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### Abstract

Approximately 50 million tons of lignin are currently produced annually as a by-product of the pulp- and paper industry, and this amount is likely to double in the future with the anticipated production of renewable fuels and chemicals from lignocellulosic biomass, as a sustainable alternative to petroleum. The latter process can be expedited by valorizing lignin, which entails making products from lignin that generate additional revenues for biorefineries so that the production of biofuels becomes more competitive with conventional gasoline. Industrially produced lignin is considered a low-value material that is used as a boiler fuel to generate heat and electricity, and as an ingredient of adhesives, cement, and drilling fluids for underwater oil wells. The aromatic nature of lignin, its ability to participate in radical-mediated cross-linking reactions, the many functional groups available for derivatization or chemical reactions, and its amenability to existing procedures for making thermoplastics, make it attractive as an additive to polymers to enhance UV-tolerance and/or other physico-chemical properties. Lignin can also be used as the basis for various nanomaterials, either per se or in combination with other polymers. This review summarizes recent developments in the synthesis of lignin-containing polymers and nanomaterials, whereby inherent variation in lignin subunit composition and structure, as a function of plant species and lignin extraction method, offer unique opportunities for fine-tuning material properties (e.g., tensile strength, hardness, elasticity) to match specific applications.

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## **Lignin-based polymers and nanomaterials**

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## **Abstract**

Approximately 50 million tons of lignin are currently produced annually as a by-product of the pulp- and paper industry, and this amount is likely to double in the future with the anticipated production of renewable fuels and chemicals from lignocellulosic biomass, as a sustainable alternative to petroleum. The latter process can be expedited by valorizing lignin, which entails making products from lignin that generate additional revenues for biorefineries so that the production of biofuels becomes more competitive with conventional gasoline. Industrially produced lignin is considered a low-value material that is used as a boiler fuel to generate heat and electricity, and as an ingredient of adhesives, cement, and drilling fluids for underwater oil wells. The aromatic nature of lignin, its ability to participate in radical-mediated cross-linking reactions, the many functional groups available for derivatization or chemical reactions, and its amenability to existing procedures for making thermoplastics, make it attractive as an additive to polymers to enhance UV-tolerance and/or other physico-chemical properties. Lignin can also be used as the basis for various nanomaterials, either *per se* or in combination with other polymers. This review summarizes recent developments in the synthesis of lignin-containing polymers and nanomaterials, whereby inherent variation in lignin subunit composition and structure, as a function of plant species and lignin extraction method, offer unique opportunities for fine-tuning material properties (e.g., tensile strength, hardness, elasticity) to match specific applications.

**Keywords:** biomass – co-polymer – encapsulation – graft – macroinitiator – valorization

### **Strategies for valorizing lignin**

Approximately 50 million tons of lignin are currently produced annually as a by-product of the pulp- and paper industry. The majority of this lignin (>95%) is used as a boiler fuel to generate heat and electricity [1], while a little over 1 million tons are used for the production of various products, including phenol-formaldehyde resins used as adhesives, additives to cement to reduce viscosity and improve reduce curing time, and as part of drilling fluids for underwater oil wells [2,3]. Meeting the biofuel production targets of the U.S. Energy Independence and Security Act of 2007 will require an increase in the number of commercial biorefineries that convert lignocellulosic biomass to renewable fuels and chemicals. This would result in an estimated production of 62 million tons of lignin per year in the United States alone [3]. Commercial production of cellulosic biofuels is lagging behind the production targets, however, in part because their price is not competitive with that of gasoline [4,5]. This gap can potentially be closed by valorizing lignin [3,5]. As the primary renewable source of aromatic molecules, lignin offers prospects for a number of other uses. This includes the production of aromatic molecules such as the industrial chemicals referred to as BTX (benzene, toluene, xylene), and drop-in transportation fuels compatible with existing internal combustion engines [6,7]. Both approaches currently require deconstruction of the lignin at high temperature, high pressure, and in the presence of catalysts [8,9], and while substantial progress has been made in recent years, additional improvements to the process are necessary before yields are sufficiently high to be economically feasible.

