Preparation and characterization of graft copolymer from dealkaline lignin and styrene

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ABSTRACT: Graft copolymerization of styrene onto dealkaline lignin by ferrous chloride and hydrogen peroxide coinitiator has been achieved successfully. The influence of temperature and reaction time as well as the amount of the styrene monomer, initiator, and catalyst on the grafting copolymerization was investigated. The optimum reaction conditions were determined as follows: c (styrene) = 20.00 mmol, c (H_2O_2) = 5.00 mmol, c ($FeCl_2$) = 0.10 mmol, T = 30°C and t = 48 h. The optimum yield (Y), total conversion (TC), grafting efficiency (GE), and degree grafted (DG) values were 96.6, 96.3, 59.5, and 53.7%, respectively. The copolymer of lignin grafted PS was separated and characterized by elemental analysis, differential scanning calorimetry, Fourier transform infrared, thermogravimetry analysis, field emission-scanning electron microscopy, gel permeation chromatography, and nuclear magnetic resonance. It was demonstrated that the solubility what the copolymer exhibited turned out to be the very reverse of the original lignin. The surface properties and structure of lignin were completely changed after grafting copolymerization. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41900.

INTRODUCTION

At present, with the depletion of fossil resources and serious environmental issues,[1,2] great attention has been turned to renewable and sustainable raw materials.[3] Lignin, representing 30% of all the nonfossil organic carbon on Earth,[4] is the second most abundant and inexpensive renewable resource, surpassed only by cellulose and hemicellulose.[2] Recently, the world production of lignin by the pulp and paper industry alone has been 50 million tonnes per year, but only 2% was used to make valuable chemicals.[5] The remainder was mainly burned as a low value fuel or directly threw away as waste material.[6,7]

Lignin is a complex phenolic polymer with a three-dimensional aromatic structure composed of methoxylated phenylpropanoids.[8] It is a highly functionalized biomacromolecule, which contains a variety of active functional groups, such as phenolic, hydroxyls, methoxyl, carboxylic, and benzyl hydrogen.[9,10] These properties offer the potential for lignin valorization.[11–13] Currently, lignin is widely used in many areas, such as polyurethane,[14] sand-fixation agent,[15,16] adsorbing material,[17,18] phenolic resin, and epoxy resin.[19,20] Therefore, there is no doubt that the rational utilization of the lignin resources will not only increase economic efficiency but also address the environmental issues.[21–23]

Grafting is considered to be one of the promising methods for modification of lignin. Over the last few decades, a huge number of studies were performed to provide more functional materials via the graft copolymerization of lignin and styrene. Koshijima and Phillips *et al.* investigated the grafting of styrene onto HCl-lignin and various Kraft softwood lignin by irradiation.[24,25] Later, the influence of lignin and lignin model compounds on the polymerization rate and molecular weight of polymer in the radiation-induced polymerization of styrene was also reported.[26] Katuščák *et al.* demonstrated the effect of the original lignin and ozonized HCl-lignin upon the polymerization of styrene.[27] Chen *et al.* studied the graft copolymerzation of calcium lignosulfonate with styrene by using ozone, H_2O_2 and $FeCl_2$.[22] Meister and Chen exploited the H_2O_2 and $CaCl_2$ initiating system to coinitiate the grafting reaction of the lignin with styrene and found that the thermal stability of lignin was efficiently enhanced by this process.[28,29] Based on this method, Bonini *et al.* studied the synthesis of copolymers between lignin from steam-exploded straw and styrene.[30] However, the
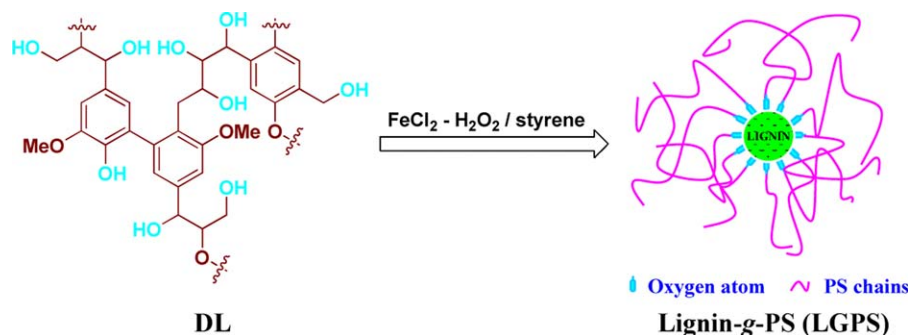
Scheme 1. A general strategy toward the copolymer of lignin grafted PS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

previously reported redox initiating system, H_2O_2 and $CaCl_2$, turned out to be unsuitable for the grafting of dealkaline lignin (DL) and styrene. It is, in this sense, imperative to make use of other more active initiator and more productive way, such as H_2O_2 and $FeCl_2$ system, which has utilized for the grafting copolymerization of methyl methacrylate on stone ground wood,[31] to prepare the thermoplastic copolymer which is a macromolecular surface-active material with excellent compatibility and adhesion.[28,29,32]

In this work, we introduced H_2O_2 and $FeCl_2$ as a coinitiator to perform the grafting of styrene onto DL via free radical polymerization (Scheme 1). The grafted copolymer was separated by dissolving the polymer blends in CH_2Cl_2 and precipitating into an excess of n-hexane. The copolymer of lignin grafted polystyrene (lignin-g-PS, LGPS) was characterized by elemental analysis, differential scanning calorimetry (DSC), Fourier transform infrared (FTIR), thermogravimetry analysis (TGA), field emission-scanning electron microscopy (FE-SEM), gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR). The influence of the reaction conditions, such as temperature, reaction time, and the concentration of styrene monomer, initiator and catalyst on the yield (Y), total conversion (TC), grafting efficiency (GE), and degree of lignin grafted (DG) was investigated and discussed.

