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Anionic polymerization of ferulic acid-derived, substituted styrene monomers☆

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ABSTRACT

Ferulic acid, a natural cinnamic acid derivative with hydroxyl and methoxy group, was quantitatively converted into protected functional styrene monomers *via* 4–vinylguaiacol (VG) as an intermediate. In a facile and scalable two-step reaction including decarboxylation followed by protection reactions, the monomers 1-ethoxy ethoxy-VG and *tert*-butyldimethylsilyl-VG were obtained in high yields. Living anionic polymerization of the acetal (1-ethoxy ethoxy-) and silyl (*tert*-butyldimethylsilyl-) protected styrenes proceeded to well-defined polymers with narrow MWD, although the reaction temperatures in THF were dependent on the protecting groups of the monomers. Deprotection of the acetal and silyl groups was conveniently attained under acidic conditions both in THF and water, resulting in well-defined poly(vinylguaiacol). In addition, demethylation with boron tribromide was performed to obtain poly(vinylcatechol) copolymers, which were used to complex Fe(III). Random copolymerization was observed for the statistical EE-VG and styrene copolymerization in THF at –95 °C. Aiming at a fully biobased approach, 4-isopropylstyrene was synthesized from cuminaldehyde by Wittig reaction, and the copolymerization of the latter with EE-VG was also performed, resulting in multi-hydroxyl functional macroinitiators after deprotection, which were employed for subsequent L-lactide and 4-methyl-ε-caprolactone grafting.

1. Introduction

Sustainable polymer materials, relying both on biobased feedstocks and biodegradable polymers, have become a central research topic in the recent decade [1,2]. Applications of high-performance materials range from chemistry to medicine, diagnostics, packaging, energy, and electronics [3–8]. To replace existing petroleum-based polymers, sustainable feedstock-based compounds must exhibit at least similar or even improved properties compared to the materials available at present. The living anionic polymerization of styrene and diene monomers is widely used for the manufacturing of thermoplastic elastomers (TPEs) [9–12]. High structural precision and a high degree of functionalization in linear polymers and block copolymers can be attained using anionic living polymerization [13–15]. Complex architectures with well-defined structure have been synthesized by anionic polymerization of hydrocarbon monomers or of monomers containing stable and protected functional groups in the presence of carbanions, such as ethers, acetals and esters [16–18]. Sustainable feedstock-based materials with specific molecular structures for special purposes can be used instead of fossil fuel-derived compounds, promising reduced environmental impact [1,19–23].

When compounds from plants are utilized as a renewable feedstock, the resulting polymers are often referred to as “bioderived”. An interesting approach recently gained popularity in science and industry, where biological fermentation is used to produce chemical commodities from agricultural feedstocks [24,25]. In most cases, such as for poly (lactide acid) (PLA), this feedstock is based on glucose obtained from corn starch.

Lignin is a complex, polyphenolic biopolymer with variable structure depending on its origin. It is the second most abundant biopolymer, produced on large scale as a byproduct of the paper industry (~70 million tons annually) [26]. Immense efforts in academia and industry have been made to transform lignin waste into chemical commodities [26–30]. A minority of lignin waste is employed in high-value applications in upcycled products, such as a fillers in tires [31,32], concrete and asphalt [33,34], and furthermore in some specialized applications such

☆ *Dedicated to Prof. Nikos Hadjichristidis, a pioneer in the field of anionic polymerization and other areas on the occasion of his 80th birthday.*

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as polymer composites [35], epoxy resins [36,37], and other materials [38–40].

Ferulic acid (3-methoxy-4-hydroxycinnamic acid) is a natural, aromatic compound that belongs to a variety of phytochemicals. It is one of the main constituents of many plant cell walls, e.g. in flax shives, oat, rice, and wheat bran [41]. Cellulose and lignin are the key structural materials of the cell wall, as they provide strength and rigidity [42]. Lignin serves as a filler in between cellulose, hemicellulose, and pectin, in particular in vascular and support tissues. Extraction of ferulic acid is attained by alkaline hydrolysis of lignin fibers [43]. Several works have focused on the biotechnological production of ferulic acid from eugenol, which is obtained from clove oil [44,45]. Fermentation-based processes offer several advantages, such as aqueous processing environments, nontoxic waste, besides the non-fossil-based feedstock. A crucial property of lignin is the prefabricated carbon scaffold consisting of different cinnamic acid derivatives that can be decarboxylated under mild condition to generate styrene derivatives. Historically, researchers found that cinnamic acid was decarboxylated to form a compound called "cinnamene" or "cinnamol", which appeared to be styrene [46–48].

Terpenes, consisting of a carbon scaffold of condensed isoprene units, are another class of naturally occurring compounds with a large diversity of chemical structures and biological activities. Cuminaldehyde (4-isopropylbenzaldehyde) is a terpene found in cumin and other related species. The aromatic aldehyde may be viewed as a natural precursor for styrene, prepared *via* the facile introduction of a polymerizable vinyl bond by Wittig olefination. Polymer scientists have increasingly exploited naturally occurring aromatic molecules as building blocks for biobased polymers [49]. Aromatic components typically increase glass transition temperatures because of quadrupolar interactions, π - π stacking, and increased sterical hindrance (4-isopropylstyrene).

The common synthesis routes for functional styrene derivatives can be divided into two strategies. The functionality is either introduced at the beginning, along with a protective group, followed by the introduction of the vinyl double bond, or vice versa [13,50,51]. The styrene vinyl group as well as the functional moiety are prone to undergo side reactions upon heating and reaction with strong electrophiles and nucleophiles.

Recently, Kamigaito and coworkers published an elegant synthetic strategy to obtain biobased functional styrenes by decarboxylation of cinnamic acids, followed by the introduction of various silyl-protecting groups [52,53]. Reversible-addition-fragmentation chain transfer (RAFT) polymerization of the protected styrene derivatives afforded poly(3-methoxy-4-hydroxy styrene) after deprotection [52]. Haraguchi *et al.* investigated the biodegradation of poly(3-methoxy-4-hydroxy styrene) by microorganisms (especially *Moraxella* and *Penicilium*) in soil [54]. They observed that vanillic acid seems to be the first biodegradation product, followed by further oxidation to the monomethyl ester of β-carboxymuconic acid, maleic and oxalic acid. Evaluation of the intermediate degradation products reveals that the degradation pathway is similar to lignin by microorganisms [54].

Catechol-containing polymers, are designed with respect to surface adhesion, complexation and antioxidant properties [55–62]. Due to the incompatibility of protic OH-functionalities and the living carbanion during the polymerization, suitable protecting chemistry was employed [51,63–66]. The first successful example of this strategy using a protective group is the synthesis of poly(4-vinylphenol), protected by *tert*-butyldimethylsilyl chloride, resulting in 4-*tert*-butyldimethylsilyloxystyrene, which was subjected to carbanionic polymerization in THF at −78 °C [64]. In previous works, catechol-containing vinyl monomers (4-vinylcatechol and 3-vinylcatechol acetonide) have been investigated with respect to kinetics, reactivity ratios, and formation of tapered block copolymers with pronounced monomer gradient [51]. The acetonide-protecting group remained stable under the polymerization conditions, but was readily removed by the addition of diluted hydrochloric acid, resulting in well-defined poly(vinylcatechol)s. Acetal protecting groups recently gained increasing attention due to their convenient access and removal in post-modifications, along with excellent stability against nucleophiles [67]. In a previous report, we introduced *p*-(1-ethoxy-ethoxy)styrene, based on ethyl vinyl ether and the respective 4-vinylphenol, for anionic polymerization, enabling rapid access to poly (hydroxy-styrene) after deprotection [68].