Additional strategies for valorizing lignin are being explored, as summarized in several recent review articles [3,10–14]. This review focuses on recent developments in lignin-based polymers and nanomaterials whose properties depend in part on the polymeric structure of lignin, and that are synthesized by exploiting lignin's inherent reactivity, specifically its ability to participate in radical-mediated cross-linking reactions and the abundance of reactive hydroxyl, carbonyl, and carboxyl moieties. These applications not only represent uses of lignin that can generate additional revenue streams but may also lead to materials with unique or enhanced properties that are difficult to attain via other means.

### **Industrial lignin is inherently variable in its composition**

When considering the use of industrial lignin for the production of high-value materials, it is important to realize that there is considerable variation in the nature of this lignin. In addition to the inherent natural variation in lignin subunit composition and structure among plant species, tissue of origin and developmental stage [15], the process by which the lignin is extracted from the biomass, and the additional chemicals added for recovery, further add to the chemical diversity, and affect molecular weight, polydispersity (the molecular weight distribution), solubility, reactivity, and, ultimately, both the market value of the lignin and the physico-chemical properties of materials derived from the lignin. **Box 1** provides a brief summary of the main sources of industrial lignin and includes references to more comprehensive descriptions. While on the one hand the variation in sources of industrial lignin complicates the development and optimization of new processes, it can also be exploited by using select sources of lignin that result in the desired material properties for specific applications.

### **Lignin-containing co-polymers with enhanced material properties**

It is difficult to imagine modern life without the use of plastics, most of which are derived from petroleum. Concerns over the depletion of worldwide petroleum reserves, the greenhouse emissions associated with its use, and the negative impact of plastic waste on terrestrial and marine environments [16,17] have spurred an interest in the use of biodegradable renewable materials that can be produced sustainably, with polymers derived from cellulose, starch, chitin and lactic acid leading the way [18,19].

The easiest way of producing lignin-based materials is by blending lignin with commercial off-the-shelf (COTS) polymers. While addition of lignin was shown to increase thermal and mechanical properties of polymer blends [20], a consistent drawback of lignin-polymer blending was lignin's immiscibility with most COTS polymers, limiting the range of applications. Miscibility could be improved via hydrogen bonding [21], but it was the ability to create block co-polymers in which COTS polymers were grafted onto lignin via covalent bonds that enabled expansion of the kinds of co-polymers that could be produced.

Radical-mediated lignin-*graft* co-polymerization with styrene, induced chemically and by radiation was first described some 50 years ago [22–24], followed by co-polymerization of lignin and acrylamide [25]. While revolutionary from the perspective of polymer science, these procedures were time-consuming and allowed little control over polymerization. This changed with the application of two polymerization methods, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT). ATRP often utilizes an alkyl halide initiator which becomes radicalized in the presence of a transition metal catalyst to facilitate polymerization of monomers [26,27], while RAFT polymerization proceeds by radicalization from the addition of a radical-generating species [28,29]. With these new polymerization methods, propagation of monomers into polymer chains is strictly determined by the reaction conditions. Two modes of grafting are employed: 'grafting from', whereby lignin serves as a macroinitiator and the chain elongation occurs on the lignin core, and 'grafting to', whereby completed polymers are grafted onto the lignin core.

Kim and Kadla [30] were the first to synthesize Kraft hardwood lignin-*graft*-poly(*N*-isopropylacrylamide) via ATRP. The macroinitiator for the polymerization was synthesized by selectively reacting phenolic hydroxyl groups with bromoisobutyryl bromide, which then yielded a reactive site for the addition of *N*-isopropylacrylamide (NIPAM) (**Figure 1**). By varying the reaction conditions, the degree of polymerization could be varied, resulting in tunable polymer properties (miscibility in water, thermal decomposition temperature). The polymer precipitated in water above 32°C, but became soluble below 32°C, as observed previously with pristine poly(NIPAM) [31]. This study demonstrated that modified industrial lignin could perform as an ATRP macroinitiator and that lignin co-polymerization was not limited by miscibility as it was with lignin-polymer blends.