EXPERIMENTAL

Materials
DL used in this study was purchased from Tokyo Kasei Kogyo (TCI), ground to a powder form and dried to constant weight in vacuum at 60°C for 24 h. Analytical grade styrene obtained from Xilong Chemical (China) was purified according to literature procedures and stored against light at −10°C in refrigerator.[29] Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4 H_2O$) and hydrogen peroxide (H_2O_2, 30%) are analytical reagents and were also obtained from the Xilong Chemicals (China). Toluene, dimethyl sulfoxide (DMSO), methanol, dichloromethane (DCM), dimethylformamide (DMF), tetrahydrofuran (THF), n-hexane, and all the other reagents were analytical reagent grade products of Rionlon BoHua (Tianjin) Pharmaceutical and Chemical (China) and used as received.

General Measurements
Elemental analysis for carbon, hydrogen, oxygen, nitrogen and sulfur were performed on a Vario EL Analyzer by using helium as the carrier gas with an associated error between replicates of 1–3%.

Glass-transition temperatures (Tg) of the DL and LGPS were determined on a NETZSCH 200F3 DSC. The software NETZSCH Proteus Analysis was used for the DSC calculations. All tests were performed under a dynamic nitrogen atmosphere at the flow rate of 30 mL/min with a sample of approximately 5.0–6.0 mg. All samples were first heated from −50°C up to 180°C at the rate of 10°C/min and then samples were subsequently cooled to −50°C at the rate of 10°C/min and then reheated up to 180°C at the rate of 10°C/min. The Tg values were recorded as the midpoint temperature of the heat capacity transition on the second heating scan.

The FTIR spectra of the DL, LGPS, and PS were determined using the Nicolet iS10 FTIR. All the samples were scanned in the range from 4000 to 400 cm^{-1} and 32 scans per sample were collected by using the KBr pellet technique.

The thermal degradation behavior of the DL and LGPS were investigated using a NETZSCH STA 449F3 TG. The samples were heated from 25 to 800°C at the heating rate of 10°C/min in a dynamic nitrogen atmosphere at the flow rate of 30 mL/min.

Morphological analysis of the DL and LGPS surface layers was taken using a JSM-6701F FE-SEM. All samples were sputter-coated with gold to make them conductive prior to FE-SEM observation.

The molecular weights and molecular weight distributions of the LGPS and PS samples were determined on a Watty DAWN HELEOS SESTEM GPC/SEC (UV and RI detectors) connected to a multiangle laser light scattering (MALLS) detector (DAWN-HELEOS, Wyatt Technologies) using MZ column at 30°C with HPLC grade THF as the eluting solvent at a flow rate of 1.0 mL min^{-1} and UV detection at 280 nm. The concentration of the samples was 2.29 mg mL^{-1} and the injection volume was 100 μL.

^1H NMR spectra of DL and LGPS were measured using a Bruker Avance 400 MHz spectrometer using DMSO-d_6 as the reference solvent. The NMR spectra were recorded at 300 K and a total of 32 scans were collected.

Graft Copolymerization of DL with Styrene
A 100 mL three-neck round-bottom flask, equipped with a thermometer, nitrogen inlet and magnetic stirring bar was charged with 200 mg of DL and 5 mL of DMSO. The mixture was stirred

until the DL was dissolved and $FeCl_2 \cdot 4\ H_2O$ in 0.5 mL of methanol was added. The reaction mixture was degassed repeatedly by four freeze-pump-thaw cycles, and then 30% H_2O_2 was added under constant nitrogen flow. After stirring for 10 min, a certain amount of deoxygenated styrene was added. The reaction mixture was maintained at required temperature under stirring for a certain period of time. In this process, the copolymer began to become turbid and precipitate out of solution after about 5 h. Once the reaction was completed, the mixture was cooled to room temperature and quenched by dilution with 80 mL of 2N HCl, and then stirred for additional 30 min. The resulting precipitate was collected by filtration, washed to neutral and dried to constant weight in vacuum at 60°C for 24 h. The crude polymer was extracted with toluene in a Soxhlet apparatus for 24 h to remove the unreacted lignin and graft copolymer with short PS chains (UL), which were toluene-insoluble.[28,29] Toluene extracts were concentrated and dissolved in DCM at 1 g mL^{-1}. The resulting yellow solution was added dropwise into an eightfold excess of n-hexane to precipitate the copolymer. The remaining residue was washed with n-hexane/ DCM ($v/v = 8 : 1$) three times, recovered, and dried under vacuum at 40°C overnight. The copolymer LGPS was obtained as filemot solid. PS was prepared at the optimum reaction conditions without DL. The product yield ($Y\%$), total conversion of styrene (TC%), grafting efficiency (GE%), and degree of lignin grafted (DG%) were defined as follows:[16,22]