More importantly, 4-*tert*-butoxystyrene is generally used as the favored protected precursor monomer for the synthesis of poly (hydroxystyrene) [69,70]. 4-*Tert*- butoxystyrene is suitable for carbanionic polymerization, but the latter requires harsh deprotection protocols. Indeed, this moiety exhibits simple benefits such as steric hindrance and high stability that enriches the chemist's toolbox in many ways. Usually, the *tert*-butyl moiety is removed under strongly acidic conditions using 1,1,1-trifluoroethanol as a solvent and trifluoromethanesulfonic acid at −5 °C [71]. Alternative removal strategies rely on trimethylsilyl iodide at 60 °C to obtain poly(hydroxystyrene) [70].

Addressing the scarcity of biobased styrenic monomers suitable for anionic polymerization, we report the synthesis of biobased functional polystyrene (co)polymers with well-defined structure, relying on naturally occurring ferulic acid and the introduction of either an acetal or a silyl protecting group. A series of different homopolymers, copolymers with styrene and 4-isopropylstyrene, and graft copolymers consisting of L-lactide and 4-methyl-ε-caprolactone (4MCL) respectively, have been prepared by living anionic polymerization to validate the versatility of the approach towards functional polymers based on renewable resources.

2. Results and discussion

2.1. Monomer synthesis

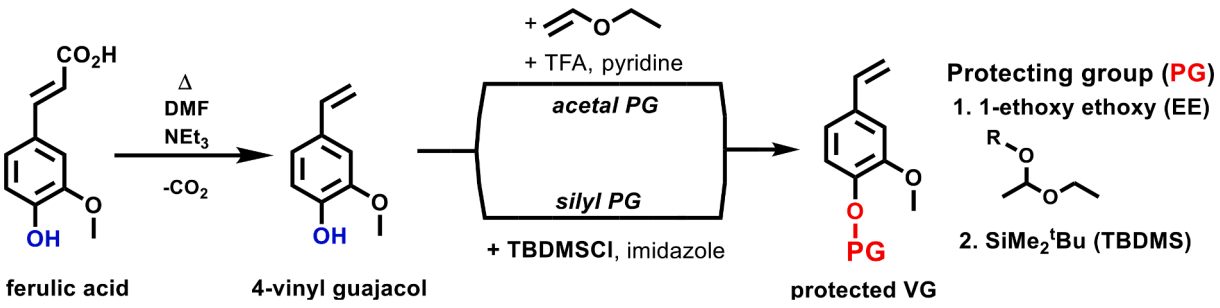
Starting from the naturally available cinnamic acid derivative ferulic acid, 4-hydroxy-3-methoxystyrene (4-vinylguaiacol, **VG**) was synthesized by decarboxylation in DMF at 100 °C in 99 % yield (Scheme 1). However, the phenolic group in the monomer has to be protected for anionic polymerization by suitable protective groups. For this purpose, two different protective groups were introduced, and the polymerization of the resulting monomerts was studied regarding polymerization behavior and subsequent deprotection. VG can be protected either by ethyl vinyl ether as an acetal, or by *tert*-butyldimethylsilyl chloride (TBDMSCl) to obtain silyl protected hydroxyl groups. Both protective groups represent stable moieties towards nucleophiles, but can be removed under acidic conditions.

The formation of acetals as a protecting group for ethyl vinyl ether with alcohols or phenols is a common strategy in organic chemistry. The protection of the phenol moiety of VG with ethyl vinyl ether using trifluoroacetate/pyridine as a catalyst proceeded quantitatively, nevertheless in only 80 % isolated yield. However, quantitative consumption of VG was achieved after seven days, and the conversion was tracked daily by NMR. The loss of EE-VG is attributed to the auto-polymerization of EE-VG, (1-ethoxyethoxy vinylguaiacol) and VG during the distillation at elevated temperatures under reduced pressure.

TBDMSCl and imidazole were applied to protect the hydroxyl group of VG. The reaction proceeded in 82 % yield without solvent. TBDMS-VG could be purified *via* distillation under reduced pressure, in contrast to literature procedures [52]. This work demonstrates an improved purification method, avoiding column chromatography and additional work-up protocols. Details of all monomer syntheses and NMR spectra are given in the Supporting Information. (Figs. S1-S3).

2.2. Polymerization of EE-VG and TBDMS-VG

Living anionic polymerization of all synthesized protected VGs was examined using *sec*-BuLi as an initiator in THF at low temperatures. For both monomers, a series of homopolymers with increasing molecular



Scheme 1. Synthesis of biobased functional styrene monomers derived from ferulic acid with different protecting groups.

weight was synthesized. Molecular weight determination was carried out by size exclusion chromatography (SEC), showing that higher molecular weights of P(EE-VG) and P(TBDMS-VG) are underestimated by SEC (eluent THF, PS calibration). Aiming at even higher molecular weights (>50 kg/mol), pronounced tailing towards molecular weights was observed (Figure S9). The results are summarized in Table 1 and Fig. 1. NMR and MALDI-TOF spectra are given in the SI (Figure S4-S8).

Due to its high reactivity, EE-VG requires very low polymerizations temperatures of −95 °C (acetone/ N_2(l)) in THF. Attempts were made to polymerize EE-VG at −78 °C (isopropanol/dry ice), but the results show that severe termination occurs during the polymerization, leading to a broad molecular weight distribution. TBDMS-VG was polymerized under standard conditions at −78 °C in THF.

In contrast to the anionic polymerization of EE-VG in THF at −95 °C, the polymerization of EE-VG in cyclohexane using *sec*-BuLi as an initiator at 25 °C did not proceed at all, indicated by the immediate disappearance of the color of the anionic species after the addition of *sec*-BuLi. This can be attributed to deactivation of the generated carbanion by nucleophilic attack at the 1-ethoxy ethoxy group. In particular, the acidic proton in vicinity to the acetal can be abstracted by the nucleophilic organo-lithium initiator or living chain end. Furthermore, initiation of TBDMS-VG resulted in a red colored solution, indicating the living chain end. However, the color of the living chain end disappeared over the course of 15 min, and only oligomers of < 2000 g/mol were detected with SEC (Figure S10 and Figure S11). These observations indicate that the TBDMS protective group is generally more stable towards strong nucleophiles than the 1-ethoxy ethoxy group. The nucleophilicity strongly depends on the temperature and on the employed solvent.

The resulting polymers of EE-VG and TBDMS-VG differ in their glass transition temperatures, T_g. Whereas the 1-ethoxy-ethoxy acetal lowers the T_g to 15 °C (Figure S12), the T_g of the polymer of TBDMS-VG was determined to be 79 °C (Figure S13). This can be attributed to the flexible ethyl side chains of EE-VG, whereas the bulky TBDMS group provides rigidity.

