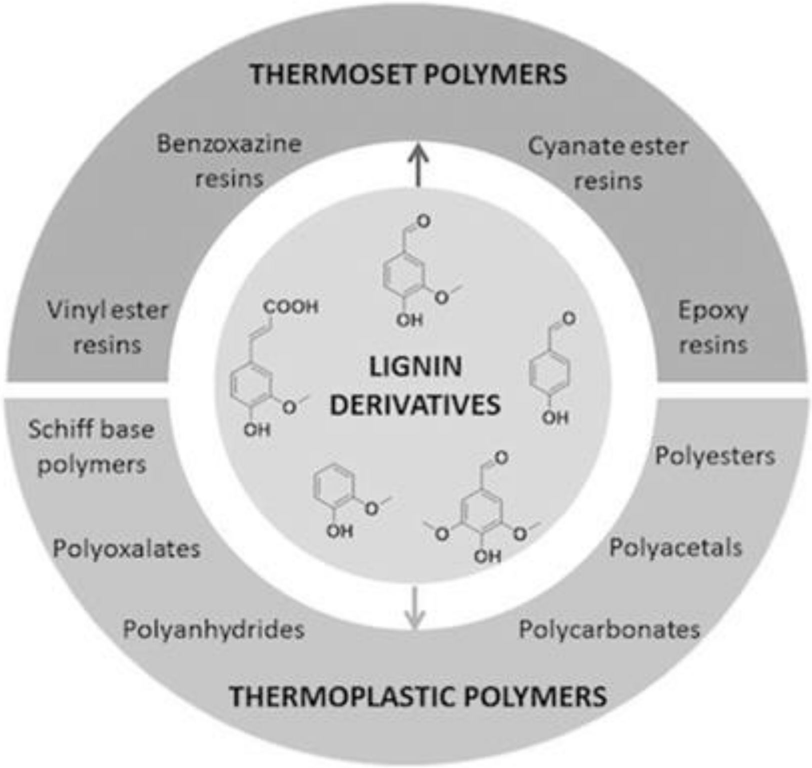
From Lignin-derived Aromatic Compounds to Novel Biobased Polymers

Audrey Llevot Etienne Grau Stéphane Carlotti Stéphane Grelier Henri Cramail

Abstract

Nowadays, the synthesis of (semi)aromatic polymers from lignin derivatives is of major interest, as aromatic compounds are key intermediates in the manufacture of polymers and lignin is the main source of aromatic biobased substrates. Phenols with a variety of chemical structures can be obtained from lignin deconstruction; among them, vanillin and ferulic acid are the main ones. Depending on the phenol substrates, different chemical modifications and polymerization pathways are developed, leading to (semi)aromatic polymers covering a wide range of thermomechanical properties. This review discusses the synthesis and properties of thermosets (vinyl ester resins, cyanate ester, epoxy, and benzoxazine resins) and thermoplastic polymers (polyesters, polyanhydrides, Schiff base polymers, polyacetals, polyoxalates, polycarbonates, acrylate polymers) prepared from vanillin, ferulic acid, guaiacol, syringaldehyde, or 4-hydroxybenzoic acid.



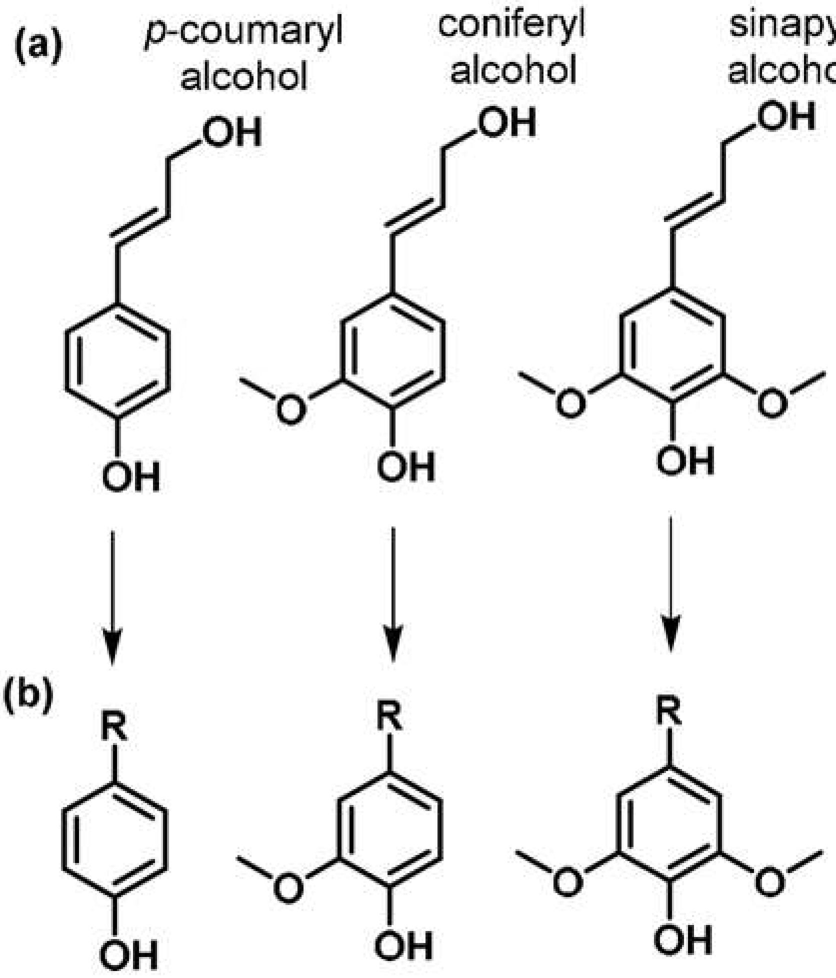
1 Introduction

Aromatic compounds constitute platform chemicals to manufacture everyday life items. In polymeric backbones, aromatic units offer rigidity, hydrophobicity, as well as resistance against fire. For instance, aromatic polyesters such as poly(alkyleneterephtalate)s are widely commercially used, due to their good thermomechanical and barrier properties, especially in food packaging and textiles.[1], [2] Indeed, the global PET predicted production is over 24 million tons for 2015.[3] Phenolic compounds are also widely used as raw materials. Among them, bisphenol-A (BPA) is an important monomer for the synthesis of polycarbonates, epoxy resins, and a popular plasticizer for thermoplastic polymers. BPA production is predicted to reach 5.4 million tons in 2015.[3] Aromatic compounds are also essential for the synthesis of high performance materials. For instance, polyaramides, such as Kevlar, are important polymers due to their high stability and rigidity.

Aromatic compounds are mainly petroleum-based and derived from benzene, xylene and cumene. In terms of sustainability, various research has recently been carried out on the investigation of biobased substitutes of aromatic petroleum-based compounds. Thus, the development of aromatic renewable polymers is drawing today an enormous interest.

Biomass constitutes the only source of available renewable carbon. Indeed, the regeneration time of carbon from biomass is measured in decades, whereas that of fossil resources reaches several million years.[4] Nowadays, the use of bio-resources for the synthesis of polymers is the subject of intensive research.[5-12] Some aromatic structures can be synthesized from natural compounds or are directly found in limited quantities in Nature. For instance, *p*-cymene can be easily synthesized from terpenes and transformed into terephtalic acid.[13] Some polyphenols contained in tannins have been investigated for the synthesis of epoxy resins.[8] Cardanol, extracted from cashew nut shell liquid,[14] the potential production of which reaches 450 000 metric tons per year, was employed as monomer for the synthesis of thermoplastics and thermosets.[15-17] Finally, hydroxymethyl furfural (HMF), synthesized from sugar dehydration, is an important aromatic building block for a wide range of applications[18, 19] and its derivatives are also used for the synthesis of biobased PET.[20]

However, the main renewable source of phenolic and, therefore, aromatic compounds is lignin. Isolated from wood or annual plant, this biopolymer constitutes the second most abundant renewable polymer after cellulose, with a world production of 40–50 million tons per year.[21, 22] The chemical structure of lignin consists of phenylpropane units originating from three aromatic alcohols (monolignol): *p*-coumaryl, coniferyl, and sinapyl alcohols (Scheme **1**). The ratio of monolignols depends on the biological species. Lignin deconstruction could lead to different phenolic molecules such as 4-substituted phenol, 4-substituted-2-methoxy phenol, or 4-substituted-2,6-dimethoxy phenol.[23-26] Nowadays, despite extensive research on the recovery of aromatic compounds from lignin,[27] the only commercial process is the production of vanillin from lignosulfonates, formed as a by-product of the sulfite pulping industry.[5, 28]



Scheme 1 Structure of a) monolignols and b) molecules potentially extracted from lignin.

The direct use of lignin for the synthesis of polymers is limited because of its ill-defined structure depending on the origin, extraction, and fragmentation processes. However, phenol–formaldehyde resins,29 polyesters, phenolic and epoxy resins,30-33 polyurethanes,34-37 or macroinitiators for ATRP polymerization38, 39 have been produced by functionalization of the hydroxyl groups of lignin.22

Together with the research on the controlled deconstruction of lignin, the synthesis of well-defined polymers from aromatic compounds potentially derived from lignin has attracted a growing interest.40 Most of the polymers produced from lignin derivatives deal with vanillin,41 ferulic acid, or guaiacol. Examples of benzaldehyde and syringaldehyde polymerizations are often described to show the influence of the *o*-methoxy group on the polymer properties. The synthesis and properties of thermosets and thermoplastic polymers synthesized from these theoretically biobased aromatic compounds will be discussed in this review.

2 Thermoset Polymers

Very few examples of thermoset polymers using aromatic compounds potentially derived from lignin have been reported. Most of them are very recent works, which describe the polymerization of vanillin. The thermomechanical properties of the polymers described in this section are summarized in Table 1.

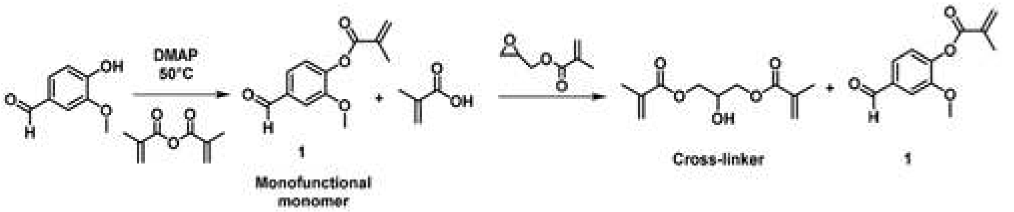
Table 1. Thermomechanical properties of lignin derivative-based thermosets

Resins	Monomer	T_g [°C]	T_d% [°C]	Curing temperature [°C]
Vinyl ester	**1**	155	50%: 405	
Cyano ester	**3**	202	5%: 340	
	5	178	5%: 326	
	6	248	5%: 357	
	7	214	5%: 337	
	8	214	5%: 348	
Epoxy	**12**	152	Max degradation: 315	
	13	97	Max degradation: 361	
	14	132	Max degradation: 338	
	15	80–110		
Benzoxazine	**18**	148	5%: 352	219
	19	82	5%: 329	232
	20	270	5%: 351	179
	21	/	333	256
	22	/	5%: 283	213
	23	255	5%: 339	250
	24	231	5%: 352	217
	25	227	5%: 322	217
	26	170	5%: 412	228

2.1 Vinyl Ester Resins

In 2012, Wool and co-workers prepared 100% biobased vinyl ester resins from vanillin methacrylate and glycerol dimethacrylate in a highly sustainable way.[42] The monomers were synthesized in a one-pot, two-step reaction without generating waste, since the by-product of step one, methacrylic acid, is a reactant of step two

(Scheme **2**). The cured resin was prepared by the free radical polymerization of **1**. The conversion reached 60% after reaction and 80% after post curing.

