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## Fe(III)-catalyzed grafting copolymerization of lignin with styrene and methyl methacrylate through AGET ATRP using triphenyl phosphine as ligand

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A novel activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP) is presented to carry out the grafting copolymerization of lignin with styrene (St) and methyl methacrylate (MMA) using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as catalyst,  $\text{PPh}_3$  as ligand and ascorbic acid (Vc) as a reducing agent for the first time. The synthesized lignin-based copolymers, L-g-PS and L-g-PMMA, were characterized by  $^1\text{H}$  NMR, FTIR, DSC, TGA and FE-SEM.  $^1\text{H}$  NMR showed the detailed structural conformation of the lignin and its copolymers, L-g-PS and L-g-PMMA. FTIR analysis confirmed that the PS and PMMA chains have been successfully grafted onto lignin backbone. The DSC indicated that the graft copolymer had two  $T_g$  values and both of them are higher than those of the original lignin. TGA showed that the thermal stability of the graft copolymers, L-g-PS and L-g-PMMA, are very different from original lignin. The surface properties and apparent structure of the lignin were completely changed after grafting with PS and PMMA chains. The GPC results showed narrow molecular weight distributions of the copolymers, which indicated that Fe(III)-catalyzed AGET ATRP for grafting copolymerization of lignin with St and MMA is well-controlled. The results obtained from these analytical methods confirm that grafting copolymerization have been successfully occurred from the surface of the lignin, and Fe(III)-catalyzed AGET ATRP provide a novel, effective, and environment friendly method to synthesize lignin-based copolymers.

### Introduction

Recently, due to the depletion of fossil fuel and the environmental awareness, the rational utilization of bioresources is recognized to be more advantageous.<sup>1,2</sup> Lignin, as the second most abundant biopolymer after cellulose, has aroused growing interest.<sup>3</sup> It is a major component with cellulose and hemicellulose of lignocellulosic plant, and represents about 10-35% of the total biomass and 30% of all the non-fossil organic carbon on Earth.<sup>4</sup> Lignin is the main by-product of conventional pulping and papermaking industry and the production of bioethanol.<sup>5</sup> However, due to the rigid and complicated three-dimensional network, low reactivity, broad chemical differences depending on source, variability of its composition and structure depending on the separation process and nature of biomass, low or no solubility in a usual solvent, and poor processability, the greatest part of industrial lignin is treated as waste material and incinerated as low-grade fuel by burning or used as a low-value product.<sup>6-9</sup>

Therefore, the question how to improve the lignin valorization has been issued.

Over the last few decades, for different purposes, the synthesis of lignin-based grafting copolymers has been carried out mainly by free-radical polymerization (FRP).<sup>10-19</sup> However, along with the atom transfer radical polymerization (ATRP) was first developed by Sawamoto and Matyjaszewski et al.,<sup>20,21</sup> it has previously been utilized for "grafting from" processes of grafting copolymerization from lignin.<sup>22-27</sup> ATRP, as an especially powerful "living"/controlled free-radical polymerization (LCFRP), has emerged as one of the most robust and versatile synthetic techniques in lignin grafting copolymerization. Generally, the surface of lignin was modified by using 2-bromoisobutryl bromide (BiBB) to synthesize the lignin-based macroinitiator. And then the grafting copolymerization of lignin with vinyl monomers was performed using the macroinitiators as initiators, some ligands, such as 1, 1, 4, 7, 10, 10-hexamethyltriethylenetetramine, *N*, *N*, *N'*, *N''*, *N'''*-pentamethylenediethylenetriamine or tris[2-(dimethylamino)ethyl]amine, in combination with  $\text{CuX}$  ( $X = \text{Cl}, \text{Br}$  or  $\text{I}$ ), were proved to be efficient catalysts via ATRP. The well-defined lignin-based copolymers, as functionalized materials, exhibited a variety of different characteristics, such as thermosensitive, ionic responsive, hydrophobic and high water resistance, and gas-switchable feature and so on. In this

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context, ATRP has been considered to be one of the most effective methods to develop lignin-based functional materials because of lignin's polyhydroxy structure.