$$Y\ (\%) = \frac{W_T}{W_L + W_S} \times 100 \tag{1}$$

$$TC\ (\%) = \frac{W_T - W_L}{W_S} \times 100 \tag{2}$$

$$GE\ (\%) = \frac{W_T - W_L - W_H}{W_T - W_L} \times 100 \tag{3}$$

$$DG\ (\%) = \frac{W_L - W_{UL}}{W_L} \times 100 \tag{4}$$

where W_T stands for the weight of total solid obtained after grafting reactions; W_L and W_S is the weight of original lignin and styrene monomer used in the grating reactions, respectively; W_H is the total weight of PS homopolymer obtained from removing the grafted product precipitate and W_{UL} is the weight of unreacted lignin and graft copolymer with short PS chains obtained from toluene-unextractable fraction.

RESULTS AND DISCUSSION

Characterization

Elemental Analysis. Elemental composition of DL and LGPS in terms of C, H, O, and S content (in percent) were analyzed. Elemental analysis of lignin were C = 51.95, H = 4.68, O = 39.11, and S = 4.26 wt %. According to this, a molecular formula of $C_9H_{9.66}O_{5.09}S_{0.28}$ was calculated with a molecular mass of 208 g mol^{-1}. The elemental analysis results of LGPS were C = 89.53, H = 7.72, O = 1.40, and S = 1.35 wt %. It can be found that the C and H contents in LGPS were greater than that in the original lignin, and the O and S contents was significantly lower. This variation may be due to the grafting of PS chains onto the lignin backbone.

DSC Thermal Analysis. The DSC thermograms of DL and LGPS are illustrated in Figure 1. Due to the amorphous struc-
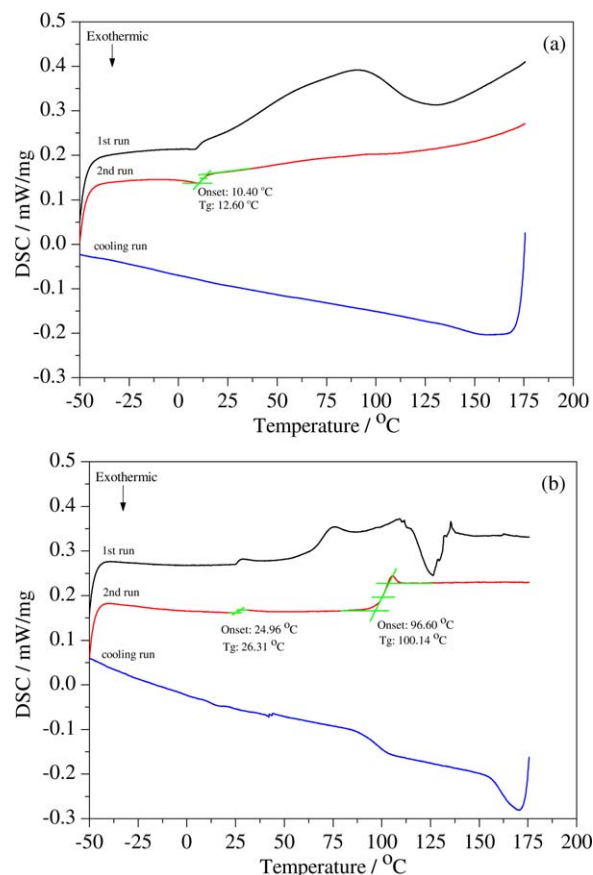

Figure 1. DSC curves of DL (a) and LGPS (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ture of the lignin, single Tg value is observed at 12.6°C [Figure 1(a)]. Unlike the lignin, two separate Tg values of LGPS are observed at 26.3 and 100.1°C as shown in Figure 1(b).[25] The lower value of Tg at 26.3°C is assigned to lignin and the higher value of Tg at 100.1°C can be assigned to the grafted PS chains on the lignin backbone. The size and flexibility of the side groups is an important factor influencing the glass transition temperature. Compared with the Tg value of the original lignin, the glass transition temperature at 26.3°C in the copolymer is increased as a result of grafting. This may be attributed to the rigid, bulky PS side branches which raise the glass transition temperature. The high value of Tg can be ascribed to the PS side chains which are wrapped in the surface of the lignin. Additionally, both Tg values of the LGPS are higher than the corresponding Tg value of the original lignin.[33,34]