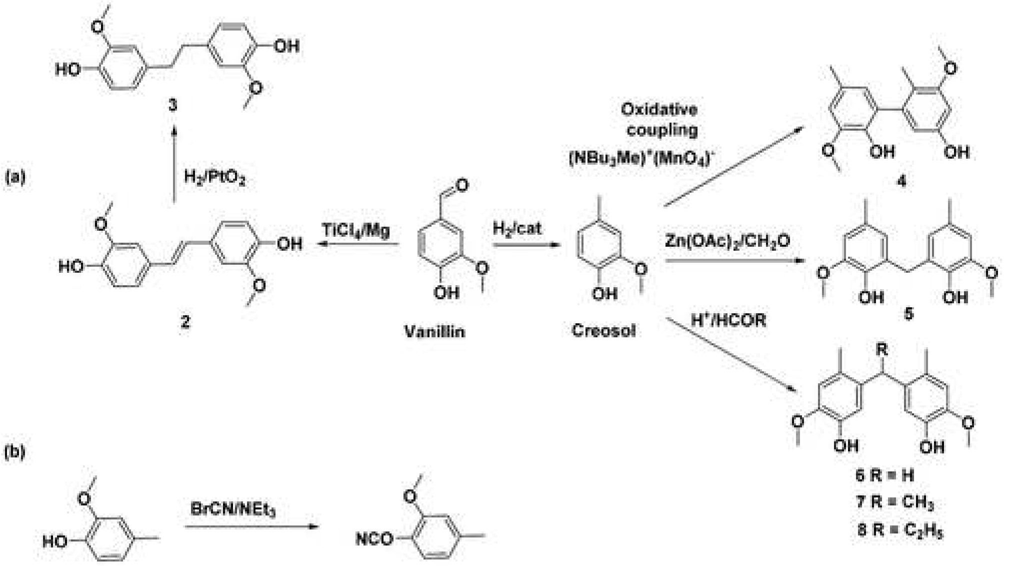


Scheme 2 The synthesis of vanillin methacrylate and glycerol dimethacrylate.

The so-formed resin is a hard transparent thermoset which exhibits a glass transition temperature (T_g) of 155 °C, a storage modulus of 3.6 GPa at 25 °C, and a 50% degradation temperature (T_d) of 405 °C. In this example, vanillin methacrylate **1** proved to be a good substitute for styrene, as the thermomechanical properties of the obtained resin are comparable to those of the typical vinyl ester resin synthesized with 45% styrene (T_g of 145 °C, storage modulus of 2.7 GPa, and 50% thermal degradation over 400 °C).

2.2 Cyanate Ester Resins

Recently, Harvey and co-workers reported two studies on the synthesis of cyanate ester thermosets from vanillin.**43**, **44** Seven bisphenols were produced from vanillin (Scheme **3**). In one study, reductive coupling (McMurry coupling) of the vanillin aldehyde in the presence of titanium tetrachloride led to **2** and, after hydrogenation, to the saturated compound **3**. In the other study, vanillin was hydrogenated to obtain creosol, which was then derivatized into several bisphenols.**45** The first method consisted of oxidative coupling creosol to produce the 2,2-biphenyl derivative **4**, because the phenol group directed the coupling to the *ortho* position. The second route employed the condensation reaction of creosol with formaldehyde, acetaldehyde, or propionaldehyde. Zinc acetate was shown to be a selective catalyst for the *ortho*-coupling of formaldehyde (**5**). Dilute HCl and HBr solutions were shown to be effective catalysts for the selective coupling of aldehydes in the *meta* position to the hydroxyl group (**6**, **7**, **8**). The bisphenols were readily converted to cyanate with cyanogen bromide under basic conditions.



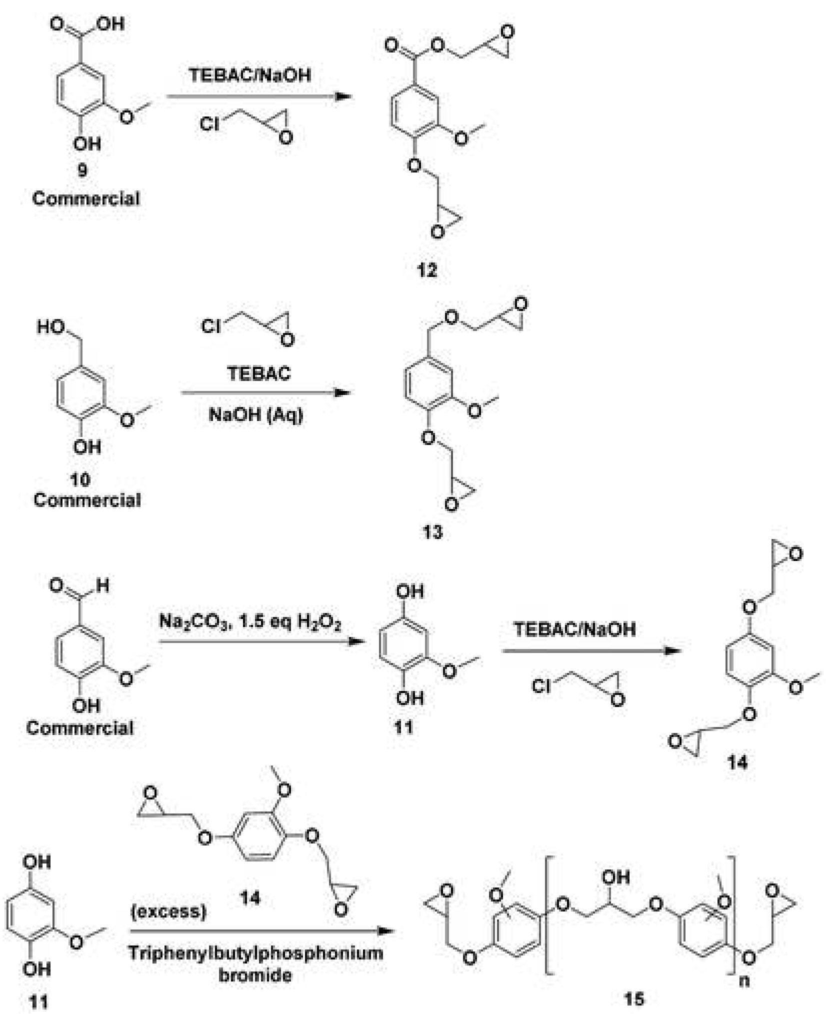
Scheme 3 The synthesis of bisphenols from vanillin (a) and of cyanate from the phenol moiety (b).

Bis(cyanate ester)s were cured at high temperature to produce cyanate ester thermosets. The bis(cyanate ester)s exhibited different behaviors and some of them were not suitable for this application. Differential scanning calorimetry (DSC) measurements showed that bis(cyanate ester)s derived from **4** and **5** were not able to complete their curing efficiently due to the rigidity of the structure and the steric hindrance around the cyanate group. The more flexible **2** has a melting point that is too high, over 220 °C, which makes it unsuitable to be used by itself. In contrast, the curing of the bis(cyanate ester)s derived from **3**, **6**, **7**, and **8** was complete. The resulting thermosets exhibit glass transition temperatures of over 200 °C and 5 wt% degradation temperatures of 300 °C. The *ortho* methoxy group of these resins leads to different properties in curing and to different thermal decomposition compared to classical resins. Despite a slight decrease in thermal stability, the vanillin-based resins present properties comparable to the petroleum-based commercial equivalents.

2.3 Epoxy Resins

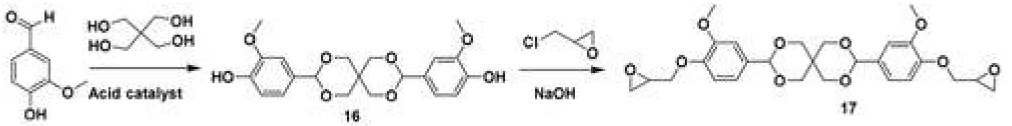
Two strategies can be developed to synthesize bisepoxides from vanillin: i) chemical modification of the aldehyde and phenolic groups, or ii) production of a bisphenol by vanillin coupling.

Caillol and co-workers reported the synthesis of epoxy resins from several bisepoxides obtained from vanillin by direct chemical modifications (Scheme 4).[46] Vanillyl alcohol, **10**, and vanillic acid, **9**, are common commercial compounds, which can be easily produced from vanillin by reduction and oxidation, respectively. 2-Methoxyhydroquinone, **11**, was prepared from vanillin by a Dakin reaction. Compounds **9**, **10**, and **11** underwent glycidylation reactions, yielding **12**, **13**, and **14**, respectively.[47] These bisepoxides reacted with isophorone diamine to produce epoxy resins in an epoxy:amine ratio of 2:1. The epoxy resins prepared from these bisepoxides exhibit T_gs ranging from 97 to 152 °C and degradation temperatures from 315 to 361 °C. These values are influenced by the structure of the monomer. Indeed, the epoxy resin synthesized from **13** exhibits a lower T_g because the additional methylene increases the flexibility and lowers the cross-linking density. On the other hand, the ester moiety of **12** induces a higher cross-linking density and so a higher T_g, but a lower degradation temperature. Vanillic bisepoxides are promising compounds as biobased alternatives to the diglycidyl ether of bisphenol A (DGEBA) (T_g = 166 °C, T_d = 360 °C). However, industrially, epoxy resins are produced from DGEBA-based oligomers, which allow a better processability and control of the thermomechanical properties. Following this trend, Caillol and co-workers prepared epoxy oligomers (**15**) from **11** and **14**, in different ratios, by the industrially used "fusion" process with triphenylbutylphosphonium bromide.[48] By tuning the length of the oligomers, the cross-linking density of the resulting material is affected, thus enabling the researchers to formulate epoxy resins with T_gs ranging from 80 to 110 °C.



Scheme 4 The synthesis of bisepoxides by chemical modification of vanillin.

Furthermore, bisphenol **16** was synthesized from dehydratation condensation between vanillin and pentaerythritol. Further reaction with epichlorhydrin led to bisepoxide **17** (Scheme 5).49

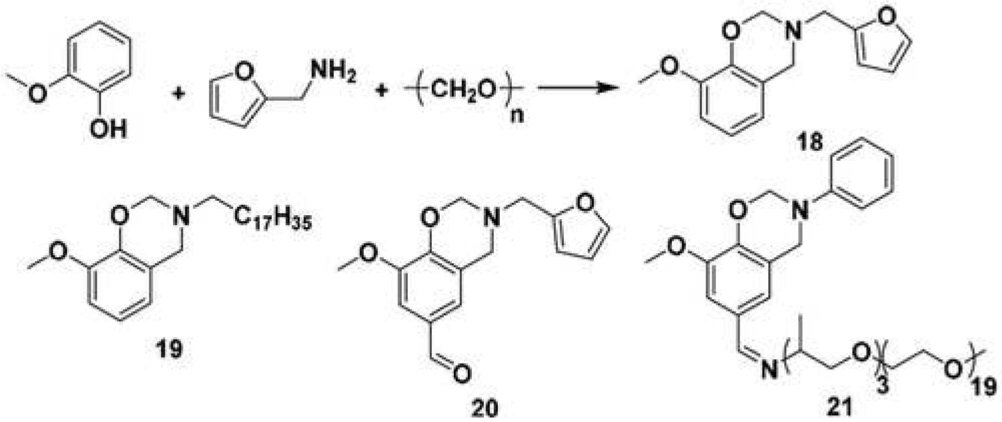


Scheme 5 The synthesis of vanillin bisepoxides by coupling with pentaerythritol.