Early studies on the grafting copolymerization of lignin with monomers by using the conventional ATRP largely relied on the use of Cu(I) complexes as catalysts, which suffered from requiring harsh reaction conditions, such as Cu(I) complexes are sensitive to air and moisture. In addition, copper and its complexes are toxic. As a means of addressing this problem, a mechanistically distinct strategy to conduct ATRP has, therefore, been developed by Matyjaszewski et al. and nominated "activators generated by electron transfer ATRP" (AGET ATRP).<sup>28-31</sup> And a class of Fe(III)-mediated catalyst system has been recently developed to induce the living polymerization to obtain well-defined polymers and block copolymers with a narrow polydispersity using AGET ATRP.<sup>32-35</sup> However, this developed AGET ATRP was just used for the homopolymerization and copolymerization. Thus, the development of initiation technique, AGET ATRP, to overcome the drawbacks of conventional ATRP by the Fe(III)-catalyzed grafting copolymerization of lignin would be highly desirable to perform and control the copolymerization of lignin with vinyl monomers which may be accessed.

In the present work, our interest has been focused on a novel, effective, and environment friendly method for the synthesis of lignin-based biomaterials through the AGET ATRP of styrene (St) and methyl methacrylate (MMA) from initiators immobilized on lignin by Fe(III)-mediated catalyst system using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as catalyst, triphenyl phosphine ( $\text{PPh}_3$ ) as ligand and ascorbic acid (Vc) as a reducing agent. The copolymers of lignin-grafted-polystyrene (L-g-PS) and lignin-grafted-poly(methyl methacrylate) (L-g-PMMA) were analyzed by  $^1\text{H}$  NMR, FTIR, TGA, DSC and FE-SEM. The GPC results showed narrow molecular weight distributions of the copolymers, which indicated that Fe(III)-catalyzed AGET ATRP is a "living"/controlled technique for grafting copolymerization of lignin with St and MMA. To our knowledge, it is the first time lignin-based copolymers have been employed by Fe(III)-catalyzed AGET ATRP techniques using  $\text{PPh}_3$  as ligand and Vc as a reducing agent.

## Experimental

### Materials

Lignin was purchased from Tokyo Kasei Kogyo Co., Ltd (Tokyo, Japan). It was ground to a powder form and dried to constant weight in vacuum at  $60\text{ }^\circ\text{C}$  for 24 h. 2-Bromoisobutyryl bromide (BiBB) ( $\geq 98\%$ ) was purchased from Beijing J&K Technology Co., Ltd (Beijing, China) and used as received. Analytical grade styrene ( $\geq 99\%$ ) and methyl methacrylate ( $\geq 99\%$ ) were obtained from Xilong Chemical Co., Ltd. (Guangzhou, China), and purified to remove the stabilizer according to literature procedures and stored against light in refrigerator at  $-10\text{ }^\circ\text{C}$ .<sup>18, 36</sup>  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\geq 99\%$ ),  $\text{PPh}_3$  ( $\geq 99\%$ ), and Vc ( $\geq 99.7\%$ ) (analytical reagent) were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China) and

used as received. Acetic anhydride, pyridine, methanol, *N,N*-dimethylformamide (DMF) and all other reagents were analytical reagent grade products of Rionlon Bohua (Tianjin) Pharmaceutical & Chemical Co. Ltd. (Tianjin, China) and used as received.

### Measurements

$^1\text{H}$  NMR was measured using a Bruker Avance 400 MHz spectrometer using  $\text{DMSO}-d_6$  or  $\text{CDCl}_3$  as the reference solvent at 300 K, and a total of 32 scans were collected.