FTIR Analysis. The FTIR spectra of DL (a), LGPS (b), and PS (c) are shown in Figure 2. The peak which appears at 3420 cm^{-1} suggests the existence of the hydroxyl groups of the phenolic and aliphatic in lignin, and meanwhile the peaks appear at 2932 and 2849 cm^{-1} may be attributed to the C—H stretching of the methylene and methyl groups in the lignin molecules.[35] The aromatic nucleus vibrations at 1600 and 1492 cm^{-1} and the C—H deformation combined with aromatic ring vibration at 1450 cm^{-1} are common characteristic absorptions of lignin.[36] The absorption at 1216 cm^{-1} corresponds to
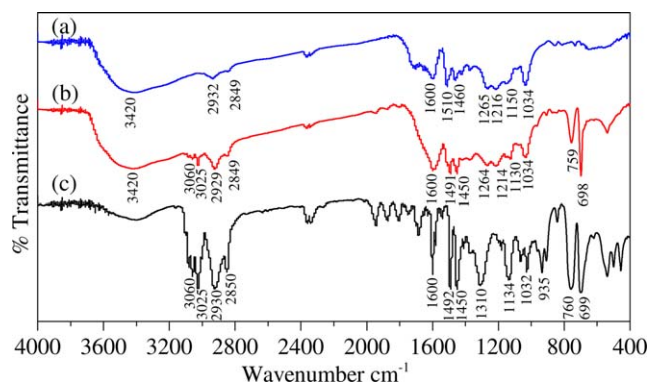
Figure 2. FTIR spectra of DL (a), LGPS (b) and PS (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the C—O—C stretching of aryl ether. The characteristic peaks of LGPS observed at 3060 and 3025 cm^{-1} can be assigned to the C—H stretching vibration of benzene ring. Absorption at 1600 and 1450 cm^{-1} are ascribed to the stretching vibration of C═C and C—C bonds in the aromatic range, respectively.[37] The strong absorption peaks at 760 and 699 cm^{-1} demonstrate the presence of monosubstituted aromatic nuclei which are attributed to the PS chains in the grafted materials.[30]

TG Analysis. Thermal stabilities of the DL and LGPS were analyzed by TGA, as shown in Figure 3. From the thermal degradation curves of the DL Figure 3(a), four thermal decomposition steps can be observed during the heating process. The lignin underwent thermal degradation, starting from the range of 25.0 to 137.3°C with 1.98% weight loss, which coincides with the weakly endothermic peak at 92.5°C on the DSC curve, corresponding to the volatilization of water molecules contained in the sample. The 41.23% weight loss in the range of 137.3 to 581.9°C is attributed to the elimination of water, sulfur dioxide, carbon monoxide, carbon dioxide and methane.[38] Moreover, the condensation reaction occurred in this process, as indicated by the exothermic peak at 384.7°C in the DSC thermogram. The third decomposition step was detected in the range of 581.9 to 703.8°C with 3.58% weight loss, with the release of the carbon dioxide and monomeric phenols into the vapor phase,

mainly due to the pyrolytic degradation of the lignin backbone structure. When the sample was heated from 703.8 to 800.0°C, a strong endothermic peak at 768.7°C was observed with 6.77% mass loss. This may be ascribed to the secondary pyrolytic degradation of the lignin backbone structure and the initial decomposition of some aromatic rings began to decompose. The weight loss tends to be stable when the temperature was above 800.0°C and the residual weight of lignin was 46.44%.

The TG curves of LGPS Figure 3(b) indicated the thermal degradation behavior of the grafted copolymer. The earlier thermal degradation was observed in the range of 25.0 to 205.3°C with 3.78% weight loss is mainly owing to the evaporation of the water and solvent molecules contained in the sample. An obvious endothermic peak of the DSC curve is observed at 420.9°C.[39] This is due to burning of the organic matter and is also consistent with the TG curve. The major difference between the TG curves of lignin and LGPS was observed obviously in the range of 266.2 to 465.8°C and the weight loss of LGPS reached 95.25%. This may be ascribed to the most fragile PS chains being broken down in this thermal region with a loss of a large number of styrene molecules. Moreover, sulfur dioxide, carbon dioxide and other low molecular weight compounds from lignin also released into the vapor phase in this thermal process. The variation of the weight loss in the range of 266.2 to 465.8°C reveals the existence of PS chains in the graft copolymer. More importantly, LGPS showed an increase in thermal stability with the onset of degradation increasing from approximately 137.3 to 266.2°C.

FE-SEM Analysis. The surface morphologies of the DL and LGPS are presented in Figure 4. From the FE-SEM microphotograph of the DL Figure 4(a), it can be observed that lignin is distributed crude with a granular structure. Moreover, there are some microscopic cavities dispersed among the particles. It is interesting that the morphological characteristic of LGPS Figure 4(b) is greatly different from the original lignin. It can be found that the apparent structure of the LGPS becomes much smoother than that of the lignin indicating the existence of the much more harmonized structure. But similar morphological structures are not observed in the lignin before grafting. This
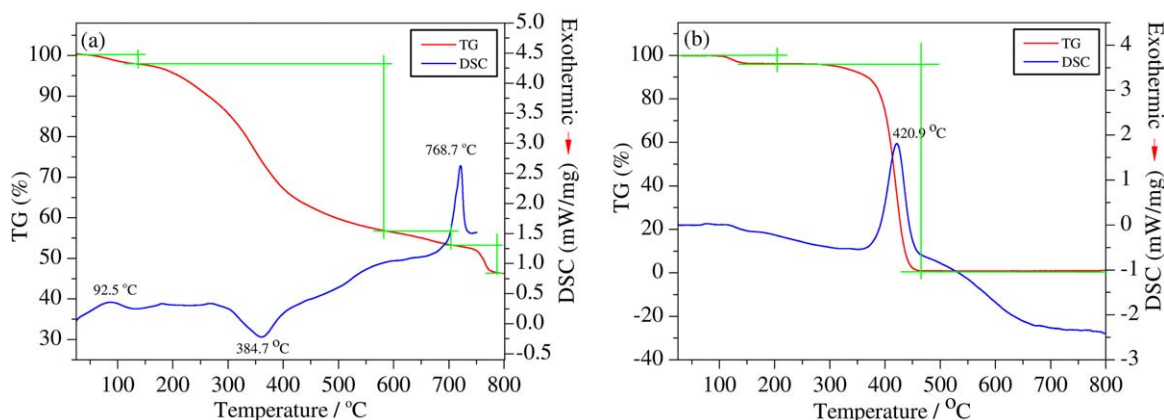