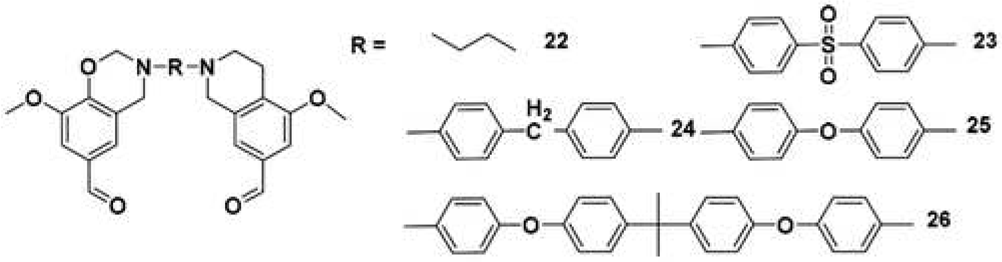
Compound **17** reacted with diaminodiphenylmethane to obtain cross-linked epoxy resins. The authors demonstrated the influence of the hydrogen bonding between the methoxy and the hydroxyl group of the resin on its mechanical properties. This phenomenon improves the impact and tensile strength of the material and is expected in all epoxy resins derived from lignin.

2.4 Benzoxazine Resins

Polybenzoxazines are a class of high-performance materials which exhibit excellent thermomechanical and chemical properties. They are synthesized in a one-pot method from phenolic derivative, primary amine, and formaldehyde. The ring-opening polymerization of benzoxazines proceeds at high temperature, producing polymeric resins bearing both phenolic hydroxyl and tertiary amine groups responsible for several hydrogen bonds in the material. Guaiacol and vanillin were employed as phenolic monomers for the synthesis of polybenzoxazines (Scheme 6 and Scheme 7). Fully biobased benzoxazines were synthesized from guaiacol (a theoritically lignin derivative), paraformaldehyde (which could be obtained by oxidation of biomethanol), and furfurylamine **18** (derived from furfural) or stearylamine **19** (a fatty acid-based amine).**50** Benzoxazine resins with a T_g of 148 °C and 82 °C from **18** and **19**, respectively, and exhibiting degradation temperatures of over 330 °C were produced. The furan moiety showed a positive influence on the polymerization by improving the curing process, cross-linking density, and thermal properties of the resulting material.



Scheme 6 The synthesis of benzoxazines from guaiacol or vanillin.



Scheme 7 The synthesis of bis-benzoxazines from vanillin.

Varma and co-workers obtained similar resins from vanillin, paraformaldehyde, and furfurylamine **20**.**51** They evidenced the role of the formyl group in curing: it undergoes decarboxylation leading to an active site in the *para* position. The resin synthesized from **20** exhibits a very high T_g of 270 °C.

Ishida and co-workers took advantage of the free aldehyde group of a partially biobased benzoxazine to functionalize it with Jeffamine M1000, and produced surfactant **21**.**52** After curing, this surfactant was used to stabilize the polymerization of styrene in mini-emulsion.

Varma and co-workers also synthesized bis-benzoxazines from vanillin and several petroleum-based diamines. The authors studied their curing behavior and the thermomechanical properties of the resulting materials (Scheme 7).**53** These characteristics were influenced by the diamine structures. The obtained materials presented high T_gs, ranging between 170 and 255 °C, and good adhesive strengths at around 200 °C, making them suitable for high-temperature adhesive applications.

The works described in this section highlight the synthesis of resins with different chemical structures from aromatic compounds potentially derived from lignin. The obtained materials present high thermomechanical properties, similar to commercial ones (Table 1).

3 Thermoplastic Polymers

The molar masses and thermal properties of the polymers described in this section are reported in Table **2**.

Table 2. Thermomechanical properties of lignin derivative-based thermoplastics

Name	Monomer	Polymerization	Mn [g mol^{-1}]	Đ	T_g [°C]	T_m [°C]	T_d [°C]
P17	Ferulic acid	Polycondensation	5450	1.50	–27	25	
P18	Vanillin	Polycondensation	16 600	1.81	–13	77	
P19	Vanillin	Polycondensation	17 800		73	234	50%: 462
P20 n = 2	Vanillin	Polycondensation	23 500	2.69	71	239	50%: 417
P20 n = 2	Syringaldehyde	Polycondensation	14 300	2.08	66	/	50%: 433
P20 n = 2	Hydroxybenzaldehyde	Polycondensation	14 000	6.66	80	203	50%: 433
P21	Vanillin	Polycondensation	11 800		13	/	5%: 357
P22	Vanillin	Polycondensation	14 700		4.4	70.1	5%: 369
P23	Ferulic acid	Polycondensation	7500	2.1	76	/	5%: 351
P24	Ferulic acid	Polycondensation	7900	1.9	35	/	5%: 349
P25	Ferulic acid	Polycondensation	10 500	2.0	26	/	5%: 347
P26	Ferulic acid	Polycondensation	8700	1.7	0.4	/	5%: 360
P27	Divanillin	Polycondensation	65 000	2.1	38	/	5%: 319
P28	Divanillin	Polycondensation	/	/	5	/	5%: 308
P29	Divanillin	Polycondensation	/	/	68	/	5%: 270
P30	Divanillin	Polycondensation	/	/	–5	/	5%: 347
P31	Divanillin	Polycondensation	/	/	102	/	5%: 310
P32	Divanillin	Polycondensation	/	/	139	/	5%: 342
P33	Divanillin	Polycondensation	/	/	102	/	5%: 305

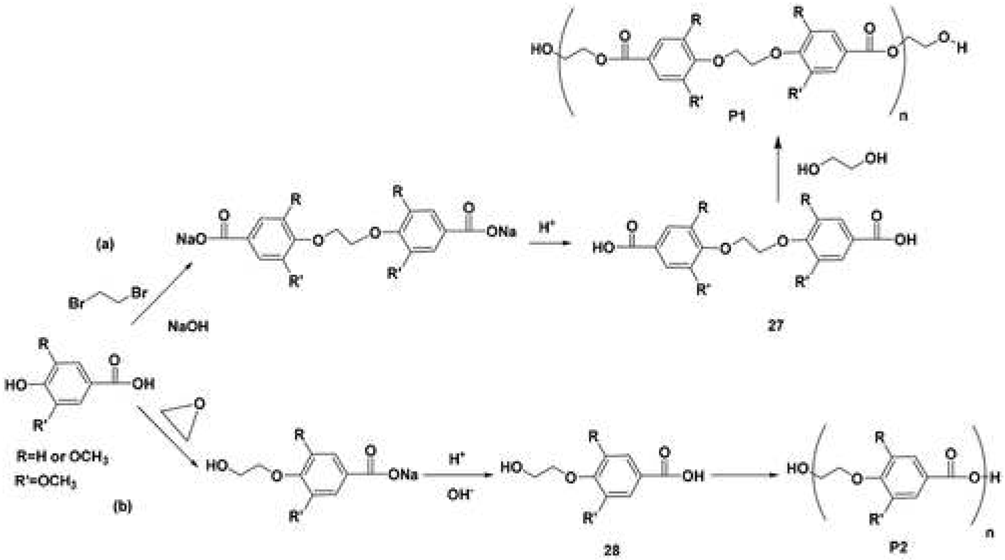
Name	**Monomer**	**Polymerization**	**Mn [g mol^{-1}]**	**Đ**	**T_g [°C]**	**T_m [°C]**	**T_d [°C]**
P34	Ferulic acid	ADMET	3100	1.81	7	/	
P35	Ferulic acid	Thiol-ene	4200	1.49	–33	/	
P36	Vanillin	ADMET	49 600	1.96	–31	/	
P37	Vanillin	Thiol-ene	15 400	1.77	–32	57.65	
P38	Vanillin	ADMET	25 600	1.88	–17	/	
P39	Vanillin	Thiol-ene	12 100	1.94	–22	68	
P40 x = 4	Ferulic acid	ADMET	10 600	2.6	18		5%: 314
P40 x = 8	Ferulic acid	ADMET	9900	2.2	7	/	5%: 314
P41 x = 4	Ferulic acid	ADMET	25 400	1.7	–8	/	5%: 291
P41 x = 8	Ferulic acid	ADMET	12 300	1.7	–22	/	5%: 334
P42	Divanillin	ADMET	11 000	1.6	17	/	5%: 310
P43	Ferulic acid	Oxidative coupling	25 000	/	56	/	210
P44	Ferulic acid	Polycondensation	21 700	1.7	82	/	332
P45	Divanillin	Schiff base	7800–9600	/	/	/	250
P46	Divanillin	Reductive coupling	10 000		/	/	300
P47	Hydroxybenzaldehyde	Polycondensation	/	/	/	/	5%: 328
P47	Vanillin	Polycondensation	10 600	2.2	129	/	5%: 308
P47	Syringaldehyde	Polycondensation	18 600	1.9	152	/	5%: 307
P48	Hydroxybenzaldehyde	Polycondensation	/	1.4	/	259	5%: 349
P48	Vanillin	Polycondensation	22 200	2.0	80	/	5%: 327
P48	Syringaldehyde	Polycondensation	21 600	1.6	98	/	5%: 320
P49	Vanillin	Polycondensation	22 000	1.6	120	/	
P50	Vanillin	Polycondensation	4000	1.9	86	/	5%: 290
P51	Ferulic acid	Polycondensation	14 600	2.57	135	/	343

Name	Monomer	Polymerization	Mn [g mol^{-1}]	Đ	T_g [°C]	T_m [°C]	T_d [°C]
P52	Ferulic acid	Polycondensation	5600	1.43	134	/	350
P53	Ferulic acid	Polycondensation	8500	2.08	129	/	337
P54	Ferulic acid	Polycondensation	17 700	2.06	130	/	343
P55	Divanillin	ADMET	29 000	1.7	160	/	5%: 380
P56	Vanillin/guaiacol	Radical	11 000	1.6	101	/	/
P57	Vanillin	Radical	17 000	1.34	120	/	<300
P58	Vanillin	Radical	56 000	1.50	–33	120	<300

3.1 Polyesters

3.1.1 First Syntheses of Polyesters from Lignin Derivatives

To the best of our knowledge, the first example of the polymerization of vanillic acid was described in 1955. Indeed, vanillic acid was converted to carboxylate by etherifying the phenolic moiety with ethylene dihalides **27** (Scheme 8a). Subsequently, the carboxylate was esterified with ethylene glycol and condensed to linear polyester, **P1**, with a T_g of 80 °C and a melting temperature (T_m) of 210 °C.54 This polymer was studied several times between 1955 and 1974.55, 56 Later, in 1981, the same strategy as well as a new one were developed by Kordsachia and co-workers to synthesize vanillic and syringic acid-based polymers.57 In the second synthetic pathway, the phenolic moiety of vanillic acid was reacted with ethylene oxide, yielding **28** (Scheme 8b). The self-condensation of **28** leads to **P2**.



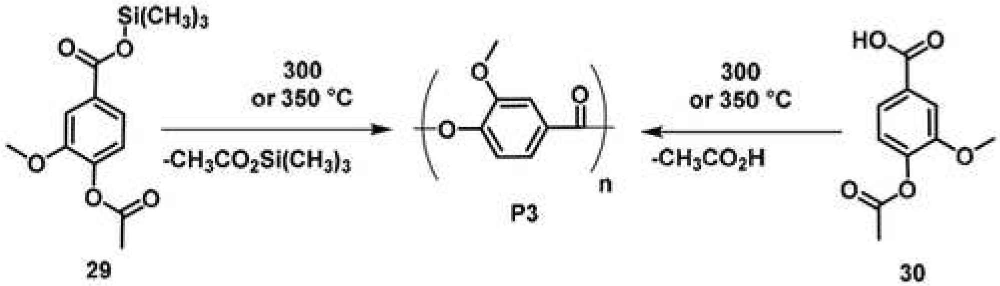
Scheme 8 The first syntheses of polyester from vanillic acid and syringic acid.

Molar masses, measured by viscometry, indicate that the first synthetic pathway (a) provides polyesters exhibiting higher molar mass, respectively 44 500 g mol^{-1} and 50 000 g mol^{-1} for vanillic acid and syringic acid in comparison to polyesters produced from the second method (b), 30 000 g mol^{-1} and 12 000 g mol^{-1}. With respect to the first method, the reported polymers showed a T_g of 69 °C and T_m of 212 °C in the case of vanillic acid and a T_g of 58 °C and T_m of 172 °C for syringic acid. From the second method, the polymers showed a T_g of 55 °C and T_m of 254 °C in the case of vanillic acid and a T_g of 45 °C and T_m of 73 °C for syringic acid. Interestingly, the polymer produced from vanillic acid exhibits thermal properties similar to polyethylene terephthalate (PET) (T_m = 265 °C, T_g = 67 °C).