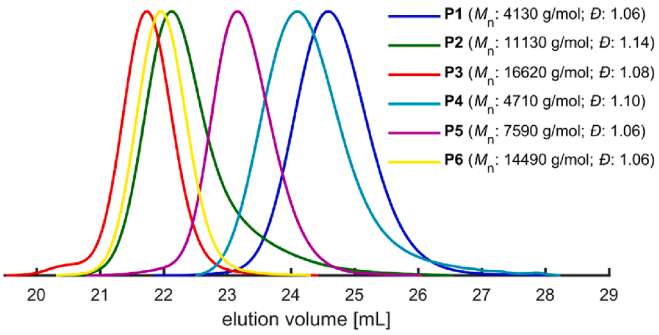


Fig. 1. SEC traces (eluent THF, PS calibration) of P1-6.

The most pronounced difference of the monomers EE-VG and TBDMS-VG was observed in the deprotection of their phenol groups. SEC traces of the deprotected homopolymers ($P1_d$-6_d) are shown in Figure S14. EE-VG is deprotected under mild conditions by the addition of diluted hydrochloric acid within one hour at 25 °C. A typical ^{1}H NMR spectrum of the deprotected homopolymer is shown in Figure S 15. However, the removal of silyl groups either requires tetrabutylammonium fluoride (TBAF) or concentrated hydrochloric acid under reflux for 24 h. The facile deprotection of acetals is an important

Table 1
Properties of homo- and copolymers of protected VG.

entry	VG + protecting group	x_{feed} Styrene, %	Composition VG+/Sty	M_n,theo, kg/mol	M_n (SEC)[a], kg/mol	$Đ$ [a]	T_g, °C
P1	1-ethoxy ethoxy	–	–	5.0	4.9	1.06	–
P2	1-ethoxy ethoxy	–		10.0	11.1	1.15	–
P3	1-ethoxy ethoxy	–	–	30.0	16.8	1.08	15
P4	TBDMS	–	–	5.0	4.8	1.10	79
P5	TBDMS	–	–	8.0	7.7	1.06	–
P6	TBDMS	–	–	20.0	14.6	1.06	–
P7	1-ethoxy ethoxy	88	10/90	10.0	11.2	1.06	81
P8	1-ethoxy ethoxy	77	25/75	10.0	9.6	1.07	95
P9	1-ethoxy ethoxy	47	50/50	10.0	12.1	1.08	45
P10	1-ethoxy ethoxy	38	75/25	10.0	9.2	1.08	35
P11	1-ethoxy ethoxy	23	90/10	10.0	11.8	1.11	30
P12	TBDMS	90	10/90	10.0	10.1	1.06	–
P13	TBDMS	75	25/75	10.0	10.8	1.08	–
P14	TBDMS	57	50/50	10.0	9.9	1.07	–
P15	TBDMS	35	75/25	10.0	15.5	1.08	–
P16	TBDMS	24	90/10	10.0	10.8	1.08	–

[a] Determined by SEC in THF (UV signal, PS calibration).

benefit of the 1-ethoxy ethoxy protecting group. In addition, the deprotection of P(EE-VG) can be performed in a one-pot reaction by adding a mixture of degassed methanol and diluted hydrochloric acid directly into the polymerization medium at −95 °C to terminate the polymerization and to deprotect the polymer. After heating to room temperature and precipitation in cold methanol, the polymer was already deprotected, resulting in well-defined poly(4-hydroxy-3-methoxystyrene) in quantitative yields. Removal of the acetal protecting group increased the T_g to 77 °C ($P3_{deprotected}$, Figure S12).

2.3. Copolymerization with styrene

EE-VG and TBDMS-VG were copolymerized with styrene in different ratios via statistical anionic copolymerization (Scheme 2), ranging from 23 to 88 % styrene content and 24–90 %, respectively to assess the reactivity of the biobased monomers in comparison to styrene. All results are given in Table 1.

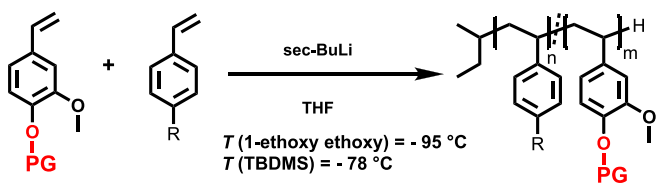
All copolymers showed narrow MWD (Figures S15-S16). The incorporated amount of styrene was determined by NMR spectroscopy (Figures S17-S18). The ratio of VG and styrene determines the T_g of the resulting copolymer (Figure S20). With increasing styrene content, the T_g increases in a linear fashion. This linear dependence of increasing T_g is an indication that the copolymer sequence is random [72]. Using the Fox-equation, the polymers follow a linear tendency shown in Fig. 2.

2.4. Copolymers with 4-isopropylstyrene

Since 4-isopropylstyrene can be obtained from a natural source, we aimed at the preparation of fully biobased polymers. In this section, we demonstrate that copolymers of 4-isopropylstyrene (4-^{i}PrS) and EE–VG are accessible *via* living anionic polymerization. Cuminaldehyde, the major terpene component of the essential oil of cumin, is used as a starting material for the synthesis of 4-^{i}PrS. This monomer can be considered as a natural substitute for styrene to generate fully biobased copolymers from functional and non-functional monomers.

Cuminaldehyde was converted to 4-isopropylstyrene (4-^{i}PrS) *via* Wittig olefination (Scheme 3, ^{1}H NMR in Figure S21). The challenging step of the Wittig reaction is the removal of the unavoidable by-product triphenylphosphine oxide (TPPO). On a gram-scale TPPO can be removed by column chromatography, but targeting larger scales is problematic due to interaction of TPPO with the column. However, the synthesis of 4-^{i}PrS was possible without purification by column chromatography. The monomer was distilled under reduced pressure und dried over CaH_2 and trioctylaluminum. Poly(4-^{i}PrS) shows interesting thermal stability. Previous works showed that compared to other *para*-alkylstyrene derivates (4-ethyl-, 4-*tert*-butyt-styrene, styrene), 4-^{i}PrS exhibits good thermal stability, confirmed by TGA measurements under N_2 and 0_2.[73].

Copolymers consisting of a large excess of 4-^{i}PrS and EE-VG (10/1 M ratio) were synthesized *via* anionic copolymerization in THF under the same conditions as described for the styrene copolymers. NMR spectrum, SEC trace and DSC curve are given in Figures S21-S24. T_g of the copolymer after removal of the 1-ethoxy ethoxy protective group is 103 °C. This copolymer, P(4-^{i}PrS-*co*-VG), was then used in a proof-of-concept reaction to serve as a macroinitiator for graft copolymers.



Scheme 2. Copolymer synthesis with styrene (derivatives), R = H, isopropyl.

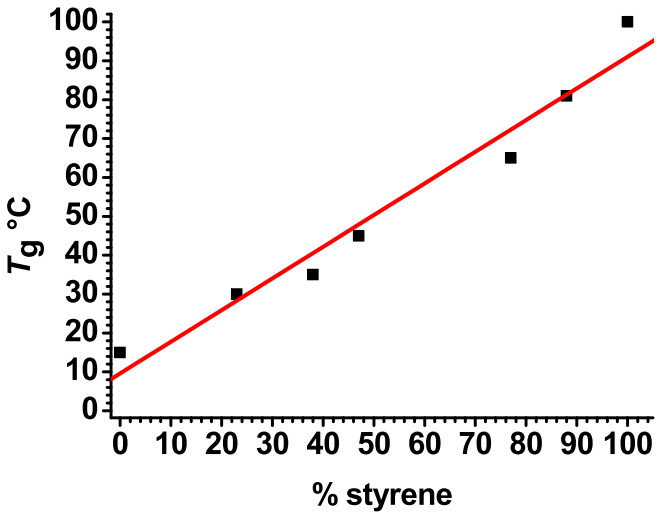


Fig. 2. T_g vs. styrene content in statistical copolymers of EE-VG and styrene (T_g of styrene taken from Literature [72]).