Figure 3. TG curves of DL (a) and LGPS (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
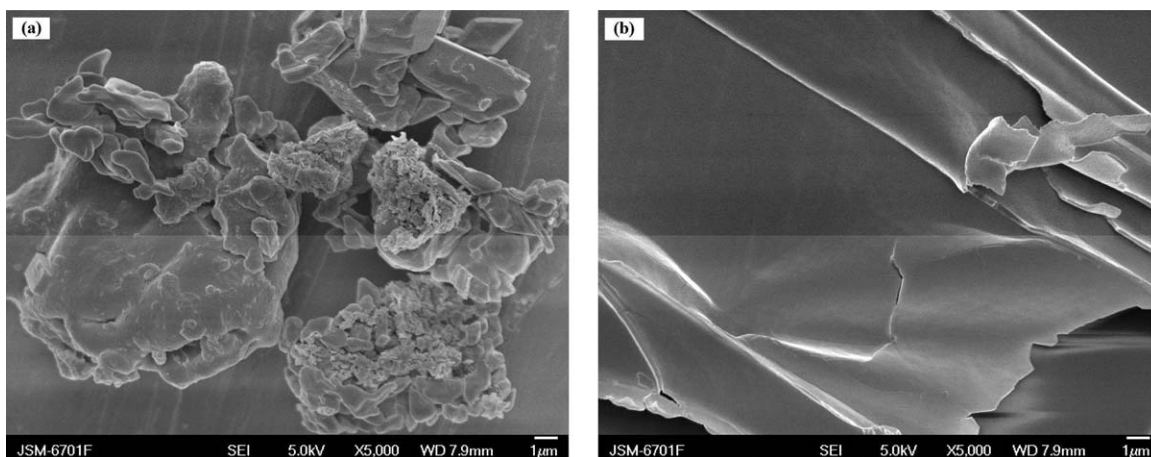
Figure 4. FE-SEM microphotographs of DL (a) and LGPS (b).

indicates that the surface morphology of lignin changed greatly after grafting PS chains.

The GPC of LGPS and PS. The molecular weights and molecular weight distributions of LGPS and PS were determined by GPC. The number-average molecular weight (Mn) and weight-average molecular weight (Mw) of LGPS are 1.78×10^4 and 7.14×10^4, respectively. The polydispersity index (PDI) is about 4.0. The Mn and Mw of PS are 3.07×10^3 and 1.48×10^4, respectively. The PDI is about 4.8.

^{1}H NMR of DL and LGPS. Detailed structural confirmation of the lignin and its copolymer were obtained by ^{1}H NMR in DMSO-d_6. The ^{1}H NMR spectra of DL and LGPS are showed in Figure 5. The signals at 6.0–7.5 ppm and 3.5–4.0 belonged to aromatic ring and methoxyl groups of DL, respectively [Figure 5(a)]. It can be seen that the peaks associated with the lignin aromatic ring are extremely weak in the lignin while they are obviously strengthened after grafting PS chains in the spectrum of LGPS [Figure 5(b)]. In addition, the peaks at 1.0–2.0 ppm, belonging to aliphatic hydrogen of PS have appeared in the
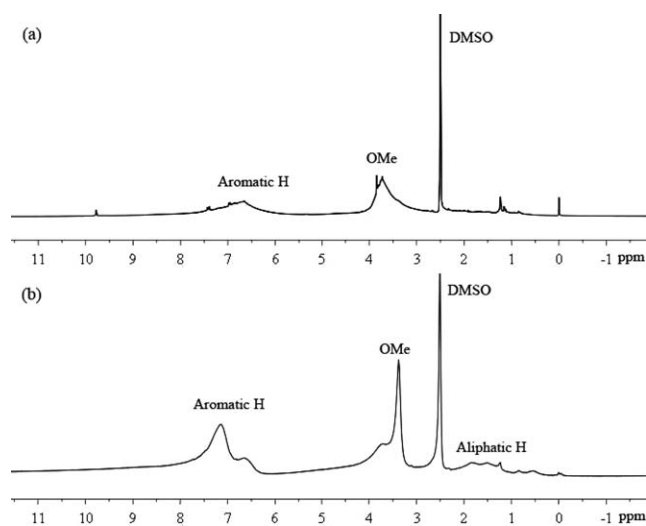
LGPS spectrum [Figure 5(b)], indicating that the PS chains have been grafted on the lignin backbone.