Glass-transition temperatures ( $T_g$ ) were measured on a NETZSCH 200F3 DSC. 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  $-50\text{ }^\circ\text{C}$  up to  $180\text{ }^\circ\text{C}$  at the rate of  $10\text{ }^\circ\text{C} / \text{min}$ , and the samples were subsequently cooled to  $-50\text{ }^\circ\text{C}$  at the rate of  $10\text{ }^\circ\text{C} / \text{min}$ , and then reheated up to  $180\text{ }^\circ\text{C}$  at the rate of  $10\text{ }^\circ\text{C} / \text{min}$ . The  $T_g$  values were recorded as the midpoint temperature of the heat capacity transition on the second heating scan.

Thermogravimetric analyses (TGA) was investigated using a NETZSCH STA 449F3 TG. Samples were heated from 25 to  $800\text{ }^\circ\text{C}$  at the heating rate of  $10\text{ }^\circ\text{C} / \text{min}$  in a dynamic nitrogen atmosphere at the flow rate of 30 mL / min.

The molecular weights and molecular weight distributions of macroinitiator L-Br, L-g-PS and L-g-PMMA were determined by a Waters 1515 gel permeation chromatograph (GPC, UV and RI detectors) equipped with a PL GEL MIXED C, guard column  $\mu\text{gel } 5\text{ }\mu\text{m}$ , Serial No. 0006162284-87 column and HPLC grade DMF with 0.1% LiBr was used as the eluting solvent ( $1.0\text{ mL min}^{-1}$ ) at  $35\text{ }^\circ\text{C}$  and UV detection at 280 nm. The columns were calibrated against polystyrene standards. Sample concentration was  $1\text{ mg mL}^{-1}$  and the injection volume was 50  $\mu\text{L}$ .

Fourier transform infrared (FTIR) analysis was performed using the Nicolet iS10 FTIR. All the samples were scanned in the range from  $4000$  to  $400\text{ cm}^{-1}$  and 32 scans per sample were collected by using the KBr pellet technique.

The surface morphology of the lignin samples before and after the grafting was observed by using a JSM-6701F FE-SEM. All samples were sputter-coated with gold to make them conductive prior to FE-SEM observation.

### Acetylation of lignin

Acetylation of lignin was performed by dissolving 0.800 g of lignin in 50 mL of pyridine/acetic anhydride (1:1, v/v) and stirring the mixture at room temperature for 48 h. The reaction solution was then added dropwise with stirring to 500 mL of ice-water. The precipitated acetylated lignin (L-Ac) was collected by filtration, washed with ice-water, and dried in vacuum until constant weight at  $50\text{ }^\circ\text{C}$  overnight. Complete acetylation was confirmed by FTIR (Fig. 3(b)).

### Synthesis of macroinitiator lignin-Br (L-Br)

Modification of both the aliphatic and the phenolic hydroxyl groups of lignin was performed by dissolving lignin (0.800 g, 2.8 mmol hydroxyl content) in 20 mL of pyridine in a 100 mL round bottom flask equipped with a magnetic stirrer, nitrogen inlet, and rubber septum. The mixture was cooled in an ice

bath under nitrogen after the formation of a homogeneous phase, and BiBB (3.862 g, 16.8 mmol) was added dropwise at 0 °C within 1 h afterward. The solution was then allowed to stir for 24 h at room temperature. The final reaction mixture was precipitated into 100 mL saturated NaHCO<sub>3</sub> solution, filtered, and repeatedly washed with distilled water until neutral. After drying in vacuum until constant weight at 50 °C for 24 h, macroinitiator lignin-Br (L-Br) was obtained. <sup>1</sup>H NMR and FTIR spectra of L-Br are shown in Fig. 1(c) and Fig. 3(c), respectively. A summary of the conditions for L-Br synthesis is shown in Scheme 1.