3.1.2 Direct Polymerization Methods

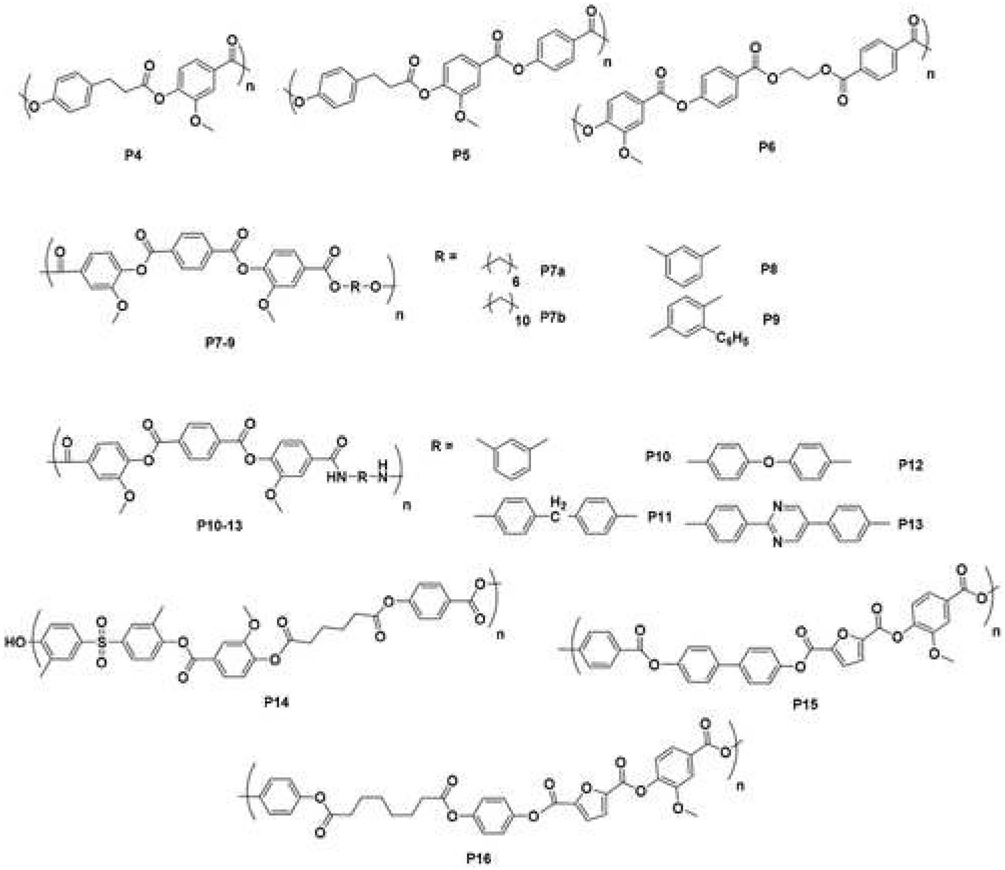
After these first polymerizations of vanillic acid, a wide number of studies on the conversion of vanillic acid, syringic acid, and 4-hydroxybenzoic acid into thermotropic polymers were reported. Thermotropic polymers are materials that exhibit liquid crystal formation in the melt form. This next section focuses on the influence of the incorporation of vanillic acid on thermotropic polymer properties. Due to their high order and aromatic structure, they possess high mechanical strength at high temperatures, extreme chemical resistance, and inherent flame retardancy.

The first report on the incorporation of vanillic acid into thermotropic polymers was from Kricheldorf and co-workers in 1995. The authors prepared polyesters derived from vanillic acid.**58** The motivation of this work was to synthesize whisker-like crystals with biodegradable properties. Homopolymers of vanillic acid were obtained via two synthetic pathways: a silylacetate method and an acetate method (Scheme **9**). For the first method, trimethylsilyl-4-acetoxy-3-methoxybenzoate, **29**, was homopolymerized, leading to poly(vanillic acid), **P3**. The second approach involved the reaction of free carboxylic acid of the 4-acetoxy-3-methoxybenzoic acid, **30,** and generated acetic acid. High reaction temperatures, between 300 and 350 °C, were required. The two synthetic methods gave different yields, crystallinity ratios, and morphologies.



Scheme 9 The synthesis of poly(vanillic acid).

Based on this work, several other thermotropic (co)polymers were synthesized from vanillic acid (Scheme **10**). First, copolyester from 4-hydroxyphenyl propanoic acid (potentially obtained from lignin) and vanillic acid, P4, were produced by the silylated method.**59** At a 1:1 molar ratio, the incorporation of vanillic acid in the polyester was lower than expected. Probably, the reactivity of the acetoxy group was decreased due to steric and electronic effects of the methoxy group in the *ortho* position. To overcome the low reactivity, Nagata and co-workers developed another synthetic pathway to synthesize 4-hydroxyphenyl propanoic acid/vanillic acid copolyesters.**60** They prepared copolymers with different compositions in pyridine, using diphenyl phosphoryl chloride and lithium bromide as condensing agents, thus improving the incorporation of vanillic acid into the polyester. A molar mass of 21 800 g mol^{-1} was reached for a composition of 30% vanillic acid. Higher vanillic acid-to-4-hydroxyphenyl propanoic acid ratios lead to higher T_gs (108 °C for 70% and 83 °C for 30%) but lower thermal degradation (356 °C for 70% and 403 °C for 30%). These binary copolymers were not thermotropic. Thus, terpolymers with 4-hydroxybenzoic acid, P5, were investigated (Scheme **10**) and were proven to be soluble, thermotropic, and to form a homogeneous nematic phase above 250 °C.



Scheme 10 The synthesis of thermotropic polymers from vanillic acid.

Sun and co-workers also investigated the properties of liquid-crystalline polymers.[61-63] They synthesized terpolymers, **P6**, by the melt polycondensation of 4-acetoxybenzoic acid, poly(ethylene terephthalate), and 5% of an acetoxy-based third monomer. Vanillic acid was used as a co-monomer and was compared to seven other molecules including bisphenol A and terephtalic acid. Vanillic acid copolymers exhibited a faster polycondensation rate, better spinnability, lower melting temperature, higher molar mass, and thermostability than all the other copolymers (**Table 3**). It also showed a highly oriented fibrillar structure.

Table 3. Properties of the terpolymers synthesized from *p*-hydroxybenzoic acid, polyethylene terephtalate, and a third monomer[61-63]

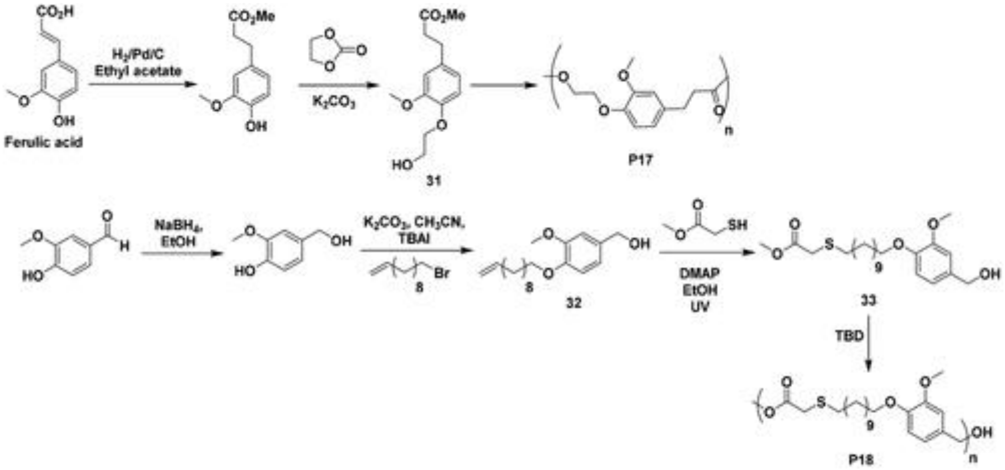
Monomer	Spinnability	T_g [°C]	T_m [°C]	T_d 5% [°C]	Mn [g mol^{-1}]	G' [GPa]	ε [%]
Vanillic acid	Very good	69	183–207	417	7 300	67	9
Bisphenol A	Bad	100	/	/		/	/
Terephtalic acid	Medium	64	196–220	/	5 400	/	/

In addition, Kudriavtsev and co-workers developed a series of polyesters, **P7–P9** and polyamides **P10–P13** employing vanillic acid (Scheme 10).64, 65 The same diols and diamines were used to produce terpolymers from vanillic acid and *p*-hydroxybenzoic acid. The polymers were cast from solutions of *N*-methylpyrrolidone on glass supports. Depending on the chemical structure of the co-monomer, elongation at break ranged from 234% and 67% for the polyesters and 14.1% and 20.8% for the polyamides.

The excellent thermomechanical properties and processability of the vanillic acid-based liquid-crystalline polymers attracted attention for biomedical applications. Indeed, recent studies have reported the synthesis of semiaromatic bioresorbable polyester from vanillic and *p*-hydroxybenzoic acid, **P14**.66-68 More precisely, polyesters derived from *p*-hydroxybenzoic acid, vanillic acid, 4,4′-sulfonylbis(2-methylphenol), and various aliphatic diacids (spacers) have been developed by the company Smith & Nephew, and in-vitro and in-vivo biocompatibility has been proven. Selected compositions, such as 50/25/12.5/12.5 in hydroxybenzoic acid/vanillic acid/4,4′-sulfonylbis(2-methylphenol)/spacer, have been shown to be processable in the nematic melt phase. However, the fibers show comparatively low tensile moduli due to the low level of molecular orientation in the nematic phase. Further developments are necessary to address the mechanical requirements for orthopedic applications.

Finally, a very recent study reported the synthesis of biobased thermotropic polyesters from 2,5-furandicarboxylic acid, 4-hydroxybenzoic acid, 4,4'-bisphenol, and vanillic acid, **P15**.19, 69 First, the polymers were formed without vanillic acid, but the rapid crystallization of the mixture from the melt did not allow it to reach a high molar mass. The introduction of vanillic acid as a co-monomer prevents crystallization during polymerization, thus allowing transesterification reactions, which decreased the formation of blocks. The polymer incorporating 20% of vanillic acid showed a T_g of 109 °C and a melting temperature of 230 °C (versus 97 °C and 336 °C without vanillin). This phenomenon was also evidenced by a similar study on the synthesis of thermotropic polymers from 4-hydroxybenzoic acid, suberic acid, 1,4-dihydroxybenzene, 2,5-furandicarboxylic acid, and vanillic acid, **P16** (Scheme 10).

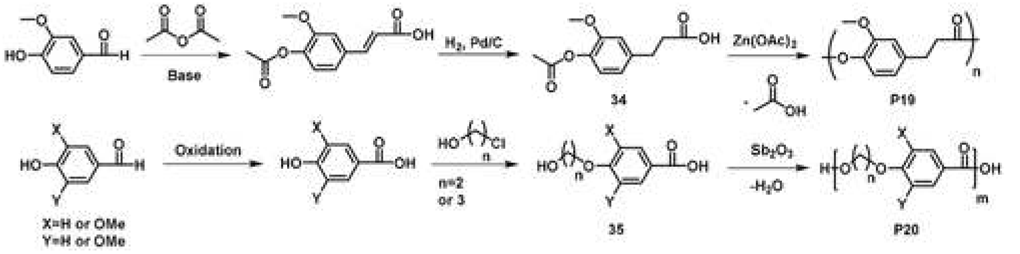
In the current context of “green” chemistry, 100% biobased polymers were synthetized from vanillin, ferulic acid, and vegetable oil derivatives. Meier and co-workers produced a polyester from ferulic acid by polycondensation (Scheme 11).70 Ferulic acid was transformed into a more reactive monomer. The carboxylic acid was first esterified with methanol and the resulting compound was hydrogenated. Hydrogenated methyl ferulate was then reacted with two equivalents of ethyl carbonate, yielding an AB monomer, **31**. **P17** was produced by the homopolymerization of **31,** performed with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a catalyst; it exhibits a molar mass of 5400 g mol^{-1} and a semicrystalline feature with a T_g of –27 °C and a T_m of 25 °C. Amorphous polymers were also synthesized by copolymerization of **31** with methyloleate and methylerucate derivatives.