The Solubility of LGPS. The solubility what the copolymer LGPS exhibited turned out to be the very reverse of the original lignin. As far as we know, DL was only soluble in DMSO and DMF, but insoluble in benzene, toluene, ethyl ether, ethyl acetate, acetone, THF, DCM, chloroform, and methanol; however, after the copolymerization with PS via free radical polymerization, it possessed the same solution behavior as PS and soluble in almost all organic solvent described previously. The reason for the change of solubility could be explained by the structure of PS long side-chain grafted onto DL results in stabilized copolymer dispersion, increasing the solubility of LGPS. On the contrary, the copolymer LGPS is not soluble in DMSO and appeared turbid, which may be caused by PS chain that is insoluble in DMSO.

The Influence of Reaction Conditions on the Graft Copolymerization

The Influence of Styrene Concentration. Figure 6(a) shows the influence of the grafting styrene onto DL matrix at different molarity of monomer ranging from 15.00 to 25.00 mmol at a fixed amount of 200 mg of lignin at 30°C for 48 h. Y and TC values for grafting styrene onto lignin increase gradually up to 20.00 mmol of styrene, but the opposite trend was observed on increasing its concentration further from 20.00 to 22.50 mmol. Then again, Y and TC values increased continuously again in tandem with raising the concentration of styrene from 22.50 to 25.00 mmol. The initial increase in Y and TC may be attributed to the regular free radical copolymerization. The decreasing trend was due to reversible phase transition of the grafted chains from a DMSO-soluble state to a DMSO-insoluble state, which ultimately has affected the penetration and diffusion of styrene molecules to the active sites on the lignin and limited the polymerization process. The secondary increase in Y and TC, mainly owing to the homopolymerization reaction, similar to bulk polymerization of styrene, occurred with the further increase in the styrene concentration. Therefore, the optimum concentration of styrene was determined to be 20.00 mmol in the point of view of the economical and practical aspects.
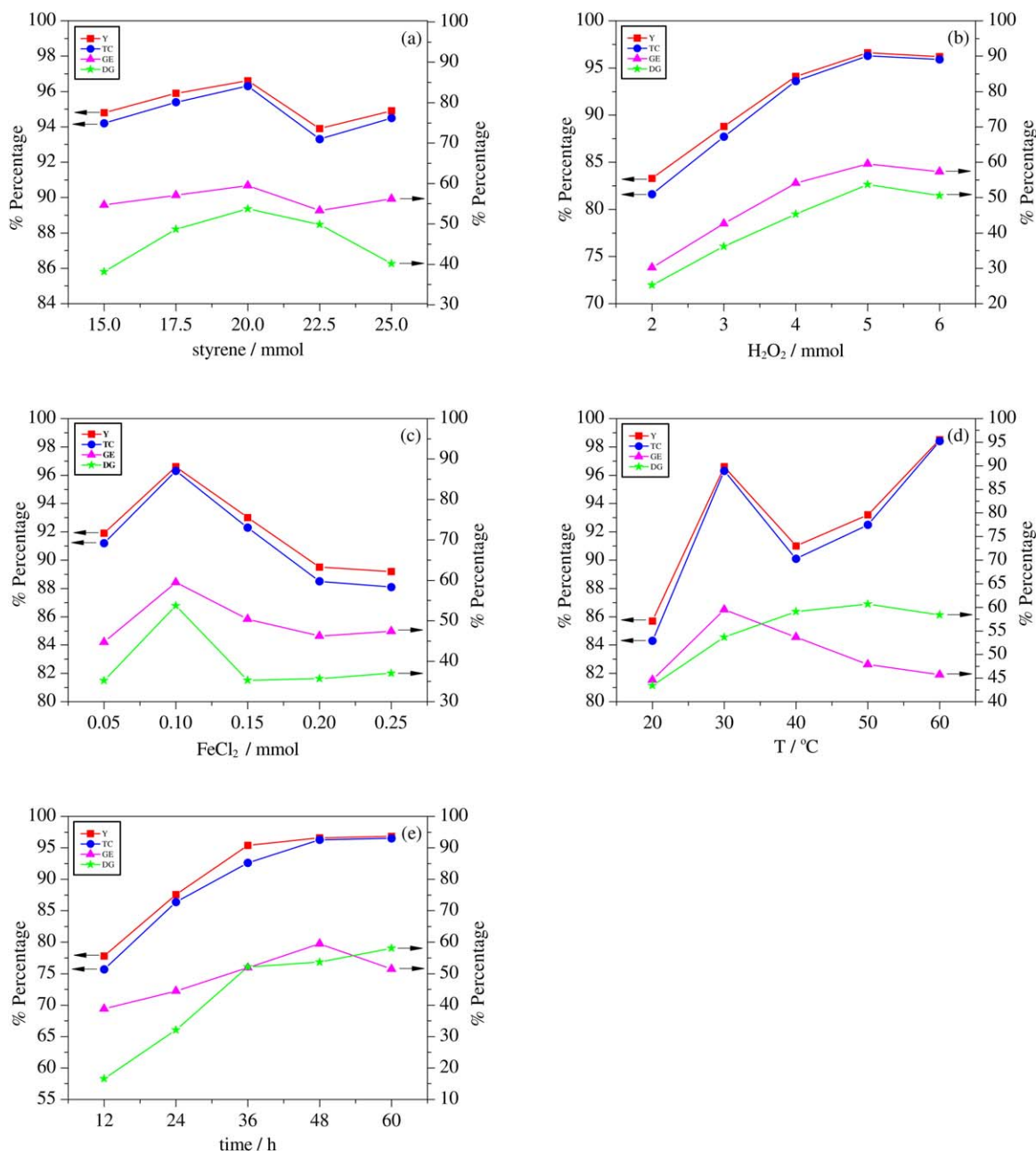