2.5. Graft copolymers and demethylation

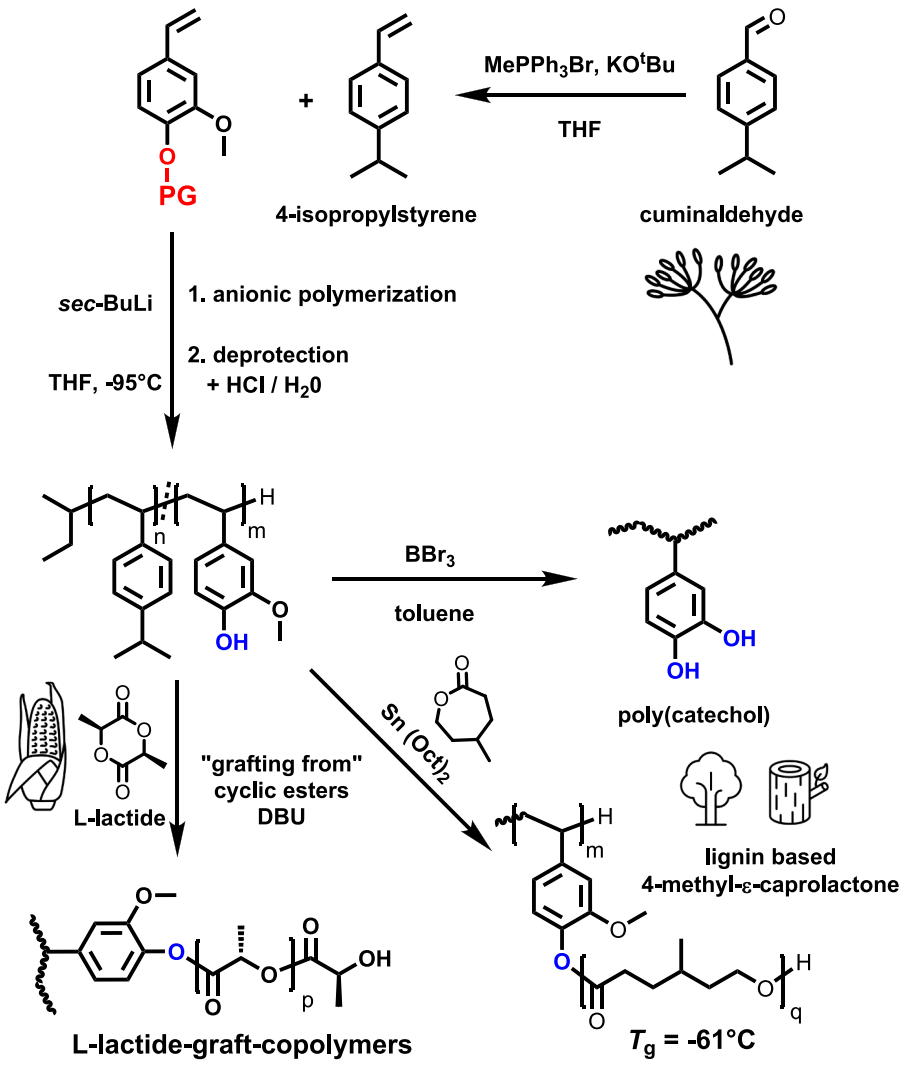
As demonstrated in previous works, poly(4-hydroxystyrene) can serve as key material to access interesting polymer features, e.g. as macroinitiators for ethylene oxide grafting [68,69,74]. The combination of the hydrophilic poly(ethylene oxide) side chains and the hydrophobic polystyrene backbone results in amphiphilic graft copolymers with promising surfactant properties [68,74].

To further expand the scope of graft copolymers using hydroxy-functionalized polystyrenes, (4-^{i}PrS$_{119}$-*co*-VG$_{12}$) was utilized as a versatile macroinitiator and precursor for the synthesis of graft copolymers. Applying the "grafting from" technique, graft copolymers of P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$) and cyclic esters were synthesized *via* ring-opening polymerization using DBU as a metal-free catalyst. It was demonstrated that P(4-^{i}PrS$_{109}$-*co*-VG$_{18}$) served as a suitable macroinitiator for L-lactide grafting. The number-average molecular weights M_n increased in direct proportion to L-lactide conversion (Fig. 3, Table 2), and the graft copolymers maintained narrow molecular weight distributions ($Đ$ =1.11–1.13).

In addition, in a proof-of-concept reaction P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$) was used as a macroinitiator to graft 4-methyl-ε-caprolactone from the phenolic hydroxyl groups using Sn(Oct)$_2$ as a catalyst. The bio-available 4MCL is a considerable alternative for flexible elastomers based on biodegradable polyesters. 4MCL is obtained in multiple steps from lignin. Lignin bio-oil provides a variety of cresols, that are hydrogenated into their respective alkyl-cyclohexanones. In a second step, Baeyer-Villiger oxidation with *m*CPBA yields methylcaprolactone derivatives.

The graft copolymer sample P19 was synthesized with Sn(Oct)$_2$ in toluene solution at 130 °C for 24 h. NMR spectra are given in Figures S27-S31. SEC shows a rather broad molecular weight distribution ($Đ$ = 1.40) with a trend towards higher molecular weights (Figure S32). This is explained by incomplete initiation of the phenolic groups of VG. Most probably due to the reduced nucleophilicity of phenolates compared to alkoxides, initiation with Sn(Oct)$_2$ can be slow. In addition, the methoxy group in the vicinity could influence the bulkiness of the macroinitiator. Moreover, the polymerization of 4MCL (P20) and P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$) in bulk within one hour at 130 °C was demonstrated. The conversion of 4MCL was accompanied by a significant increase in melt viscosity.

The versatility of P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$) is displayed by the clean removal of the methoxy substituent at the aromatic ring of vinylguaiacol. The demethylation was performed using boron tribromide in dry toluene for 24 h- reaction time, resulting in well-defined poly(4-



Scheme 3. Synthesis of biobased functional styrene monomers, anionic copolymerization, demethylation, and "grafting from" ring-opening polymerization of cyclic esters (PG = protecting group).

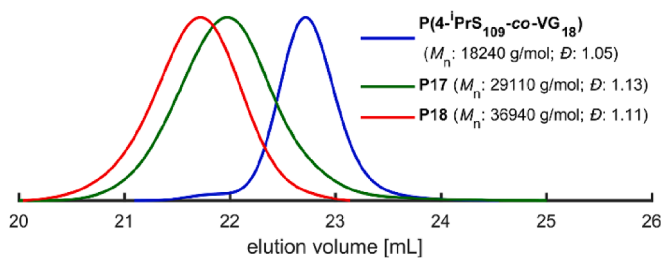


Fig. 3. SEC traces (eluent THF, PS calibration) of P(4-^{i}PrS$_{106}$-*co*-VG$_{18}$) and P (4-^{i}PrS$_{119}$-*co*-VG$_{12}$-*g*-L-lactide); P17 and P18.

isopropylstyrene-*co*-vinylcatechol) (P(4-^{i}PrS$_{119}$-*co*-VC$_{12}$)) in quantitative yield (Fig. 4). The demethylation resulted in copolymers of P(VC) and P(4-^{i}PrS) with a T_g of 93 °C (Figure S25). The total disappearance of the methoxy signal at 3.58 ppm in ^{1}H NMR in Fig. 4 confirmed complete demethylation. SEC in Figure S 32 shows that the MWD remains unchanged.