Scheme 11 The synthesis of ferulic acid and vanillin-based polyesters by polycondensation in a sustainable way.

The polycondensation of vanillin derivatives and fatty acid derivatives was also investigated by the same group (Scheme 11).71 The intermediate **32** was prepared by reduction of the aldehyde moiety to alcohol and the etherification of the phenol moiety with an undecenoic acid derivative. The thiol-ene addition of methylthioglycolate on **32** leads to an AB monomer **33**, able to undergo homopolymerization, yielding **P18**. The latter is a semicrystalline polymer with a T_g of –13 °C and a T_m of 77 °C. Polymers with a higher crystallinity were also synthesized by copolymerization of **33** with fatty acid-derived esters.

In 2010, Miller and co-workers reported the synthesis of biorenewable poly(ethylene terephthalate) mimics, P19, derived from lignin and acetic acid (Scheme 12).72 The reaction of vanillin and acetic anhydride leads to both a Perkin reaction and acetylation of the phenolic group. The resulting compound was hydrogenated and the generated acetyldihydroferulic acid, **34**, was homopolymerized, yielding **P19**. Zinc acetate proved to be the most efficient catalyst. **P19** exhibits a molar mass of 17 800 g mol^{-1} (degree of polymerization around 100), a melting temperature of 234 °C, a transition temperature of 73 °C and a 50% thermal decomposition at 462 °C. All these values are similar to the corresponding values of PET (T_m = 265 °C, T_g = 67 °C, T_d 50% = 470 °C).

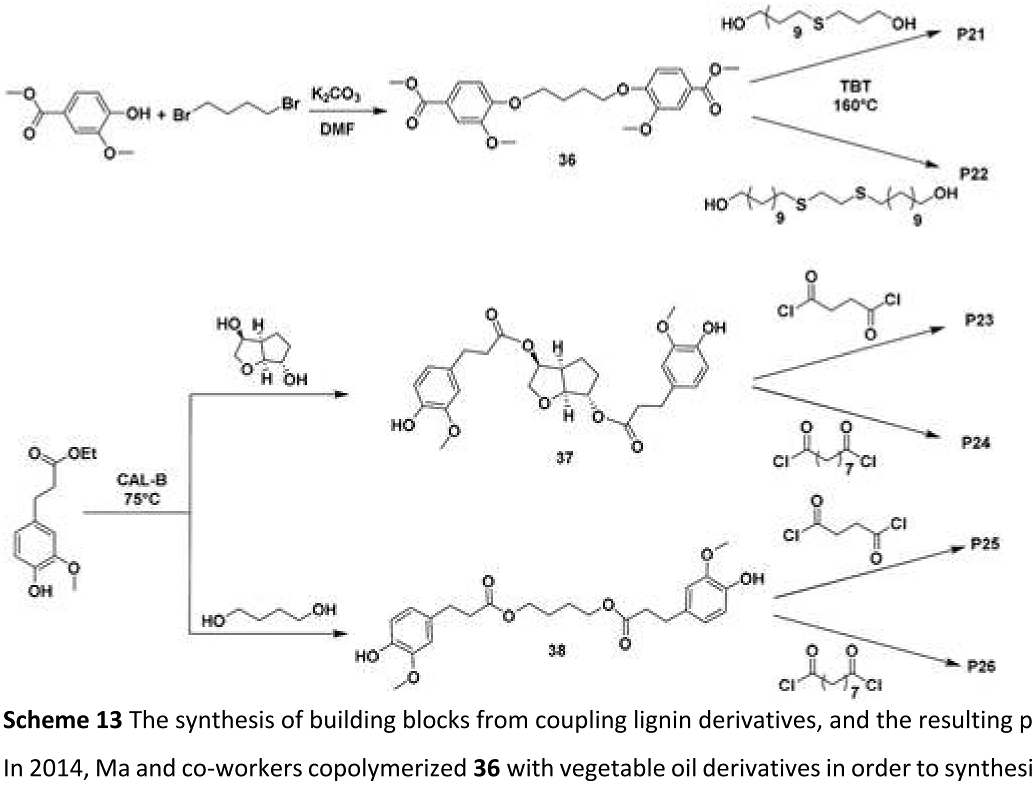


Scheme 12 The synthesis of poly(alkylenehydroxybenzoate)s from lignin derivatives.

The same group also synthesized poly(alkylenehydroxybenzoate)s (PAHBs) from three lignin derivatives, vanillin, 4-hydroxybenzoic acid, and syringic acid (Scheme 12), in order to target materials with a wide range of thermomechanical properties.73 These aromatic aldehydes were oxidized into the corresponding carboxylic acids and the phenol moiety was derivatized with 2-chloroethanol or 3-chloropropan-1-ol. The resulting hydroxy acid monomers (AB), **35**, were homopolymerized, yielding **P20**, using antimony oxide as a catalyst. The thermomechanical properties of **P25** vary with respect to the aromatic unit substitution. Indeed, substitution on the aromatic ring increases the free volume of the polymer chains, which decreases the glass transition temperature. Additionally, the length of the aliphatic segment between the aromatic units also has an impact on the thermal properties. The thermal stability of all the polymers is high (Table 3). In this series of polymers, the glass transition temperature was tuned between 50 and 70 °C and the melting temperature between 170 and 239 °C.

3.1.3 Synthesis and Polymerization of Symmetrical Difunctional Monomers

An alternative path toward difunctional monomers from vanillin or lignin derivatives is based on the coupling of phenolic substrates. This coupling could occur either on the phenol, yielding dicarbonyl, or on the carbonyl, yielding bisphenol (Scheme 13). For instance, the diester **36** was synthesized via the Williamson ether synthesis reaction of two equivalents of methylvanillate and one equivalent of 1,4-dibromobutane.74 The bisphenols **37** and **38** were obtained via a chemoenzymatic pathway. First, ethyl dihydroferulate was synthesized, from vanillin by reaction with malonic acid, piperidine, and pyridine, followed by hydrogenation. The transesterification of this compound with isosorbide, 1,3-propanediol, and 1,4-butanediol was performed in the presence of lipase. One of the main advantages of using *Candida Antarctica* lipase B (CAL-B) lies on its inactivity toward phenol. In each case, a yield of about 90% was achieved without the presence of by-products after a reaction time of three days.75 These building blocks were used for polyester synthesis.

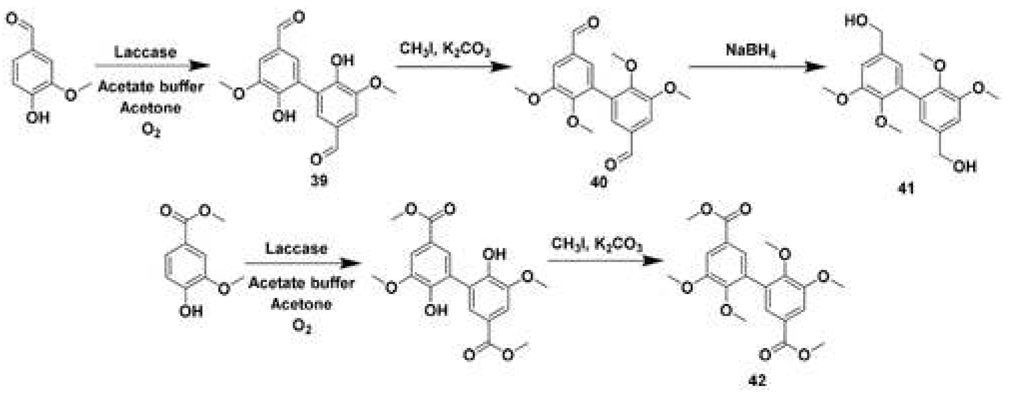


Scheme 13 The synthesis of building blocks from coupling lignin derivatives, and the resulting polymers.

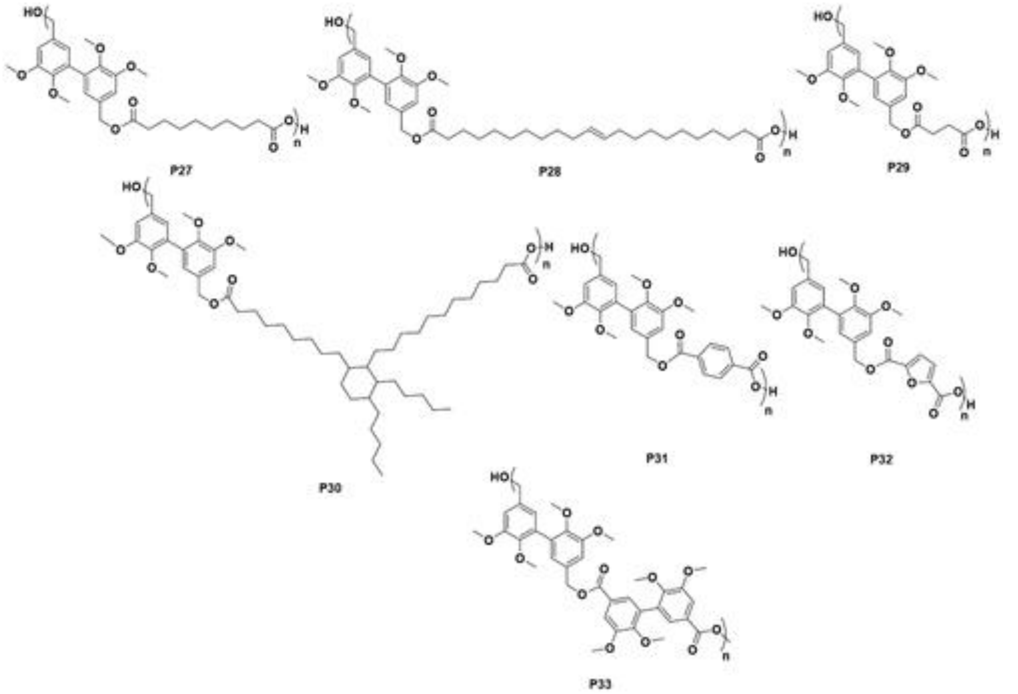
In 2014, Ma and co-workers copolymerized **36** with vegetable oil derivatives in order to synthesize fully biobased semiaromatic polyesters (Scheme 13).74 The vegetable oil-based diols were prepared via thiol-ene addition on undecenol. The resulting polyesters **P21** and **P22** exhibit molar masses of, respectively, 11 800 and 14 700 g mol^{-1} and dispersities around 2. The shorter aliphatic chain of **P21** leads to a polyester with better thermal stability (T_d 5% of 357 °C versus 339 °C), a higher Young's modulus (99.7 MPa versus 66.2 MPa) and a lower strain-at-break (22.8% versus 43.7%) than **P22**. Moreover, **P21** is amorphous, with a T_g of 13.0 °C, whereas **P22** is semicrystalline, with a T_g of –4.4 °C and a T_m of 70.1 °C.

A similar study concerning the influence of aliphatic or cycloaliphatic segments on the thermomechanical properties of polyesters was conducted on **37** and **38** by Allais and co-workers.76 The bisphenols were copolymerized with diacyl chloride (succinic or azelaic) in *o*-dichlorobenzene or in bulk, yielding low molar mass polymers (3700 g mol^{-1} < Mn < 5200 g mol^{-1}), **P23–26**. The glass transition temperatures were tuned from 0.4 °C to 75.6 °C by the design of the monomers. All the polymers exhibit good thermal stability with 5% weight loss at temperatures over 347 °C.