The difference in mechanical and thermal material properties between lignin-poly(ethylene glycol) and lignin-poly(methyl methacrylate) blends and their lignin-*graft*-polymer equivalents generated using ATRP with Kraft lignin-based macroinitiators was elegantly

demonstrated by Hilburg *et al* [32]. Lignin-polymer blends displayed higher glass transition temperatures ( $T_g$ ), but similar mechanical properties to their parent homopolymers. In contrast, lignin-*graft* co-polymers displayed nearly ten-fold greater fracture resistance (toughness), two-fold greater elongation percentage, and significantly higher  $T_g$  compared to the blends. To optimize applications of lignin-*graft*-poly(methyl methacrylate) (PMMA), Shah *et al* [33] used it as an additive filler to PMMA in 0.5%, 1%, and 2% concentrations. Their results indicated a filler concentration of 1% provided thermal and mechanical properties exceeding those of 0.5% and 2% blends, and far-exceeding those of pristine PMMA. However, perhaps more importantly than the results themselves, these studies emphasized the ease of using industrial lignin as a ‘grafting-from core’ via ATRP.

Two alternative polymerization methods that can be used to synthesize lignin co-polymers are ring-opening polymerization (ROP) and click chemistry. As the name implies, ROP involves a polymerization reaction in which a cyclic molecule is opened, which upon reaction creates a reactive group that can react with the next cyclic molecule [35]. An example of ROP involving lignin is the synthesis of lignin-*graft*-poly(lactic acid), which was blended with poly(L-lactide) (PLLA) and electrospun into nanofibers. The nanofibers displayed antioxidant activity, likely resulting from the addition of lignin, and were biologically compatible with mammalian cell growth [34]. Click chemistry refers to an efficient chemical reaction in mild solvents between two molecules containing different reactive moieties [36] (**Figure 1**). Han *et al.* [37] synthesized a variety of lignin-based co-polymers via solvent-free, copper-free Huisgen azide-alkyne cycloaddition, a form of thermal click chemistry (**Figure 1**). These authors demonstrated the ability to crosslink lignin efficiently with poly(ethylene glycol) (PEG), poly( $\epsilon$ -caprolactone) (PCL), and poly(lactic acid) (PLA), all of which have current applications in biomedical settings [38–40], thus offering new opportunities for valorizing lignin.

### **Lignin in polymer nanocomposites**

Polymer nanocomposites refer to polymers containing nanoparticle components that enhance the material properties of the polymer [41]. For example, the addition of inorganic nano-scale clay particles in organic polymers such as nylon-6 resulted in increased modulus and heat deflection temperature and better flame-retardant properties [42], which is relevant in many applications, including automobiles. Optimal performance hinges on the ability to uniformly disperse the nano-clay (termed exfoliation) [43], but this is challenging due to its hydrophilic nature, and typically requires a cationic surfactant and use of mini-emulsion polymerization [44]. Jairam *et al* [45] isolated lignin from the residues of a biorefinery that processed sugarcane bagasse, and chemically modified the lignin with quarternary amine groups to create a cationic surfactant able to incorporate nano-clay into polystyrene co-butyl acrylate latex. They subsequently demonstrated that the presence of lignin in this nanocomposite substantially enhanced tolerance to high levels of UV-radiation that would make these polymers suitable for use on Mars or outer space [46].

An entirely different clay-containing nanocomposite derived from lignin was synthesized by Parsell *et al* [47]. Rather than using isolated lignin as the basis of the nanocomposite,

they used phenolic monomers obtained by subjecting biomass to hydrodeoxygenation with a Zn/Pd catalyst in the presence of hydrogen to generate dihydroeugenol (DHE) as the major product [47]. Reactive epoxides were formed after demethylation of DHE with HBr and reaction with epichlorohydrin. Polymerization in the presence of nano-clay and diethylenetriamine resulted in a nanocomposite where mechanical properties improved as the proportion of clay (up to 12%) increased. Compared to the use of lignin *per se*, a clear benefit of the use of defined monomers for the synthesis of phenolic co-polymers is the ability to exert stricter control over the structure of the final product. The process used for monomer generation is, however, energy intensive and the current maximum product yield is reported as 54%. While high for a catalytic conversion process, a substantial portion of the lignin is left unused.