< Scheme 1.cdx >

#### General procedure for the grafting copolymerization of lignin with St and MMA via AGET ATRP

In a general procedure, a mixture of L-Br (200 mg, 0.232 mmol) was added to a dried 25 mL three-neck round-bottomed flask equipped with a magnetic stirred bar and dissolved in DMF (4 mL), and then FeCl<sub>3</sub>·6H<sub>2</sub>O (63 mg, 0.232 mmol), PPh<sub>3</sub> (183 mg, 0.696 mmol), Vc (21 mg, 0.116 mmol) and St or MMA (46.4 mmol) were added to the mixture under stirring. The reaction mixture was bubbled with nitrogen for 20 min to degas and then transferred into a preheated oil bath held at 110 °C for St and 90 °C for MMA to polymerize under stirring for 24 h. Then the reaction mixture was cooled to room temperature and precipitated into 150 mL of methanol, filtered, and repeatedly washed with methanol for three times. The obtained copolymers were dried in vacuum until constant weight at 50 °C overnight. The synthesis strategy of lignin-based copolymers is shown in Scheme 2.

< Scheme 2.cdx >

## Results and discussion

### Synthesis of acetylated lignin L-Ac

Lignin was acetylated to determine the number of aliphatic and the phenolic hydroxyl groups by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> with 10 mg of 4-nitrobenzaldehyde (PNB) as an internal standard (Fig. 1(b)). The content of hydroxyl groups per mass of lignin were calculated according to Equation 1, and the result was 3.47 mmol (OH) /g (lignin).

$$\text{mol(OH)/mass(L - Ac)} = \frac{1}{3 \times 151.12} \times \frac{A_b + A_{b'}}{A_e} \times \frac{m_{\text{PNB}}}{m_{\text{L-Ac}}} \quad (1)$$

Where  $A_e$  is the <sup>1</sup>H NMR integration area ( $\delta = 10.16$  ppm) of aldehyde protons in PNB;  $A_b$  and  $A_{b'}$  are the <sup>1</sup>H NMR integration area ( $\delta = 2.30$ - $1.70$  ppm) of -OCH<sub>3</sub> protons in L-Ac; 3 is the number of protons of OCH<sub>3</sub>; 151.12 is the molecular weight of PNB;  $m_{\text{PNB}}$  and  $m_{\text{L-Ac}}$  are actual mass of PNB and L-Ac, respectively.

### Synthesis of lignin macroinitiator L-Br

Lignin was modified by using BiBB in the presence of pyridine to create active initiating sites for controlled AGET ATRP. The content of active initiating sites was determined by <sup>1</sup>H NMR in

DMSO-*d*<sub>6</sub> in which PNB was also used as an internal standard (Fig. 1(c)). The moles of bromine atoms per lignin macroinitiator mass were determined according to Equation 2. The content of bromine atoms was calculated to be 2.32 mmol (Br) /g (L-Br).

$$\text{mol(Br)/mass(L - Br)} = \frac{1}{6 \times 151.12} \times \frac{A_f + A_{f'}}{A_e} \times \frac{m_{\text{PNB}}}{m_{\text{L-Br}}} \quad (2)$$

Where  $A_e$  is the <sup>1</sup>H NMR integration area ( $\delta = 10.16$  ppm) of aldehyde protons in PNB;  $A_f$  and  $A_{f'}$  are the <sup>1</sup>H NMR integration area ( $\delta = 2.10$ - $1.60$  ppm) of -COC(CH<sub>3</sub>)<sub>2</sub>Br protons in L-Br; 6 is the number of protons of COC(CH<sub>3</sub>)<sub>2</sub>Br; 151.12 is the molecular weight of PNB;  $m_{\text{PNB}}$  and  $m_{\text{L-Br}}$  are actual mass of PNB and L-Br, respectively.