2.6. Complexation properties of P(4-^{i}PrS-co-VC)

After successful demethylation of vinylguaiacol, the resulting polyvinylcatechol (PVC) was investigated with respect to the resulting complexation properties. It is known that catechols show remarkable complexation affinities to metal ions. It is noteworthy that iron III, (Fe^{3+}) cations form stable tris-complexes with catechols. The catechol complexation activity with Fe^{3+} cations depends on the pH value. First, no complexation was observed when mixing a solution of $FeCl_3$ in methanol with a solution of P(4-^{i}PrS-*co*-VC) in acetone. Only under alkaline conditions catechols show deprotonation of the hydroxyl groups. After the addition of sodium hydroxide in water, the formation of a dark precipitate was observed. The complexation leads to an insoluble polymer network (Fig. 5). The reversibility of the complexation was demonstrated by adding hydrochloric acid to the solution to dissolve the complex, reducing the number of coordinating catechols on the iron center at low pH (Fig. 5).

3. Conclusion

Currently there are hardly any biobased styrene derivatives that are amenable to anionic polymerization. Ferulic acid was quantitatively transformed into 4-vinylguaiacol and novel hydroxyl-protected biobased styrene monomers. Acetal and silyl protective group were introduced to protect the phenols of VG. Living anionic polymerization in THF at low temperatures of these protected phenolic styrene derivatives resulted in well-defined polymers with controlled molecular weights

Table 2
Graft copolymers and demethylation of poly(4-isopropylstyrene-*co*-3-methoxy-4-hydroxystyrene).

entry	composition	Macroinitiator /precursor M_n (SEC)[a] kg/mol	% VG[a]	monomer	M_n (SEC)[b] kg/mol	$Đ$ [b]	T_g, [c] °C
P17	P(4-^{i}PrS$_{109}$-*co*-VG$_{18}$)	18.2	14	lactide	29.1	1.13	–
P18	P(4-^{i}PrS$_{109}$-*co*-VG$_{18}$)	18.2	14	lactide	36.9	1.11	49
P19	P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$)	19.4	9	4MCL	31.9	1.40	−60
P20	P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$)	19.4	9	4MCL	33.3	1.79	−58
		Demethylation with BBr_3					
P21	P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$)	19.4	9		20.9	1.09	93

[a] %VG determined by NMR.
[b] SEC (eluent THF, PS calibration).
[c] DSC (see Figures S 24–26, S33).

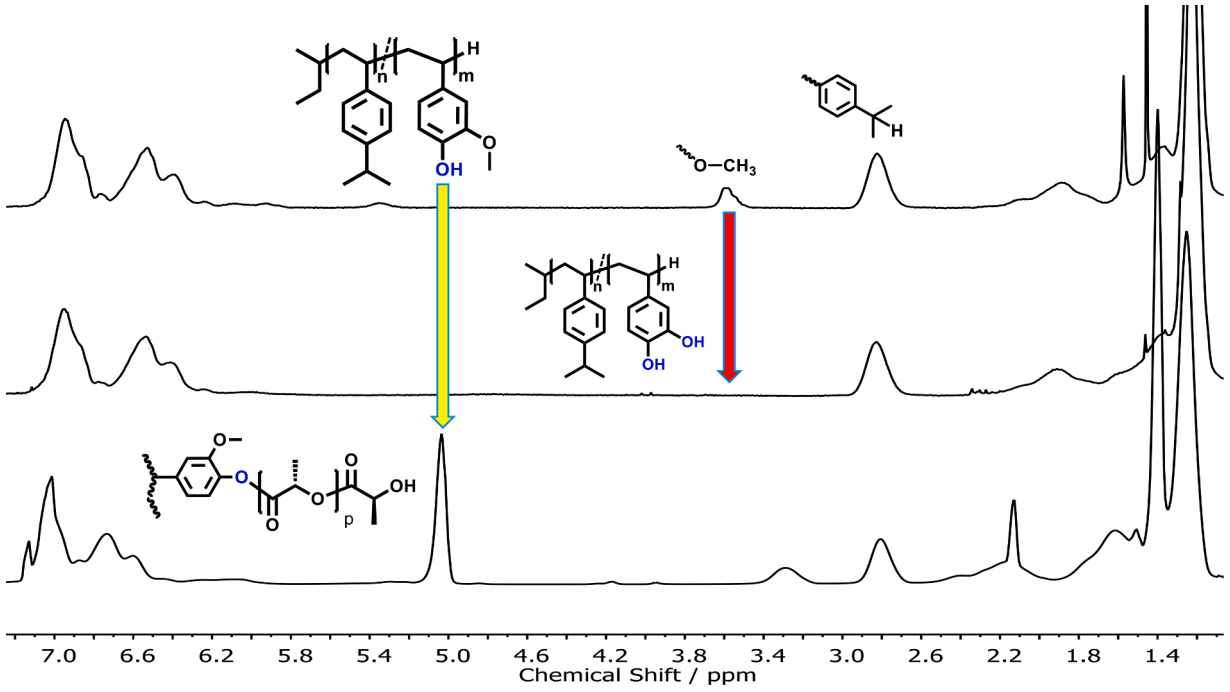


Fig. 4. Deprotection, demethylation and graft copolymers of VG. Top: ^{1}H NMR spectrum of P(4-^{i}PrS$_{119}$-*co*-VG$_{12}$) (400 MHz, C*D*Cl$_3$, 25 °C), middle: P21, P(4-^{i}PrS$_{119}$-*co*-VC$_{12}$) (400 MHz, C*D*Cl$_3$, 25 °C), bottom: P19, P(4-^{i}PrS$_{109}$-*co*-VG$_{18}$)-*g*-P(L-lactide) (400 MHz, toluene-d_8, 25 °C).

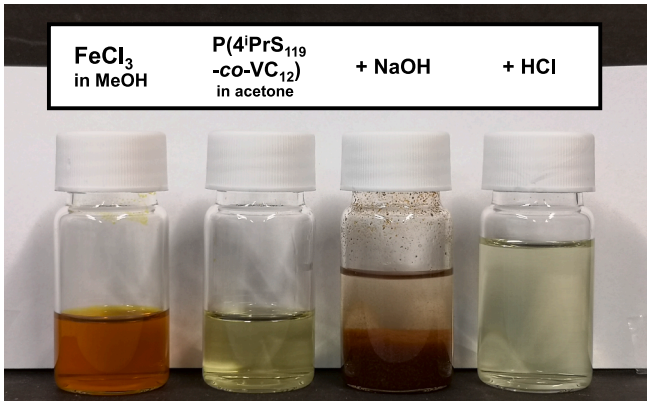


Fig. 5. Complexation properties of P(4-^{i}PrS-*co*-VC) in alkaline and acidic solution.

and narrow molecular weight distributions. The removal of acetal and silyl protective groups was accomplished by treatment under different acidic conditions to generate multi-hydroxyl-functional polystyrenes. These polymers were used as macroinitiators for the synthesis of graft copolymers of L-lactide and 4-methyl-ε-caprolactone *via* ring-opening polymerization. Furthermore, demethylation was successfully demonstrated, resulting in copolymers with catechol functionalities without molecular weight distribution broadening. In addition, well-defined copolymers of 4-^{i}PrS and VC containing catechol moieties can be applied as complexing agents and surface coatings with improved biodegradability.