A similar approach is also being explored for the synthesis of lignin-derived methacrylate co-polymers via RAFT. A large collection of lignin-based methacrylate monomers were generated as proof of concept for valorization of pyrolysis oils [48–52]. With variation in bio-oil constituents as a function of biomass source, the intent was to provide a foundation for controlled synthesis of tunable co-polymers. For example, syringyl methacrylate was polymerized to poly(syringyl methacrylate) with a  $T_g$  above 200°C, a level unmatched by any lignin-*graft*-polymer to date [52]. Moreover, the  $T_g$  of poly(syringyl methacrylate) is tunable based on the degree of polymerization, thus can be tailored towards commercial thermoplastic applications with strict temperature requirements.

### **Lignin in 3D printing resins**

Fused deposition modeling (FDM) or 3D printing is a melt extrusion method to create three-dimensional objects with the help of a nozzle that adds layers of a thermoplast polymer according to a specific design. Successful resins for 3D printing need to be able to withstand high shear forces, have suitable rheological properties, need to set quickly once deposited, and need to adhere strongly to the previously deposited layer. The most common thermoplast used in 3D printing is the petroleum-based acrylonitrile butadiene styrene (ABS). Nguyen *et al* [53] investigated whether lignin could be used to replace some of the ABS. Substitution of 40% of the ABS with organosolv lignin ( $M_w$  3,000 Da), mixed in a blender, resulted in a brittle polymer. Addition of 10% acrylonitrile butadiene rubber, however, counteracted the negative effect of lignin addition and resulted in a polymer with a five-fold greater tensile strength that was suitable for 3D printing. Interlayer adhesion of the printed materials could be enhanced further by addition of 10% carbon fibers. This application required lignin with a high proportion of syringyl residues; the use of guaiacyl-rich Kraft lignin from softwood resulted in high flow resistance. The use of such a high proportion of lignin in a resin compatible with 3D printing offers exciting opportunities to valorize lignin on a large scale, similar to use of lignin in thermoplastics [52-55] and polyurethane foams [56–58]. In these applications mechanical properties could be fine-tuned by varying the molecular weight of the lignin and the proportion of lignin during co-polymer formation.

### **Lignin-based nanoparticles for use in biomedical applications**

Lignin is also being used in nanotechnology. This is a discipline focusing on particles in the nanometer scale, which tend to have unique physico-chemical properties that make

them attractive for a variety of uses, including electronics, coatings, and medicine. In the latter category, nanotechnology is used for diagnostic and/or therapeutic purposes, for example through ‘smart’ delivery of bio-active agents to specific cells or tissues. This will typically involve a nanocarrier that is guided to its target cells through the addition of ligands. The bio-active agent is either attached to or encapsulated in the nanocarrier [59,60]. Most of this research is still in the proof-of-concept stage and involves cell and tissue culture experiments rather than whole organisms.