Figure 5. ^{1}H NMR spectra of DL (a) and LGPS (b) in DMSO-d_6.

Figure 6. Influence of reaction conditions on the percentages of Y, TC, GE, and DG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Influence of H_2O_2 Concentration. The graft copolymerization of styrene and DL was studied at different concentrations of H_2O_2 ranging from 2.00 to 6.00 mmol, keeping constant concentrations of styrene (20.00 mmol) and $FeCl_2$ (0.10 mmol). After the reaction proceeded at 30°C for 48 h, the results are shown in Figure 6(b). It can be seen that Y, TC, GE, and DG values showed a linear growth with the increase in the H_2O_2 concentration from 2.00 to 4.00 mmol. When the concentration of H_2O_2 was up to 5.00 mmol, the highest Y, TC, GE, and DG values were achieved to be 96.6, 96.3, 59.5, and 53.7%, respectively. After that, increasing the concentration of H_2O_2 even further had little influence on the graft copolymerization. The

most likely cause is the rapid decomposition of H_2O_2 in the presence of Fe^{2+}, leading to the generation of hydroxyl radicals which are eventually involved in the generation of lignin radicals for grafting reaction.[40] Additionally, raised concentration of H_2O_2 increases the amount of the free radicals which can therefore enhance the possibility of initiating reactive sites on the lignin whereon styrene can be grafted.

The Influence of $FeCl_2$ Concentration. The influence of different concentrations of $FeCl_2$ ranging from 0.05 to 0.25 mmol on the reaction was studied at constant concentrations of styrene (20.00 mmol) and H_2O_2 (5.00 mmol) at 30°C for 48 h [Figure 6(c)]. It is
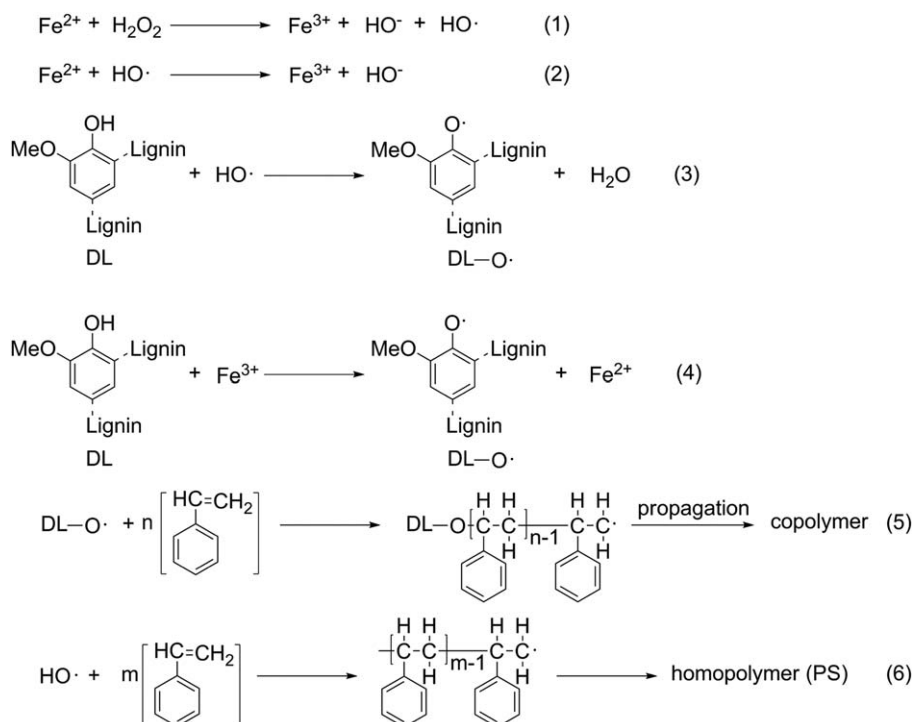
Scheme 2. The possible reaction mechanism of grafting styrene onto DL.

established that the grafting reaction did not occur without Fe^{2+}. When the content of $FeCl_2$ was up to 0.10 mmol, the values of Y, TC, GE, and DG reached the corresponding maxima at 96.6, 96.3, 59.5, and 53.7%, respectively, and decreased gradually on taking $FeCl_2$ concentration beyond it. This behavior can be explained by the logic that the increase in $FeCl_2$ concentration will result in generation of more free radical sites on the lignin backbone, which may lead to the initial increasing trend in both Y and TC values. It is known that Fe^{2+} reacts with H_2O_2 to generate highly reactive hydroxyl radicals ($\cdot OH$) in Fenton's reaction. However, with further increase in $FeCl_2$ concentration, the hydroxyl radicals formed in Fenton's reaction will be quenched by excess Fe^{2+}. Moreover, free radicals may interact with each other to terminate the polymerization and, as a result, decrease the rate of graft copolymerization and hence lead to a drop of the graft yield and the TC of styrene.