<Fig. 1.TIF>

### Grafting copolymerization of L-Br with St and MMA by AGET ATRP

The grafting copolymerization of lignin with St and MMA through Fe(III)-catalyzed AGET ATRP were first studied. Lignin-based macroinitiators L-Br were employed to perform "grafting from" AGET ATRP of St and MMA using FeCl<sub>3</sub>·6H<sub>2</sub>O as catalyst, PPh<sub>3</sub> as ligand, and Vc as reducing agent. The grafting copolymerization was carried out by fixed the amount of L-Br at 0.200 g (0.464 mmol Br) and conducted with the same molar ratio of monomers to bromine initiating sites ( $[\text{monomer}]/[\text{L-Br}]/[\text{Fe(III)}]/[\text{PPh}_3]/[\text{Vc}] = 200/1/1/3/0.5$ ) in DMF for 24 h. The Fe(III)-catalyzed AGET ATRP of lignin with St and MMA were carried out under stirring at 110 and 90 °C, respectively. Fe(III)-catalyzed AGET ATRP is a very attractive method to conduct the grafting copolymerization of lignin with St and MMA because of the use of environment friendly and low-cost iron catalyst. Moreover, the copolymers, precipitated out of methanol, needed no further purification and dried in vacuum to obtain sand brown or light yellow products. These circumstances hold for both the two investigated copolymers: L-g-PS and L-g-PMMA.

The molecular weights and the polydispersity index (PDI) of macroinitiator L-Br, L-g-PS and L-g-PMMA copolymers were determined by GPC. The results are summarized in Table 1 and the GPC traces are showed in Fig. 2. The number-average molecular weight ( $M_n$ ) of L-Br are determined to be  $M_n = 7200$  g mol<sup>-1</sup>, and PDI = 2.86, respectively. It can be found that the  $M_n$  of L-g-PS is 44800 g mol<sup>-1</sup> and the value of PDI = 1.11, and the  $M_n$  of L-g-PMMA is 38400 g mol<sup>-1</sup> and the value of PDI = 1.06, respectively. As can be seen, the molecular weight distributions are narrow and both the PDI values of copolymers are all close to one, which is expected since AGET ATRP is "living"/controlled during the grafting copolymerization. In addition, the lignin-based copolymer L-g-PS shows bimodal GPC trace obviously maybe due to the high dispersity of macroinitiator L-Br and different grafting degree from L-g-PMMA. These low values of PDI imply that with FeCl<sub>3</sub>/PPh<sub>3</sub> in the presence of Vc the grafting copolymerization was well-controlled and the controllability over molecular weights and molecular weight distributions is very good. Furthermore, it has been proven that AGET ATRP is a very



suitable and effective technique to carry out the grafting copolymerization of lignin with St and MMA.

<Table 1>

<Fig. 2.EPS>

#### The proposed mechanism of AGET ATRP for L-Br with St and MMA

The proposed mechanism of the grafting copolymerization from lignin with St and MMA via Fe(III)-catalyzed AGET ATRP is shown in Scheme 3. Graft polymerization of vinyl monomers St and MMA onto lignin was carried out in DMF solution using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as catalyst,  $\text{PPh}_3$  as ligand, Vc as reducing agent, and BiBB modified lignin-based macroinitiator L-Br as initiator. The high oxidation state of transition metal complexes  $\text{Fe}^{\text{III}}\text{Cl}_3/\text{PPh}_3$  maybe the mainly catalytic precursor, while the added reducing agent Vc could react with the complex  $\text{Fe}^{\text{III}}\text{Cl}_3/\text{PPh}_3$  to form the low oxidation state ATRP catalyst  $\text{Fe}^{\text{II}}\text{Cl}_2/\text{PPh}_3$  which was generated in situ by electron transfer.<sup>37</sup>