Tortora *et al* [61] prepared oil-filled lignin microcapsules (LMCs) of 0.3-1.1  $\mu\text{m}$  in diameter from softwood Kraft lignin using an oil-in-water emulsion at high pH, whereby high-intensity sonication was used to form the LMCs and crosslink the lignin fragments. Following encapsulation of the hydrophobic, fluorescent model drug Coumarin-6 in these LMCs, they showed efficient delivery of the LMCs into Chinese hamster ovary cells (in tissue culture) with low cytotoxicity. Nanocapsules can also be based on a metal-phenolic network (MPN). In these structures, ferric ( $\text{Fe}^{3+}$ ) cations serve to arrange and stabilize lignin fragments. Bartzoka *et al* [62] used a low-power sonication protocol to synthesize lignin MPN nanocapsules (0.4-6  $\mu\text{m}$  in diameter) that exploited Kraft lignin- $\text{Fe}^{3+}$  complexation and lignin’s propensity to participate in  $\pi$ - $\pi$  stacking. These lignin nanocapsules were effective delivery vehicles for Coumarin-6. Tardy *et al* [63] used a different approach to nanocapsule synthesis by using softwood Kraft lignin nanoparticles as scaffold cores around which tannic acid and  $\text{Fe}^{3+}$  created an MPN shell, after which the lignin core was dissolved, leaving behind a hollow MPN nanocapsule with a diameter between 0.3-1.9  $\mu\text{m}$ . While the noted application was towards a Fenton reaction-based detoxification of environmental contaminants, these MNP nanocapsules may also be of interest for delivery of therapeutic molecules. Another application involving the interaction between lignin and metal cations involved silver-doped lignin nanoparticles (40-70 nm in diameter) displaying antimicrobial activity against a range of bacteria [64]. Negatively charged lignin nanoparticles were prepared from Kraft lignin via pH-drop flash precipitation in ethylene glycol. The use of silver ions to eliminate harmful bacteria may become more important as antibiotic resistance continues to increase at an alarming rate [65], and the use of these particles helps reduce the concentration of reactive silver in the environment.

Delivery of therapeutic DNA and RNA shows promise to treat certain types of cancer and genetic disorders resulting from aberrant gene expression [58], and lignin-based nanomaterials are being explored for these applications. Liu *et al* [66] synthesized nanoparticles of 100-200 nm in diameter that were able to bind DNA via electrostatic interactions by grafting (via ATRP) a shell of the cationic poly-(2-dimethylaminoethyl methacrylate) (PDMAEMA) onto a Kraft lignin core. The resulting nanoparticles were able to deliver plasmid DNA into a variety of mammalian cells in tissue culture. The properties of these nanoparticles depended on the chain length of the PDMAEMA: co-polymers with shorter chains displayed lower cytotoxicity, but also lower transfection efficiency.

The preparation of lignin macroinitiators used in the synthesis of lignin-co-polymer nanoparticles was greatly simplified by Lieveonen *et al* [67]. They developed a solvent-exchange dialysis of softwood Kraft lignin dissolved in tetrahydrofuran (THF). As the THF

was slowly replaced by water, nanoparticles were formed that were amenable to cationic surface-charge modification with poly(diallyldimethylammonium chloride) (PDADMAC). Nanoparticles produced by this same process were subsequently chemically and enzymatically-oxidized to enhance stability, dispersion, and applicability towards biomedical applications [68].

Richter *et al* [69] applied a modified solvent exchange technique using lignin flash-precipitated from different solvent-antisolvent mixtures. Kraft lignin dissolved in ethylene glycol was precipitated with nitric acid, and organosolv lignin dissolved in acetone was precipitated with water, both of which provided nanoparticles (45-250 nm in diameter) with surface charges compatible with PDADMAC.

Hollow lignin nanotubes and solid lignin nanorods synthesized inside the pores of a sacrificial aluminum membrane template [70] were shown by Ten *et al* [71] to have affinity for DNA. These DNA-carrying lignin nanotubes can enter HeLa cells (human cells grown in tissue culture) and deliver the DNA. The source of the lignin (plant species and extraction method) affected their elastic properties and subcellular localization within the cells, with nanotubes made from pine lignin isolated with thioglycolic acid able to penetrate the highly restrictive nuclear envelope.