CRediT authorship contribution statement

Christoph Hahn: Writing – original draft, Visualization, Validation, Methodology, Data curation, Conceptualization. **Sebastian Becker:** Investigation, Formal analysis, Data curation. **Axel H.E. Müller:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Holger Frey:** Writing – review & editing, Writing – original draft, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary material

Supplementary material to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2024.113004.

References

[1] Y. Zhu, C. Romain, C.K. Williams, Sustainable polymers from renewable resources, Nature 540 (7633) (2016) 354–362, https://doi.org/10.1038/nature21001.

[2] K. Satoh, Controlled/living polymerization of renewable vinyl monomers into bio-based polymers, Polym. J. 47 (8) (2015) 527–536, https://doi.org/10.1038/pj.2015.31.

[3] A. Lendlein, B.F. Pierce, L. Ambrosio, D. Grijpma, Advanced functional polymers for medicine: multifunctional biomaterials, Acta Biomater. 8 (12) (2012) 4199, https://doi.org/10.1016/j.actbio.2012.09.036.

[4] D. Hofmann, M. Entrialgo-Castaño, K. Kratz, A. Lendlein, Knowledge-based approach towards hydrolytic degradation of polymer-based biomaterials, Adv. Mater. 21 (32–33) (2009) 3237–3245, https://doi.org/10.1002/adma.200802213.

[5] M. Ulbricht, Advanced functional polymer membranes, Polymer 47 (7) (2006) 2217–2262, https://doi.org/10.1016/j.polymer.2006.01.084.

[6] F. Aeschelmann, M. Carus, Biobased Building Blocks and Polymers in the world: capacities, production, and applications-status quo and trends towards 2020, Ind. Biotechnol. 11 (3) (2015) 154–159, https://doi.org/10.1089/ind.2015.28999.fae.

[7] C.T. Black, K.W. Guarini, K.R. Milkove, S.M. Baker, T.P. Russell, M.T. Tuominen, Integration of self-assembled diblock copolymers for semiconductor capacitor fabrication, Appl. Phys. Lett. 79 (3) (2001) 409–411, https://doi.org/10.1063/1.1383805.

[8] C.T. Black, K.W. Guarini, Y. Zhang, H. Kim, J. Benedict, E. Sikorski, I.V. Babich, K. R. Milkove, High-capacity, self-assembled metal–oxide–semiconductor decoupling capacitors, IEEE Electron. Device Lett. 25 (9) (2004) 622–624, https://doi.org/10.1109/LED.2004.834637.

[9] A. Requardt, Walter Bock (1895–1948) und die Erfindung des Buna, Jahrbuch Des Kölnischen Geschichtsvereins 82–83 (1) (2015) 291–333, https://doi.org/10.7788/jbkgv-2015-0109.

[10] Walter Bock, E. T. Polymerization product of butadiene-1.3 hydrocarbons and process of making same:US1898522A.

[11] Walter Bock, E. T. Artificial rubber: US1826846A.

[12] K. Knoll, N. Nießner, Styrolux + and styroflex + - from transparent high impact polystyrene to new thermoplastic elastomers: syntheses, applications and blends with other styrene based polymers, Macromol. Symp. 132 (1) (1998) 231–243, https://doi.org/10.1002/masy.19981320122.

[13] A. Hirao, S. Kubota, T. Sueyoshi, K. Sugiyama, Living anionic polymerization of functionalized monomers, 2. anionic polymerization of p-alkenylstyrene derivatives, Macromol. Chem. Phys. 202 (7) (2001) 1044–1052, https://doi.org/10.1002/1521-3935(20010401)202:7<1044:AID-MACP1044>3.0.CO;2-T.

[14] A. Hirao, S. Loykulnant, T. Ishizone, Recent advance in living anionic polymerization of functionalized styrene derivatives, Prog. Polym. Sci. 27 (8) (2002) 1399–1471, https://doi.org/10.1016/S0079-6700(02)00016-3.

[15] T. Ishizone, R. Kato, Y. Ishino, A. Hirao, S. Nakahama, Protection and polymerization of functional monomers. 15. Anionic living polymerizations of 2-(3-vinylphenyl)-1,3-dioxolane and related monomers, Macromolecules 24 (7) (1991) 1449–1454, https://doi.org/10.1021/ma00007a002.

[16] K. Se, O. Watanabe, Y. Isono, T. Fujimoto, Synthesis and characterization of model block-graft copolymers via anionic polymerization: Introduction of poly(isoprene) and poly(ethylene oxide) as graft chains, Makromol. Chem. Macromol. Symp. 25 (1) (1989) 249–261, https://doi.org/10.1002/masy.19890250123.

[17] T. Ishizone, K. Okamoto, A. Hirao, S. Nakahama, Protection and Polymerization of Functional Monomers. 29. Syntheses of Well-Defined Poly[(4-vinylphenyl)acetic acid], Poly[3-(4-vinylphenyl)propionic acid], and Poly(3-vinylbenzoic acid) by Means of Anionic Living Polymerizations of Protected Monomers Bearing Bicyclic Ortho Ester Moieties, Macromolecules 32 (5) (1999) 1453–1462, https://doi.org/10.1021/ma981492r.

[18] H. Mori, A. Hirao, S. Nakahama, Protection and polymerization of functional monomers. 21. Anionic living polymerization of (2,2-dimethyl-1,3-dioxolan-4-yl) methyl methacrylate, Macromolecules 27 (1) (1994) 35–39, https://doi.org/10.1021/ma00079a006.

[19] M. Winnacker, J. Sag, Sustainable terpene-based polyamides via anionic polymerization of a pinene-derived lactam, Chem. Comm. 54 (7) (2018) 841–844, https://doi.org/10.1039/C7CC08266E.

[20] M.R. Thomsett, J.C. Moore, A. Buchard, R.A. Stockman, S.M. Howdle, New renewably-sourced polyesters from limonene-derived monomers, Green Chem. 21 (1) (2019) 149–156, https://doi.org/10.1039/C8GC02957A.

[21] P.A. Wilbon, F. Chu, C. Tang, Progress in renewable polymers from natural terpenes, terpenoids, and rosin, Macromol. Rapid Comm. 34 (1) (2013) 8–37, https://doi.org/10.1002/marc.201200513.

[22] Schlaad, H., Ed. Bio-synthetic Polymer Conjugates Adv. Polym. Sci., Springer Berlin Heidelberg, 2013 10.1007/978-3-642-34350-6.

[23] Zhao, J.; Schlaad, H. Synthesis of Terpene-Based Polymers. In *Bio-synthetic Polymer Conjugates*; Schlaad, H., Ed.; Advances in Polymer Science; Springer Berlin Heidelberg, 2013; pp 151–190. DOI: 10.1007/12_2012_166.

[24] B. Erickson, Nelson, P. Winters, Perspective on opportunities in industrial biotechnology in renewable chemicals, Biotechnol. J. 7 (2) (2012) 176–185, https://doi.org/10.1002/biot.201100069.

[25] W. Schutyser, T. Renders, S. van den Bosch, S.-F. Koelewijn, G.T. Beckham, B. F. Sels, Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading, Chem. Soc. Rev. 47 (3) (2018) 852–908, https://doi.org/10.1039/C7CS00566K.