Then a conventional ATRP process was proceeded to complete the copolymerization of lignin with PS or PMMA. The complex  $\text{Fe}^{\text{II}}\text{Cl}_2/\text{PPh}_3$  obtained bromide atom from Lignin-Br by oxidation process and generated free radical Lignin $\cdot$  and species  $\text{BrFe}^{\text{III}}\text{Cl}_2/\text{PPh}_3$ . Then the radical Lignin $\cdot$  reacted with monomers M (St or MMA) to generate free radical Lignin-M $\cdot$  which could be reacted with  $\text{Fe}^{\text{III}}\text{Cl}_3/\text{PPh}_3$  further to achieve the copolymers Lignin-M-Br. At the same time, the complex  $\text{Fe}^{\text{III}}\text{Cl}_3/\text{PPh}_3$  was reduced to active species  $\text{Fe}^{\text{II}}\text{Cl}_2/\text{PPh}_3$  and triggered a new cycle of reaction once again. The redox process could make the system effectively to maintain a very low concentration of free radicals, thereby greatly reduced the termination of free radical reaction. In the overall grafting copolymerization, the reduction of the high oxidation state complexes  $\text{Fe}^{\text{III}}\text{Cl}_3/\text{PPh}_3$  to the low oxidation state complexes  $\text{Fe}^{\text{II}}\text{Cl}_2/\text{PPh}_3$  is extremely significant for AGET ATRP.<sup>38, 39</sup>

<Scheme 3>

#### Characterization of lignin-based copolymers

**FTIR analysis.** Fig. 3 shows the FTIR spectra for lignin, L-Ac, L-Br, L-g-PS, and L-g-PMMA. The peak which appears at  $3400\text{ cm}^{-1}$  suggests the existence of the hydroxyl groups of the phenolic and aliphatic in lignin, and meanwhile the peaks appear at  $2935$  and  $2845\text{ cm}^{-1}$  may be attributed to the C-H stretching of the methylene and methyl groups in the lignin molecules (Fig. 3(a)). The aromatic nucleus vibrations at  $1600$  and  $1510\text{ cm}^{-1}$  and the C-H deformation combined with aromatic ring vibration at  $1450\text{ cm}^{-1}$  are all common characteristic absorptions of lignin. The absorption at  $1765$  and  $1195\text{ cm}^{-1}$  correspond to the C=O stretching vibration of acetyl and the C-O-C asymmetric stretching vibration of L-Ac, respectively (Fig. 3(b)). As shown in Fig. 3(c), the FTIR spectrum of L-Br shows the absorption peaks at  $1740$  and  $1266\text{ cm}^{-1}$  corresponding to stretching vibration of the C=O and C-O band from 2-bromoisobutyryl ester moiety, respectively. The appearance of  $\text{CH}_3$  formation vibration at  $1389$  and  $1368\text{ cm}^{-1}$

along with a dramatic decrease in the OH stretching band at  $3400\text{ cm}^{-1}$ , confirmed the attachment of 2-bromoisobutyryl groups. Fig. 3(d) shows FTIR spectrum of the grafted copolymer L-g-PS. The characteristic absorption peaks at  $3060$  and  $3025\text{ cm}^{-1}$  can be assigned to the C-H stretching vibration of benzene ring. And the strong absorption peaks at  $760$  and  $698\text{ cm}^{-1}$  demonstrate the presence of mono-substituted aromatic nuclei which are attributed to the PS chains in the grafted materials. The FTIR spectrum of grafted copolymer L-g-PMMA is shown in Fig. 3(e), where a strong absorption peak is seen at  $1730\text{ cm}^{-1}$  due to the C=O stretching vibration of PMMA which successfully grafted on the surface of lignin. Moreover, there is stretching vibration of  $\text{CH}_3$  at  $1450\text{ cm}^{-1}$  and the adsorption peak at  $1150\text{ cm}^{-1}$  because of the combination of lignin and  $\text{CH}_2$  symmetric vibration. The absorption peak at  $1190\text{ cm}^{-1}$  is attributed to asymmetric vibration. In addition, the adsorption peaks at  $1240$  and  $1268\text{ cm}^{-1}$  are due to the symmetric vibration and asymmetric vibration of C-O, respectively.