In order to produce difunctional symmetrical monomers, we investigated the enzymatic coupling of several phenolic compounds potentially derived from lignin.77 Employing a laccase from *Trametes Versicolor*, we developed a process to synthesize bisphenyl compounds. This process presents several advantages: i) the divanillin formation occurs at room temperature under oxygen (which could be replaced by air), and employs a low-toxicity co-solvent (10% acetone); ii) the product extraction is easy and the purity is high (95%) due to the solvent conditions, which enables reactant solubility while the dimer precipitates out of the solution; iii) a low enzyme loading is employed and can be reused, which makes the process economically valuable. The excellent purity of the obtained bisphenyl compounds together with their easy large-scale synthesis constitute important parameters for the production of synthons for polymer synthesis. We chemically modified some of the dimers and polymerized them. A methylated divanillyl diol, **41**, and a methylated dimethylvanillate dimer, **42**, were synthesized from divanillin and dimethylvanillate, respectively, and employed as (co)monomers for the design of renewable (semi)aromatic polyesters (Scheme 14).78 The methylation of the phenol allowed polymerization in bulk and prevented the phenol moiety from being involved in the polycondensation. The reactivity of **41** and **42** towards polycondensation was investigated on the copolymerization with dimethyl sebacate and 1,10-decanediol. Polyester molar masses of 65 000 g mol^{-1} were reached for **41** and 20 000 g mol^{-1} for **42**. Considering this difference in reactivity, a series of polyesters were synthesized by the transesterification of **41** with several diesters of aromatic, aliphatic, or cycloaliphatic structures (Scheme 15). The polyesters displayed glass transition temperatures ranging from –5 to 139 °C, influenced by the structure of the co-monomer and 5 wt% loss a temperatures above 300 °C.



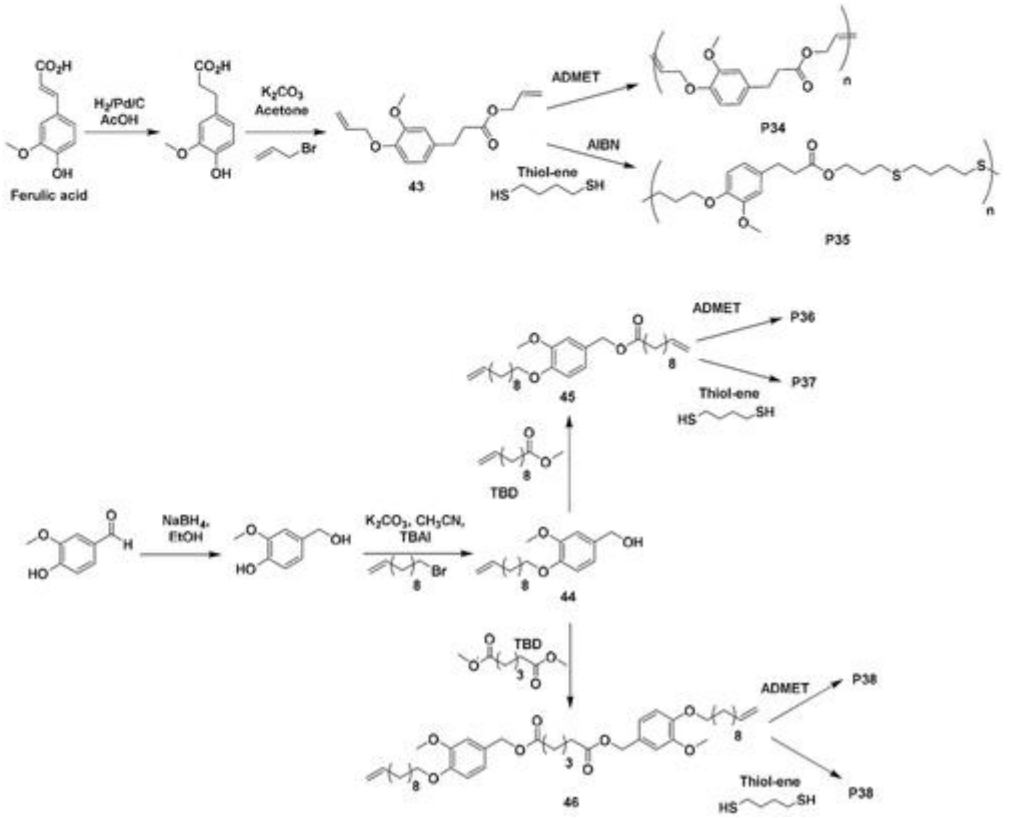
Scheme 14 The synthesis of methylated divanillyl diol, 41, and methylated dimethyl divanillate, 42, from vanillin, with their respective yields.



Scheme 15 The structures of polyesters synthesized from methylated divanillyl diol 4 and diesters with different structures.

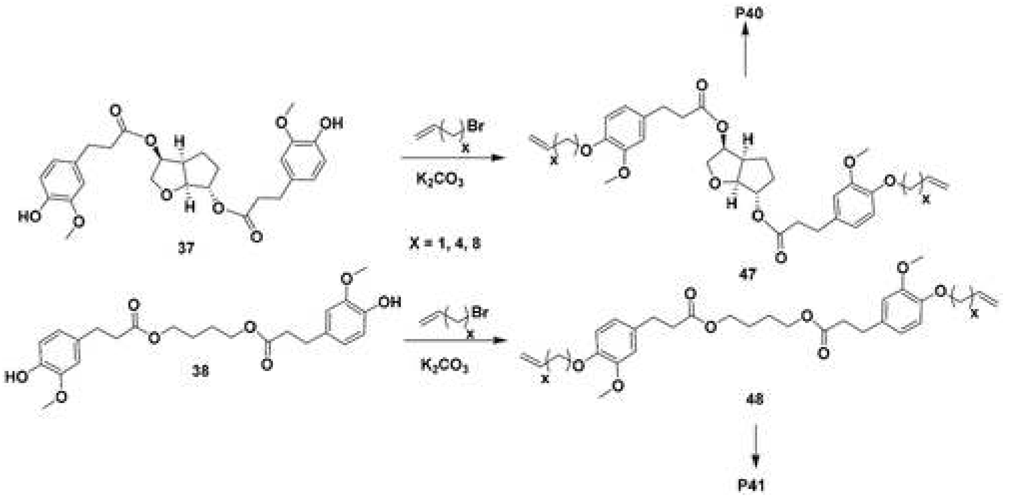
3.1.4 Synthesis and Polymerization of bis-Unsaturated Esters

Other polymerization techniques were also employed to produce polyesters from lignin derivatives (Scheme 16). Indeed, Meier and co-workers prepared bis-unsaturated esters from ferulic acid and vanillin, which were polymerized via the ADMET or thiol-ene methodologies.[71], [79] First, hydrogenation of the internal double bond of ferulic acid was performed to avoid side reactions during polymerization. The resulting compound reacted with allyl bromide, leading simultaneously to the formation of the allyl ester from the carboxylic acid and an allyl ether on the phenol moiety. Among seven tested catalysts, only Hoveyda Grubbs 2nd generation, Zhan, and M51 (Umicore company) metathesis catalysts were able to oligomerize the bis-unsaturated **43**, leading to **P34** with molar masses between 2150 g mol^{-1} and 3050 g mol^{-1}. The polyaddition of **43** was performed with 1,4-butanedithiol and AIBN as radical initiator, yielding **P35**. In comparison to ADMET, a slightly higher molar mass was observed (4150 g mol^{-1}). These techniques led to amorphous polymers, with a low glass transition temperature of –33 °C for **P35**, due to the presence of a long alkyl chain. The same group also provided two bis-unsaturated compounds, **45** and **46**, from the intermediate compound **40** derived from vanillin. Compound **44** was prepared by reduction of the aldehyde moiety into alcohol, and etherification of the phenol moiety with an undecenoic acid derivative. In order to get difunctional compounds **45** and **46**, the alcohol was esterified with methyl undecenoate in a 1:1 molar ratio, or with dimethyl adipate, a biobased compound, in a 2:1 molar ratio, respectively. Compounds **45** and **46** were polymerized by ADMET or thiol-ene addition to lead to **P36**–**P39**. The difference with the previous study is the length of the alkyl chain between the aromatic moiety and the double bond. This longer chain allows higher molar masses to be reached by ADMET. The polymers synthesized via thiol-ene polyaddition are semicrystalline, whereas the ones synthesized by ADMET are amorphous (Table 2).



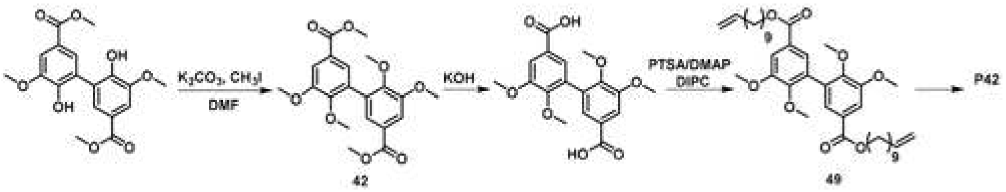
Scheme 16 The synthesis of ferulic acid and vanillin-based polyesters by ADMET polymerization and thiol-ene addition.

Allais and co-workers modified the bisphenols **37** and **38** derived from ferulic acid to obtained bis-unsaturated esters by etherification with three bromoalkenes (3-bromoprop-1-ene, 6-bromohex-1-ene, and 10-(bromodec-1-ene)) (Scheme 17).[80] ADMET polymerization of **47** and **48** was conducted under different conditions, yielding **P40** and **P41**. Although the polymerization of allyl monomers only gave oligomers, optimized conditions led to polymers with molar masses ranging from 9900 to 25 900 g mol^{-1}, depending on the employed monomer. Amorphous polymers were obtained with low glass transition temperatures, from –21.6 to 18.2 °C and 5 wt% loss temperatures between 291 and 333 °C.



Scheme 17 The synthesis of polyesters by ADMET polymerization from bisphenol-based polyesters.

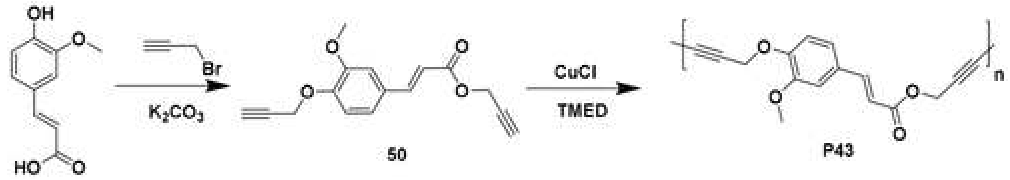
We also reported the synthesis of a bis-unsaturated diester, **49**, and its polymerization by ADMET.[81] Diester **49** was obtained from methylated dimethylvanillate dimer **42** and undecenol (Scheme 18). ADMET polymerization was performed in Polarclean solvent, which was selected for its high boiling point, its compatibility with Grubbs catalyst, and its sustainability.[82] The highest polymer molar masses, 11 000 g mol^{-1}, were achieved employing Grubbs 1st generation and Hoveyda Grubbs 2nd generation catalysts. The obtained polymer, **P42**, showed no isomerization of the double bond. **P42** exhibits a T_g of 17 °C due to its C12 aliphatic chain and a good thermal stability with a 5 wt% loss temperature of 310 °C.



Scheme 18 The synthesis and polymerization via ADMET of the diester obtained by the esterification of a biphenyl compound and undecenol.