[26] A. Gandini, The irruption of polymers from renewable resources on the scene of macromolecular science and technology, Green Chem. 13 (5) (2011) 1061, https://doi.org/10.1039/C0GC00789G.

[27] M. Zirbes, L.L. Quadri, M. Breiner, A. Stenglein, A. Bomm, W. Schade, S. R. Waldvogel, High-temperature electrolysis of kraft lignin for selective vanillin formation, ACS Susta. Chem. Eng. 8 (19) (2020) 7300–7307, https://doi.org/10.1021/acssuschemeng.0c00162.

[28] R. Rinaldi, R. Jastrzebski, M.T. Clough, J. Ralph, M. Kennema, P.C.A. Bruijnincx, B. M. Weckhuysen, Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis, Angew. Chem. Int. Ed. 55 (29) (2016) 8164–8215, https://doi.org/10.1002/anie.201510351.

[29] P. Ferrini, R. Rinaldi, Catalytic biorefining of plant biomass to non-pyrolytic lignin bio-oil and carbohydrates through hydrogen transfer reactions, Angew. Chem. 126 (33) (2014) 8778–8783, https://doi.org/10.1002/ange.201403747.

[30] J.H. Lora, W.G. Glasser, Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials, J. Polym. Environ. 10 (1/2) (2002) 39–48, https://doi.org/10.1023/A:1021070006895.

[31] Lignin Filler for Tires. *Chem. Eng. News* 1957 *35* 22 28–32. DOI: 10.1021/cen-v035n022.p028a.

[32] Z. Kramárová, P. Alexy, I. Chodák, E. Špirk, I. Hudec, B. Košíková, A. Gregorová, P. Šúri, J. Feranc, P. Bugaj, M. Ďuračka, Biopolymers as fillers for rubber blends, Polym. Adv. Technol. 18 (2) (2007) 135–140, https://doi.org/10.1002/pat.803.

[33] *Waste Materials Used in Concrete Manufacturing*; Elsevier, 1996.

[34] A.K. Mullick, Use of lignin-based products in concrete, in: Waste Materials Used in Concrete Manufacturing, Elsevier, 1996, pp. 352–429, https://doi.org/10.1016/B978-081551393-3.50010-7.

[35] Y. Xu, L. Yuan, Z. Wang, P.A. Wilbon, C. Wang, F. Chu, C. Tang, Lignin and soy oil-derived polymeric biocomposites by "grafting from" RAFT polymerization, Green Chem. 18 (18) (2016) 4974–4981, https://doi.org/10.1039/C6GC00859C.

[36] R.J. Li, J. Gutierrez, Y.-L. Chung, C.W. Frank, S.L. Billington, E.S. Sattely, A lignin-epoxy resin derived from biomass as an alternative to formaldehyde-based wood adhesives, Green Chem. 20 (7) (2018) 1459–1466, https://doi.org/10.1039/C7GC03026F.

[37] J.F. Stanzione, P.A. Giangiulio, J.M. Sadler, J.J. La Scala, R.P. Wool, Lignin-based bio-oil mimic as biobased resin for composite applications, ACS Susta. Chem. Eng. 1 (4) (2013) 419–426, https://doi.org/10.1021/sc3001492.

[38] J.T. Sutton, K. Rajan, D.P. Harper, S.C. Chmely, Lignin-containing photoactive resins for 3D printing by stereolithography, ACS Appl. Mater. & Interf. 10 (42) (2018) 36456–36463, https://doi.org/10.1021/acsami.8b13031.

[39] M. Alinejad, C. Henry, S. Nikafshar, A. Gondaliya, S. Bagheri, N. Chen, S.K. Singh, D.B. Hodge, M. Nejad, Lignin-based polyurethanes: opportunities for bio-based foams, elastomers, coatings and adhesives, Polymers 11 (7) (2019), https://doi.org/10.3390/polym11071202.

[40] Y. Xu, J. Zhao, Q. Gan, W. Ying, Z. Hu, F. Tang, W. Luo, Y. Luo, Z. Jian, D. Gong, Synthesis and properties investigation of hydroxyl functionalized polyisoprene prepared by cobalt catalyzed co-polymerization of isoprene and hydroxylmyrcene, Polym. Chem. 11 (12) (2020) 2034–2043, https://doi.org/10.1039/C9PY01808E.

[41] A. Gossauer, Struktur und Reaktivität der Biomoleküle: Eine Einführung in die organische Chemie, Wiley-VCH, 2006.

[42] Die Chemie der Pflanzenzellwand:Ein Beitrag zur Morphologie, Physik, Chemie und Technologie der Cellulose und ihrer Begleiter; Springer Berlin Heidelberg, 2013.

[43] A.U. Buranov, G. Mazza, Extraction and purification of ferulic acid from flax shives, wheat and corn bran by alkaline hydrolysis and pressurised solvents, Food Chem. 115 (4) (2009) 1542–1548, https://doi.org/10.1016/j.foodchem.2009.01.059.

[44] J. Overhage, A. Steinbüchel, H. Priefert, Biotransformation of eugenol to ferulic acid by a recombinant strain of ralstonia eutropha H16, Appl. Environ. Microbiol. 68 (9) (2002) 4315–4321, https://doi.org/10.1128/AEM.68.9.4315-4321.2002.

[45] R. Plaggenborg, J. Overhage, A. Loos, J.A.C. Archer, P. Lessard, A.J. Sinskey, A. Steinbüchel, H. Priefert, Potential of rhodococcus strains for biotechnological vanillin production from ferulic acid and eugenol, Appl. Microbiol. Biotechnol. (2006) 745–755, https://doi.org/10.1007/s00253-005-0302-5.

[46] M. Berthelot, Sur les caractères de la benzine et du styrolène, "Sur les caractères de la benzine et du styrolène, comparés avec ceux des autres carbures d'hydrogène", Bulletin De La Société Chimique De Paris 1867 (2) (1867) 289–298.

[47] Fittig, R.; Petri, C. Untersuchungen über die ungesättigten Säuren. I. Weitere Beiträge zur Kenntnifs der Fumarsäure und Maleïnsäure. *Justus Liebigs Ann. Chem.* **1879**, *195* (1-2), 56–179. DOI: 10.1002/jlac.18791950103.

[48] E. Kopp, Recherches sur l'acide cinnamique et sur le cinnamèn, Comptes. Rendus. 1845 (21) (1845) 1376–1380.

[49] P.J. Deuss, M. Scott, F. Tran, N.J. Westwood, J.G. Vries de, K. Barta, Aromatic monomers by in situ conversion of reactive intermediates in the acid-catalyzed depolymerization of lignin, J. Am. Chem. Soc. 137 (23) (2015) 7456–7467, https://doi.org/10.1021/jacs.5b03693.