The Influence of Reaction Temperature. The influence of the reaction temperature varied from 20 to 60°C with constant concentrations of styrene (20.00 mmol), $FeCl_2$ (0.10 mmol), and H_2O_2 (5.00 mmol) for 48 h was investigated. The results are shown in Figure 6(d). It is observed that there is significant variation of Y and TC values with temperature. The reaction was initiated very slowly by $FeCl_2$ and H_2O_2 when the grafting reaction was carried out below 20°C. Along with the increase of the reaction temperature from 20°C to 30°C, Y, TC, GE, and DG values increased sharply and reached the maxima at 96.6, 96.3, 59.5, and 53.7%, respectively. Subsequently, Y, TC, and GE values dropped down gradually when the reaction temperature was further raised. As the temperature increased, the concentration of hydroxyl radicals formed by the reduction of H_2O_2 by Fe^{2+} increased to generate more reactive graft sites on the lignin to

induce the graft copolymerization. The decreasing trend of Y and TC values took place mainly due to the decrease of the reactivity and reaction ratio. The secondary increase in Y and TC values was observed when the temperature was raised continuously above 40°C. This may be due to the energy that speeds up the movement of the molecules and motivates the homopolymerization of the styrene.

The Influence of Reaction Time. The graft copolymerization has been performed at different reaction times ranging from 12 to 60 h at 30°C under definite concentrations of styrene (20.00 mmol), $FeCl_2$ (0.10 mmol), and H_2O_2 (5.00 mmol) [Figure 6(e)]. The results show that Y, TC, and DG values increase smoothly when the reaction time is prolonged from 12 to 48 h and then level off, while GE value decreases after 48 h. This is probably attributed to the generation of more and more hydroxyl radicals and monomer radicals which interact with the active sites on the lignin backbone as the reaction time is increased. Leveling off indicates that prolonging the reaction time has little influence on the grafting reaction but results in the formation of more styrene

The Possible Reaction Mechanism
The possible reaction mechanism is shown in Scheme 2. Graft polymerization of PS onto DL was carried out in DMSO solution using $FeCl_2$ and H_2O_2 as a redox coinitiator. Hydroxyl radicals (HO·) produced by the reaction of H_2O_2 by Fe^{2+} [Reaction (1)].[16] The resulted HO· reacts again with Fe^{2+} to yield Fe^{3+} [Reaction (2)].[41] In the formation of an active center on lignin which acts as the backbone, the radical species HO· may attack the lignin hydroxyl to produce macroradicals (DL-O·) [Reaction (3)] or to initiate homopolymerization of styrene [Reaction (6)]. In addition, Fe^{3+} could also abstract hydrogen

from Ph—OH group of DL to produce phenoxy radicals [Reaction (4)]. The lignin radicals species (DL-O·) is expected to be reactive and reacted with the monomers styrene to give the graft copolymer [Reaction (5)]. Termination of the graft copolymerization could be through a combination of the radicals or a chain transfer and polymerizations of styrene initiated by simple radical leads to the formation of homopolymer.

CONCLUSIONS

The graft copolymer from DL and styrene has been successfully formulated via free radical polymerization by using $FeCl_2$ and H_2O_2 as a redox coinitiator. The copolymer LGPS was separated by dissolving the polymer blends in CH_2Cl_2 and precipitating into an excess of n-hexane. The influence of reaction conditions, such as the reaction temperature, time, and the concentration of the styrene monomer, $FeCl_2$ and H_2O_2 on the values of Y, TC, GE, and DG was investigated. The optimum reaction conditions were determined as follows: c (styrene) = 20.00 mmol, c (H_2O_2) = 5.00 mmol, c $(FeCl_2)$ = 0.10 mmol, $T = 30°C$, and $t = 48$ h. The optimum Y, TC, GE, and DG values were 96.6, 96.3, 59.5, and 53.7%, respectively. The DSC indicated that the graft copolymer had two Tg values and both of them are higher than those of the original lignin. The elemental analysis illustrated that the chemical structure of lignin has changed after grafting PS chains. FTIR analysis of the DL and LGPS confirmed the formation of the graft copolymer. The graft copolymer LGPS showed an increase in thermal stability, as the onset of degradation temperature increased from approximately 137.3 to 266.2°C. More interesting is the fact that the apparent structure of the lignin changed greatly after grafting long PS chains, which was shown on FE-SEM micrographs. The copolymer LGPS has the same solution behavior as PS in many organic solvent but insoluble in DMSO. Additionally, further studies on the graft copolymerization of DL with other vinyl monomers are in progress in an effort to develop better lignin biological materials which are much more functional, available and practical.

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