3.1.5 Synthesis and Polymerization of bis-Acetylenic Esters

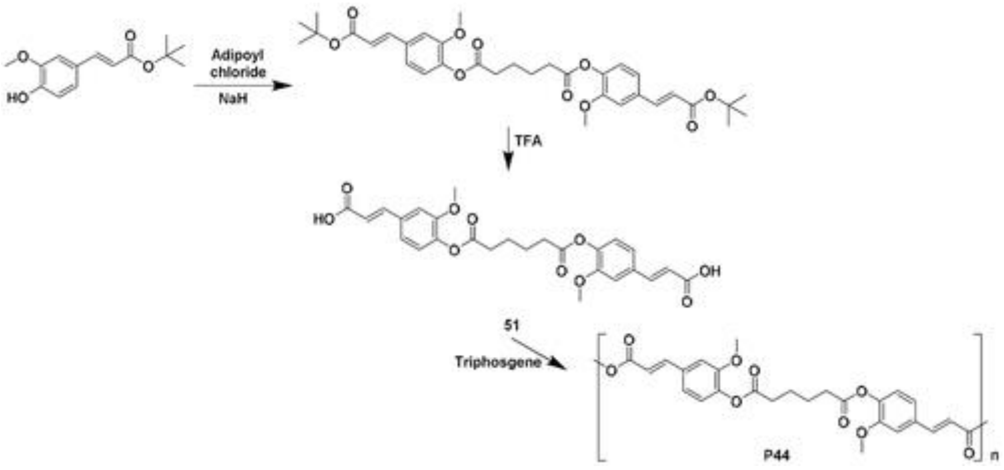
Ogaw and co-workers synthesized a bisacetylene monomer, **50**, from ferulic acid and polymerized it by oxidative coupling polymerization (Scheme 19).[83] This polymerization technique is a living polymerization, which occurs without a termination step. The presence of diacetylene groups in the polymer chain enables cross-linking. Compound **50** was prepared by reacting ferulic acid with propargyl bromide. The oxidative coupling polymerization of **50** led to **P43** with a molar mass of 25 000 g mol^{-1}, a T_g of 56 °C and a degradation temperature of 201 °C. The good solubility of **P43** in organic solvents enables the cast polymer to give a transparent film. Acetylene groups started to cross-link under heating and UV irradiation, leading to an increase of the polymer thermomechanical properties.



Scheme 19 Polymerization by the oxidative coupling of bisacetylenic esters derived from ferulic acid.

3.2 Polyanhydrides

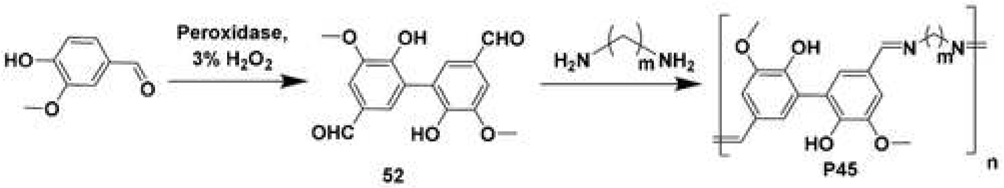
The synthesis of biodegradable polyesters from ferulic acid is very interesting due to their antioxidant properties. Polyanhydrides constitute a class of polymers that are easily hydrolysable. For these reasons, Uhrich and co-workers prepared ferulic-containing poly(anhydride ester)s (Scheme 20).[84]] *t*-Butyl ferulate synthesized by a Knoevenagel condensation reaction (t-butanol was reacted with Meldrum's acid to form a malonic acid monoester, which was immediately reacted with vanillin), underwent a coupling reaction with adipoyl chloride. After deprotection, the diacid **51** was recovered. Polycondensation of **51** with triphosgene led to polyanhydride **P44** with a molar mass of 21 700 g mol^{-1}, a T_g of 82 °C, and a degradation temperature of 332 °C. The hydrolytic degradation of **P44** led to products with antioxidant and antibacterial properties similar to free ferulic acid.



Scheme 20 The synthesis of poly(anhydride ester) from ferulic acid.

3.3 Schiff Base Polymers

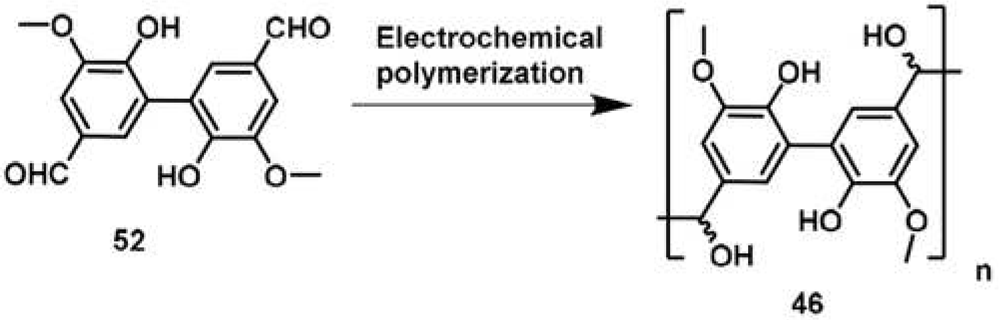
The oxidative coupling of vanillin leading to dialdehyde compounds is also suitable for Schiff base polymerization. Razzaq and co-workers synthesized **52** by the oxidative dimerization of vanillin following an enzymatic pathway reported by Vosburg and co-workers in 2010, employing Horseradish Peroxidase.85 The dialdehyde compound **52** and alkyl diamine (1,2-diaminoethane, 1,3-diaminopropane, 1,6-diaminohexane) were refluxed in ethanol, leading to polymer **P45** with a degree of polymerization between 25 and 32 (Scheme 21).85 The three polymers were stable up to 250 °C. The polymer synthesized with 1,6-diaminohexane complexed with Cu(II), Fe(II), and Co(II).



Scheme 21 The synthesis of Schiff base polymers from divanillin.

3.4 Electrochemistry Route

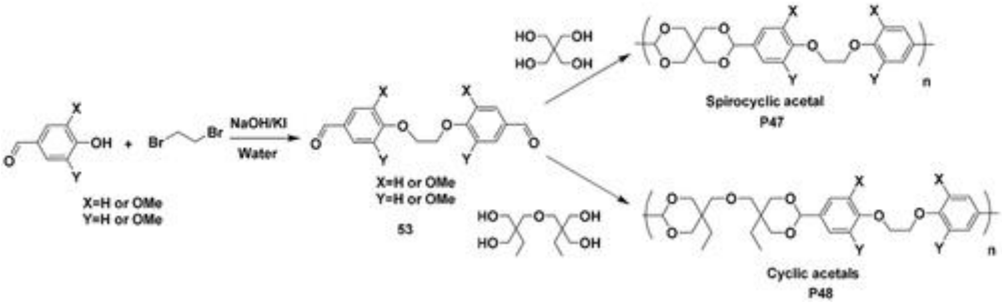
Divanillin was also polymerized by an electrochemical route yielding polyvanillin **P46** (Scheme 22).86 Polyvanillin was prepared by the reductive coupling of the aldehyde group of divanillin using an electrochemical polymerization cell (catholyte: 0.175 M divanillin, 1 M NaOH in water, anolyte: 1 M NaOH (aq), conditions: 12 V, 1.1 A, 3 h, 25 °C). **P46** was obtained with a molar mass of about 10 000 g mol^{-1} and dispersity of 1.5. The polymer exhibits good thermal stability with an onset temperature of 300 °C.



Scheme 22 Polymerization by the reductive coupling of divanillin.

3.5 Polyacetals

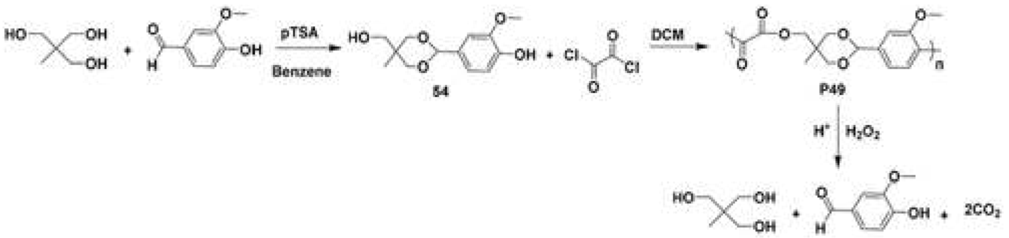
Dialdehydes are also important monomers for the synthesis of polyacetals, a class of biodegradable polymer, as acetal linkages are sensitive to hydrolysis. Miller and co-workers synthesized cyclic and polycyclic polyacetal ethers from lignin-based aromatics.87 4-Hydroxybenzaldehyde, vanillin, and syringaldehyde were investigated in this study. The dialdehydes **53** were prepared by the reaction of lignin derivatives with 1,2-dibromoethane using sodium hydroxide and potassium iodide in water.87 Polycondensation of the dialdehydes **53** with tetraol yields cyclic polyacetal ethers (**P47)** in the case of di-trimethylolpropane and spirocyclic acetal (**P48**) in the case of pentaerythritol (Scheme 23). Molar masses ranging between 10 600 and 22 200 g mol^{-1} were reached. Polymers from 4-hydroxybenzaldehyde are semicrystalline, whereas polymers synthesized from vanillin and syringaldehyde are amorphous due to the presence of methoxy groups. Spirocyclic polyacetals exhibit higher glass transition temperatures than the cyclic equivalent ones (for vanillin: 129 °C versus 80 °C). As already reported, syringaldehyde-based polymers show higher glass transitions than vanillin-based ones (152 °C for the spirocyclic one and 98 °C for the cyclic equivalent). All the polymers present high 5 wt% degradation temperature, between 307 and 349 °C.



Scheme 23 The synthetic pathway of polyacetals from lignin derivatives.

3.6 Polyoxalates

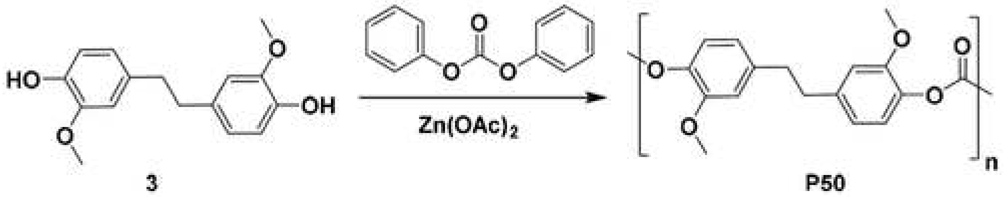
In 2013, Lee and co-workers synthesized poly(vanillin oxalate), **P49**, as inflammation-responsive antioxidant polymeric prodrug (Scheme 24).88 4-(5-(Hydroxymethyl)-5-methyl-1,3-dioxan-2-yl)-2-methoxyphenol, **54**, was synthesized from vanillin and 2-methylpropane-1,3-diol. The step growth polymerization of **54** using oxalyl chloride led to the polyoxalate **P49**, which exhibits a molar mass of 22 000 g mol^{-1} with a dispersity of 1.6 and a glass transition temperature of 120 °C. As poly(vanillin oxalate) has an hydrophobic backbone, it could be formulated into nanoparticles by a conventional emulsion method. Poly(vanillin oxalate) releases vanillin during H_2O_2 and acid-mediated hydrolytic degradation due to the presence of acid-cleavable acetal linkages in its backbone. H_2O_2 was chosen because it is an essential metabolite in living organisms and it could serve as a potential biomarker of various oxidative stress-associated inflammatory diseases. The nanoparticles showed excellent biocompatibility, antioxidant, and anti-inflammatory activity and could potentially be used as therapeutics.



Scheme 24 The synthesis of poly(vanillin oxalate) and vanillin release of under H_2O_2 stimulus.