[50] P. Tiedemann von, E. Kersten, J. Ewald, T. Linder, C. Fuchs, M. Wagner, H. Frey, A nonconventional approach toward multihydroxy functional polystyrenes relying on a simple grignard reagent, Macromolecules 53 (9) (2020) 3370–3379, https://doi.org/10.1021/acs.macromol.0c00541.
[51] D. Leibig, A.H.E. Müller, H. Frey, Anionic polymerization of vinylcatechol derivatives: reversal of the monomer gradient directed by the position of the catechol moiety in the copolymerization with styrene, Macromolecules 49 (13) (2016) 4792–4801, https://doi.org/10.1021/acs.macromol.6b00831.
[52] H. Takeshima, K. Satoh, M. Kamigaito, Bio-based functional styrene monomers derived from naturally occurring ferulic acid for poly(vinylcatechol) and poly (vinylguaiacol) via controlled radical polymerization, Macromolecules 50 (11) (2017) 4206–4216, https://doi.org/10.1021/acs.macromol.7b00970.
[53] H. Takeshima, K. Satoh, M. Kamigaito, Scalable synthesis of bio-based functional styrene: protected vinyl catechol from caffeic acid and controlled radical and anionic polymerizations thereof, ACS Susta. Chem. Eng. 6 (11) (2018) 13681–13686, https://doi.org/10.1021/acssuschemeng.8b04400.
[54] H. Hatakeyama, E. Hayashi, T. Haraguchi, Biodegradation of poly(3-methoxy-4-hydroxy styrene), Polymer 18 (8) (1977) 759–763, https://doi.org/10.1016/0032-3861(77)90177-X.
[55] X. Zhang, M.C.D. Carter, M.E. Belowich, G. Wan, M. Crimmins, K.B. Laughlin, R. C. Even, T.H. Kalantar, Catechol-functionalized latex polymers display improved adhesion to low-surface-energy thermoplastic polyolefin substrates, ACS Appl. Polym. Mater. 1 (6) (2019) 1317–1325, https://doi.org/10.1021/acsapm.9b00130.
[56] Y. Miao, F. Xie, J. Cen, F. Zhou, X. Tao, J. Luo, G. Han, X. Kong, X. Yang, J. Sun, J. Ling, Fe^{3+}@polyDOPA-b-polysarcosine, a T1-weighted MRI contrast agent via controlled NTA polymerization, ACS Macro Lett. 7 (6) (2018) 693–698, https://doi.org/10.1021/acsmacrolett.8b00287.
[57] E.A. Pillar, R.C. Camm, M.I. Guzman, Catechol oxidation by ozone and hydroxyl radicals at the air-water interface, Environ. Sci. Tech. 48 (24) (2014) 14352–14360, https://doi.org/10.1021/es504094x.
[58] J.H. Waite, Mussel power, Nat. Mater. 7 (1) (2008) 8–9, https://doi.org/10.1038/nmat2087.
[59] L.Q. Xu, D. Pranantyo, K.-G. Neoh, E.-T. Kang, S.-L.-M. Teo, G.D. Fu, Synthesis of catechol and zwitterion-bifunctionalized poly(ethylene glycol) for the construction of antifouling surfaces, Polym. Chem. 7 (2) (2016) 493–501, https://doi.org/10.1039/C5PY01234A.
[60] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface chemistry for multifunctional coatings, Science 318 (5849) (2007) 426–430, https://doi.org/10.1126/science.1147241.
[61] A. Charlot, V. Sciannaméa, S. Lenoir, E. Faure, R. Jérôme, C. Jérôme, C. van de Weerdt, J. Martial, C. Archambeau, N. Willet, A.-S. Duwez, C.-A. Fustin, C. Detrembleur, All-in-one strategy for the fabrication of antimicrobial biomimetic films on stainless steel, J. Mater. Chem. 19 (24) (2009) 4117, https://doi.org/10.1039/B820832H.
[62] N. Lüdecke, M. Bekir, S. Eickelmann, M. Hartlieb, H. Schlaad, Toward protein-repellent surface coatings from catechol-containing cationic poly(2-ethyl-2-oxazoline), ACS Appl. Mater. & Interf. 15 (15) (2023) 19582–19592, https://doi.org/10.1021/acsami.2c22518.
[63] A. Hirao, R. Goseki, T. Ishizone, Advances in living anionic polymerization: from functional monomers, polymerization systems, to macromolecular architectures, Macromolecules 47 (6) (2014) 1883–1905, https://doi.org/10.1021/ma401175m.
[64] A. Hirao, K. Yamaguchi, K. Takenaka, K. Suzuki, S. Nakahama, N. Yamazaki, Polymerization of monomers containing functional groups protected by trialkylsilyl groups, Makromol. Chem., Rapid Commun. 3 (12) (1982) 941–946, https://doi.org/10.1002/marc.1982.030031218.
[65] S. Nakahama, A. Hirao, Protection and polymerization of functional monomers: anionic living polymerization of protected monomers, Prog. Polym. Sci. 15 (2) (1990) 299–335, https://doi.org/10.1016/0079-6700(90)90031-U.
[66] A. Lancelot, A.A. Putnam-Neeb, S.L. Huntington, J.M. Garcia-Rodriguez, N. Naren, C.L. Atencio-Martinez, J.J. Wilker, Increasing the scale and decreasing the cost of making a catechol-containing adhesive polymer, Macromolecules (2023), https://doi.org/10.1021/acs.macromol.2c02499.
[67] D.P. Sweat, X. Yu, M. Kim, P. Gopalan, Synthesis of poly(4-hydroxystyrene)-based block copolymers containing acid-sensitive blocks by living anionic polymerization, J. Polym. Sci. Part A Polym. Chem. 52 (10) (2014) 1458–1468, https://doi.org/10.1002/pola.27138.
[68] A. Natalello, C. Tonhauser, H. Frey, Anionic polymerization of para -(1-Ethoxy ethoxy)styrene: rapid access to poly(p -hydroxystyrene) copolymer architectures, ACS Macro Lett. 2 (5) (2013) 409–413, https://doi.org/10.1021/mz400147z.
[69] C. Schüll, H. Frey, Controlled Synthesis of Linear Polymers with Highly Branched Side Chains by "Hypergrafting": Poly(4-hydroxy styrene)- graft -hyperbranched Polyglycerol, ACS Macro Lett. 1 (4) (2012) 461–464, https://doi.org/10.1021/mz200250s.
[70] A. Wolf, A. Walther, A.H.E. Müller, Janus triad: three types of nonspherical, nanoscale janus particles from one single triblock terpolymer, Macromolecules 44 (23) (2011) 9221–9229, https://doi.org/10.1021/ma2020408.
[71] D.A. Conlon, J.V. Crivello, J.L. Lee, M.J. O'Brien, The synthesis, characterization, and deblocking of poly(4-tert-butoxystyrene) and poly(4-tert-butoxy-.alpha.-methylstyrene), Macromolecules 22 (2) (1989) 509–516, https://doi.org/10.1021/ma00192a002.
[72] Koltzenburg, S.; Maskos, M.; Nuyken, O. *Polymere: Synthese, Eigenschaften und Anwendungen*; Springer Berlin Heidelberg, 2014. DOI: 10.1007/978-3-642-34773-3.
[73] P. Tiedemann von, J. Blankenburg, K. Maciol, T. Johann, A.H.E. Müller, H. Frey, Copolymerization of Isoprene with p -Alkylstyrene monomers: disparate reactivity ratios and the shape of the gradient, Macromolecules 52 (3) (2019) 796–806, https://doi.org/10.1021/acs.macromol.8b02280.
[74] J. Zhao, G. Mountrichas, G. Zhang, S. Pispas, Thermoresponsive core−shell brush copolymers with poly(propylene oxide)- block -poly(ethylene oxide) side chains via a "Grafting from" technique, Macromolecules 43 (4) (2010) 1771–1777, https://doi.org/10.1021/ma902590w.