### **Future prospects**

As mentioned in the Introduction and highlighted in the various applications described in this article, the variation in lignin structure, polydispersity and chemical reactivity can be exploited for various applications of lignin-based materials, as illustrated clearly by, for example, superior material properties with syringyl-rich lignin in 3D printing resins [53]. Advances in genetics, biochemistry, and analytical chemistry have resulted in a better understanding of lignin biosynthesis and structure, as well as the ability to manipulate lignin biosynthesis *in planta* through transgenic approaches [72–76]. The anticipated advances in the ability to edit plant genomes with tools like CRISPR/Cas9 [74,75] will enable an even more fine-tuned approach whereby specific amino acids critical for substrate specificity in enzymes involved in lignin biosynthesis [77,78] can be changed. The natural variation in subunit composition, degree of polymerization, and distribution of interunit-bonds, combined with the potential to generate angiosperm lignins essentially composed of a single monomer [79], or of monomers normally present in only trace amounts, such as 5-hydroxyguaiacyl residues [80] and the recently discovered caffeyl residues [81], offers a wide array of starting materials for lignin-based polymers and nanomaterials with tunable properties. Caffeyl lignin, with its intrinsically linear structure, is of particular interest, if (when) it becomes available on an industrial scale as the result of successful plant genetic engineering.

The reduced complexity in lignin structure resulting from genetic engineering approaches is of particular relevance for use in biomedical settings, where regulatory approval from, for example, the U.S. Food and Drug Administration, is contingent upon detailed compositional and structural information. This information is challenging to obtain for lignin, due to its inherent variation in structure. In the meantime, characterization of phenolic co-polymers generated from monomers obtained by pyrolysis of lignin [51] or

catalytic hydrodeoxygenation [46] can serve to define targets for engineering lignin with reduced complexity.

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## **Box 1: Characteristics of the main sources of industrial lignin**

### **Lignin composition as a function of plant species**

Lignin subunit composition varies as a function of plant species. Grasses (sugarcane, sorghum, miscanthus, maize) produce lignin consisting of guaiacyl (G) and syringyl (S) residues, with a small proportion of *p*-hydroxyphenyl (H) residues. Lignin from angiosperm dicots (e.g. deciduous trees, alfalfa) consists of a mixture of G and S residues, whereas softwood lignin (from gymnosperm trees) consists of predominantly guaiacyl (G) residues. Lignin composition can also vary as a function of developmental stage and tissue [14].

### **Kraft lignin**

This type of lignin is the by-product of pulp and paper mills that use the Kraft process (sodium hydrosulfide, sodium hydroxide, high temperature) [83]. Despite being the most widely used pulping process, the large volumes of Kraft lignin are mostly used as boiler fuel. Recovery of sulfur-containing Kraft lignin from the 'black liquor' rich in process chemicals is accomplished by lowering the pH, which causes the lignin to aggregate [83]. An initial patented recovery process was developed by Westvaco [84], followed more recently by the LignoBoost [85,86] and LignoForce [87] processes that enable use of Kraft lignin for other applications, including in co-polymers.

### **Lignosulfonates**

The sulfite process is used to produce pulp and paper, especially from softwood species, and generates a soluble form of lignin that is currently the most abundant source of industrial lignin used in various applications. It can be used in batteries, animal feed, adhesives, and as a dispersing agent to concrete [2,3]. A version of this process was patented by the Norwegian company Borregaard (BALI™: Borregaard Advanced Lignin) and generates the food flavoring compound vanillin as a by-product [88].

### **Organosolv lignin**

Organosolv lignin is extracted from plant biomass with organic solvents at elevated temperature, often in the presence of acid catalysts [89]. Due to the limited use of process chemicals, organosolv lignin is considered a pure and relatively uniformly distributed form of lignin. Several companies produce organosolv lignin on pilot and commercial scale [89]. For example, BioLignin™ is formed following extraction of lignocellulosic biomass in formic and acetic acid at atmospheric pressure [90] and results in a lignin containing formyl and acetyl groups, with a linear structure based on mass spectrometry analyses [91].

### **Lignin extracted with dilute acid or hydrothermal treatments**

Biorefineries that convert lignocellulosic biomass into renewable chemicals or fuels via a biochemical (as opposed to thermochemical) route require a pretreatment to enable cellulolytic enzymes access to cellulose [92]. When lignocellulosic biomass is pretreated at high temperature and pressure (160-210°C, 1-1.5 MPa), either with or without the presence of an acid catalyst (sulfuric acid, phosphoric acid), lignin depolymerizes and is redistributed [93,94], making the biomass more amenable to enzymatic saccharification. Depending on the conditions, condensation reactions may occur that increase the molecular

weight. The lignin is ultimately recovered from the solid residues remaining after fermentation.