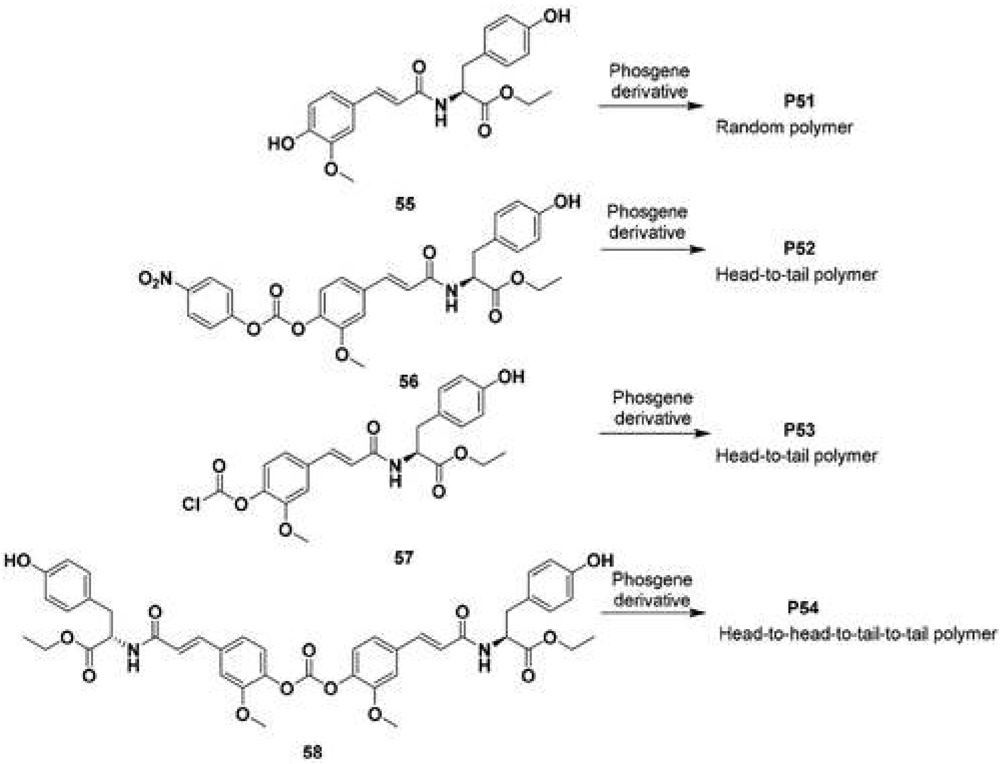
3.7 Polycarbonates

Polycarbonates are a class of material between the commodity and the engineering plastics. They are synthesized by the transesterification of bisphenols and phosgenes or carbonates. Harvey and co-workers synthesized polycarbonate **P50** by a transesterification reaction between the bisphenol **3** and diphenylcarbonate (Scheme 25).89 The non-optimized reaction conditions led to a polymer with a molar mass of 4000 g mol^{-1}. A T_g of 86 °C and 5 wt% loss temperature of 290 °C were measured but these values are affected by the low molar mass. The authors expect that a higher reaction temperature or the use of phosgene would increase the molar mass of the polymer.



Scheme 25 The synthesis of polycarbonates from vanillin.

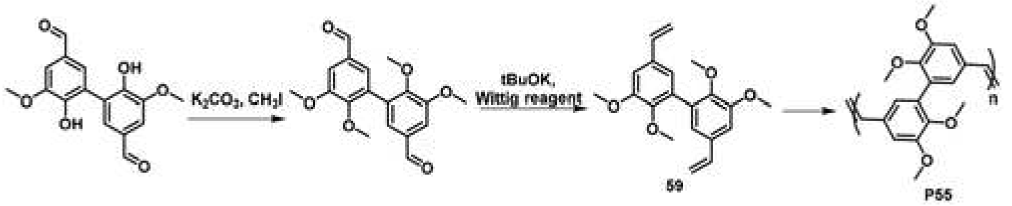
Biocompatible and biodegradable poly(carbonate-amide)s were also synthesized from ferulic acid and tyrosine (Scheme 26).90 The peptidic coupling of ferulic acid and tyrosine led to the bisphenol **55**. **P51**, obtained by polycondensation of **55** with diphosgene, is a regio-random polymer. However, good control of the regio-selectivity was achieved by the design of other monomers. Using BA' monomer, **56** and **57** were synthesized to produce a regio-regular head-to-tail polymer. To reach this goal, the phenol of the ferulic acid moiety was activated to a *p*-nitrophenylcarbonate, **56**, or to a chloroformate, **57**. Their polymerization respectively led to the targeted regio-regular polymers **P52** and **P53,** with regio-selectivities of 63% and 90%, respectively. The A'AAA' diphenol **58** was synthesized to produce, by polycondensation with phosgene, a regio-regular head-to-head-to-tail-to-tail polymer, **P54.** In this study, the obtained polymers exhibited molar masses between 6000 and 19 000 g mol^{-1}, T_gs of around 130 °C, and degradation temperatures of around 340 °C. Although the thermomechanical properties were not influenced by the regio-selectivity, the fluorescence properties were impacted. These biodegradable and biocompatible materials are therefore interesting for sensing or imaging applications.



Scheme 26 The synthesis of poly(carbonate-amide)s from ferulic acid.

3.8 Conjugated Polymers by ADMET Polymerization

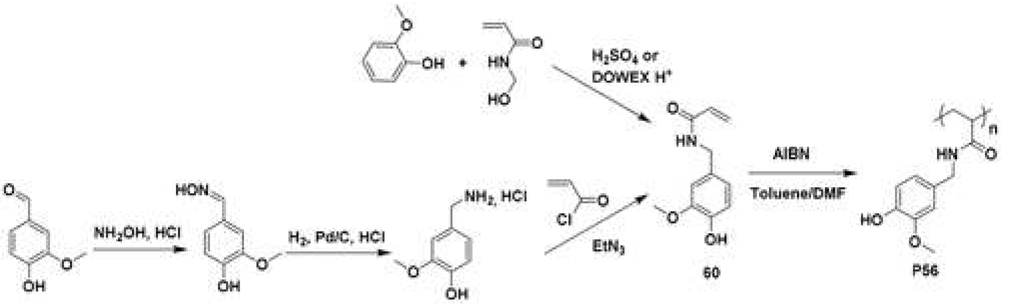
Dihaldehydes are key intermediates in polymer chemistry as they can undergo a wide range of chemical modifications and thus lead to polymers with different structures and properties. We performed a Wittig reaction on methylated divanillin yielding a divinyl compound, **59** (Scheme 27).81 The ADMET polymerization of **59** in Polarclean solvent yielded **P55**. The highest polymer molar mass, 29 000 g mol^{-1}, was achieved employing Hoveyda Grubbs 2nd generation catalyst. The polymers displayed only *trans* configuration of the vinylene bonds. **P55** exhibited high thermomechanical properties, due to the conjugation of the double bond and the aromatic ring. Indeed, the T_g was observed at around 160 °C by DSC, while dynamic mechanical analysis (DMA) revealed a glass transition temperature (T_α) at 209 °C. The 5 wt% loss temperature occured at 380 °C.



Scheme 27 The synthesis of divinyl compound from divanillin and ADMET polymerization.

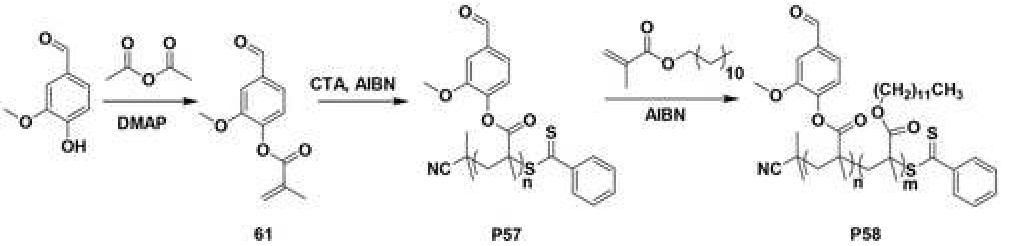
3.9 Radical Polymerization

Lignin derivatives were also modified into acrylamide and acrylate derivatives and polymerized by radical polymerization. Thermoplastic polymers with lignin derivatives as side chain groups are obtained (Scheme 28). Roger and co-workers synthesized the acrylamide derivative **60** from guaiacol and vanillin.91 The first pathway involves the Friedel–Craft alkylation reaction of *N*-hydroxymethylacrylamide with guaiacol. The second approach is based on vanillin and requires a three-step reaction: the oxime is prepared, reduced and the resulting amine reacts with acryloyl chloride. The obtained acrylamide **60** was polymerized by free radical polymerization, employing AIBN as initiator. Despite a screening of the conditions, polymers with relatively low molar masses below 11 000 g mol^{-1} were obtained; branched structures and broad molar mass distributions were observed at high conversion. These observations can be attributed to the phenoxy radicals known to inhibit radical polymerization by acting as scavengers. Polymers **P56** displayed a T_g of around 100 °C, and showed antibacterial activity.



Scheme 28 The synthesis of thermoplastic polymers by the radical polymerization of lignin-derived acrylamides.

Controlled radical polymerization was used to synthesize homopolymers and block copolymers from vanillin-derived acrylate.92 An acrylate derivative, **61**, was synthesized from vanillin by esterification of the phenolic group with methacrylic anhydride (Scheme 29). **61** was polymerized by reversible addition–fragmentation chain transfer (RAFT), yielding **P57** with a molar mass of 17 000 g mol^{-1} and a dispersity of 1.34. **P57** was employed as a macro-chain transfer agent (CTA) for the polymerization of lauryl methacrylate, a fatty acid derivative, yielding the copolymer **P58** with a molar mass of 56 000 g mol^{-1} and a dispersity of 1.50. The vanillin homopolymer **P57** exhibits a T_g of 120 °C and a degradation temperature over 300 °C, similar to the values of polystyrene. The copolymer **P58** self-assembles into body-centered cubic nanospheres. Other morphologies could be reached by increasing the volume fraction of vanillin.



Scheme 29 The synthesis of thermoplastic polymers by the radical polymerization of lignin-derived acrylates.

In conclusion, a multitude of thermoplastic polymers have been synthesized from vanillin, ferulic acid, syringaldehyde, hydroxybenzaldehyde, and guaiacol by different polymerization methods. Due to chemical modifications or copolymerization, the resulting polymers cover a wide range of thermal properties (see Table 2).

4 Conclusion

The majority of the studies described in this review were published very recently, showing the growing interest of researchers in the synthesis of lignin-based derivatives polymers. The preparation of thermosets with different structures such as vinyl ester resins, cyanate ester, epoxy, and benzoxazine resins from vanillin or guaiacol have led to various high-performance materials. Different polymerization techniques were also employed for the synthesis of thermoplastic polymers. Indeed, although in the past decades lignin derivatives have been widely used for thermotropic polymers, in the current context of sustainability, mainly vanillin-based thermoplastic polymers have been recently re-explored. For instance, vanillin, syringaldehyde, or ferulic acid have been used for the synthesis of PET mimic polymers or for designing fully biobased copolymers with fatty acids and a wide range of other polymers such as Schiff base polymers, polyacetals, polyanhydrides, and polyacrylates. Through all these examples of polymerization, lignin derivatives were proven to enhance the rigidity and thermostability of the obtained polymers. It is important to notice that the presence of methoxy substituent(s) on the aromatic ring, due to the inherent structure of lignin, affects the thermomechanical properties polymers by decreasing the crystallinity or increasing some mechanical properties such as impact strength. Despite this difference with petroleum-based molecules, lignin derivatives have proven good substitutes for aromatic molecules such as styrene, terephtalic acid, or bisphenol-A. A wide range of applications can be reached with such lignin derivative-based polymers, such as high-performance materials or for biomedical applications. All these applications in the field of polymer materials valorize the extensive research carried out on the fractionation of lignocellulosic biomass. Indeed, before producing and commercializing renewable polymers derived from lignin, it is essential to develop green, efficient, and economic processes to produce selectively and on a large scale small aromatic molecules from lignin. Improved processes should include both the fractionation of lignocellulosic biomass and the depolymerization of lignin. Moreover, this review only focuses on the use of bioresources; in terms of sustainability, the impact of the overall reactions should be also considered.

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