### **Alkali lignin**

Lignin can be extracted from biomass because of its solubility in alkaline solutions (typically NaOH) at moderate temperatures (60-120°C). This extraction procedure works especially well for lignin from the biomass of grass species (sugarcane, sorghum, maize, wheat) in biorefineries due to the high extractability of grass lignin in alkaline solutions [95], but is also used to extract lignin from woody species, in which case the lignin is referred to as soda lignin. Constant *et al* [96] conducted a detailed comparison of different industrial lignins, including alkali lignin.

### **Molecular weight of industrial lignin**

The molecular weight ( $M_w$ ) of industrial lignin generally ranges between 1,000 and 5,000 Da as measured by size exclusion chromatography (SEC). Individual values vary considerably, however, with  $M_w$  values for lignosulfonates reported as low as 1,100 [97] and as high as 61,000 Da [98]. This variation reflects different sources of lignin (species, isolation conditions), the experimental setup for the SEC, and the potential for condensation reactions prior to and during SEC that create high-molecular-weight polymers, and makes comparisons among studies somewhat challenging.

**Figure 1.** Four different reaction mechanisms to create lignin co-polymers. In all reaction schemes lignin is represented as a single phenolic structure, labeled ‘L’, for the sake of simplicity. The wavy bond represents the larger polymeric structure, and the substituents  $R_1$  and  $R_2$  can be -H, -OH or -OCH<sub>3</sub>. Brackets mark the repeat structure of the different polymers.

**Scheme I:** Formation of lignin-*graft-N*-isopropylacrylamide (NIPAM) via atom transfer radical polymerization (ATRP) based on Kim and Kadla [29]. A lignin macroinitiator is formed from the reaction of lignin with 2-bromo*isobutyryl* bromide (gray) in ethylacetate containing triethylamine. The reaction between the lignin macroinitiator and NIPAM (magenta) is catalyzed by Cu(I)-PMDTA, formed from mixing Cu(I)Br and *N,N,N',N'',N''*-pentamethylenediethylenetriamine (PMDTA), in a mixture of water and dimethylformamide (DMF) at 50°C.

**Scheme II:** Formation of lignin grafted with polyacrylamide via reversible addition-fragmentation chain-transfer polymerization (RAFT), based on Gupta and Washburn [98]. Both phenolic and aliphatic hydroxyl groups of lignin can react with acyl chloride xanthate (blue) to create a macroinitiator. The reaction with acrylamide (burgundy) takes place in DMF at 70°C in the presence of azobis-(isobutyronitrile) (AIBN) as catalyst.

**Scheme III:** Formation of lignin-poly( $\epsilon$ -caprolactone) (PCL)/poly(L-lactic acid) (PLLA) co-polymer involving solvent-free ring opening polymerization, based on Kai et al. [33]. Lignin is mixed with  $\epsilon$ -caprolactone (red), L-lactide (dark blue) and stannous octoate (Sn(Oct)<sub>2</sub>; Sn(II)ethyl hexanoate) at 130°C. The polymers can be grafted to both aliphatic and phenolic hydroxyl groups. The number of PCL and PLLA repeat units (marked by brackets) of the different chains can vary, as indicated by the different indices ( $n, m, x, y$ ).

**Scheme IV:** Thermal click chemistry involving a Huisgen cycloaddition reaction between an azide and alkyne at elevated temperature (75°C) based on Han et al. [36]. The lignin azide is generated by first reacting lignin with bromobutyryl chloride (gray) and subsequently with sodium azide (purple). Lignin poly( $\epsilon$ -caprolactone) (PCL; red) with a reactive alkyne moiety is generated by a ring opening polymerization between lignin and  $\epsilon$ -caprolactone in the presence of stannous octoate (Sn(Oct)<sub>2</sub>) followed by a reaction with propargyl bromide (orange) in the presence of potassium carbonate. The cycloaddition reaction between the azide and alkyne results in a lignin-PCL-lignin co-polymer.