<Fig. 3.EPS>

**$^1\text{H}$  NMR analysis.**  $^1\text{H}$  NMR spectra of L-g-PS and L-g-PMMA copolymers are shown in Fig. 4. Lignin was determined by  $^1\text{H}$  NMR in  $\text{DMSO}-d_6$  and the broad signals at  $\delta = 6.10\text{--}7.50\text{ ppm}$  and  $\delta = 3.30\text{--}4.00\text{ ppm}$  belong to aromatic protons and methoxy protons, respectively (Fig. 1(a)). Due to much lower weight fraction of lignin (<10%, Table 1), the lignin peaks for the grafted copolymers are difficult to see from  $^1\text{H}$  NMR spectra in Fig. 4(a) L-g-PS and in Fig. 4(b) L-g-PMMA.<sup>22, 26</sup> The signals at  $\delta = 6.23\text{--}7.39\text{ ppm}$  (a in Fig. 4(a)) were attributed to the aromatic protons in the lignin and PS main chains. The signals at  $\delta = 1.17\text{--}2.24\text{ ppm}$  were assigned to the methylene and methyne protons in the PS chains (b in Fig. 4(a)). The signal at  $\delta = 1.27\text{ ppm}$  (c in Fig. 4(a)) was assigned to the methyl protons of isobutyryl groups in macroinitiator L-Br. The signal at  $\delta = 3.95\text{ ppm}$  (d in Fig. 4(a)) was assigned to the methyne protons in the chain ends of PS chains because of the electron-attracting function of  $\omega\text{-Br}$  atom which from L-Br. As shown in Fig. 4(b), the signals at  $\delta = 3.59\text{ ppm}$  (e in Fig. 4(b)) and  $\delta = 3.77\text{ ppm}$  (e' in Fig. 4(b)) could be assigned to the protons of methoxy ( $\text{CH}_3\text{-O-}$ ) in the main and ends of PMMA chains, respectively.<sup>40</sup> The signals at  $\delta = 0.56\text{--}2.09\text{ ppm}$  (f in Fig. 4(b)) were attributed to methyl and methylene protons in the PMMA chains. The signal at  $\delta = 2.06\text{ ppm}$  (g in Fig. 4(b)) was assigned to the methyl protons in the chain ends of PMMA also due to the electron-attracting function of  $\omega\text{-Br}$  atom. The signal at  $\delta = 1.24\text{ ppm}$  (c in Fig. 4(b)) due to the methyl protons of isobutyryl groups in macroinitiator L-Br, which indicated that PMMA chains were successfully attached onto lignin backbone. These results indicated that Fe(III)-catalyzed AGET ATRP is an effective method for the grafting copolymerization of lignin with PS and PMMA.

<Fig. 4.TIF>

**Thermal stability.** Thermal stabilities of lignin, L-Br, and its copolymers were analyzed by thermogravimetric analysis (TGA), as shown in Fig. 5. Lignin underwent maximum thermal degradation beginning at around 310 °C. When lignin is modified with BiBB the thermal stability is lowered, and the thermal degradation of macroinitiator L-Br was earlier observed at around 240 °C. It is mainly owing to the elimination of HBr from 2-bromoisobutryl ester moiety upon the heating process.<sup>22,41</sup> Both lignin and modified L-Br showed higher thermal stability above 460 °C, mainly due to the pyrolytic degradation of the lignin backbone structure.<sup>26</sup> The weight loss tends to be stable when the temperature was above 800.0 °C and the residual weight of lignin and L-Br were 46.11 % and 29.65 %, respectively. However, after grafting with PS and PMMA with much lower weight fraction of lignin, the thermal stability of lignin-based copolymers are very different. As can be seen, L-*g*-PS showed a major degradation between 360 to 450 °C and the thermal stability is tended to stabilize above 450 °C. Somewhat differently, L-*g*-PMMA displayed lower initial decomposition temperature and the degradation occurred in two distinguish steps between 208 to 360 °C for the first step and 360 to 450 °C for the second step. The first step of degradation may be due to the decomposition of methyl ester, and the second step of degradation may be related to the decomposition of the residual PMMA moiety. Both the lignin-based copolymers showed thermal stability when the temperature was above 800.0 °C, with about 1.02 % and 4.78 % residual weight of L-*g*-PS and L-*g*-PMMA, respectively.

<Fig. 5.EPS>

**Thermal behaviour.** The glass transition temperature ( $T_g$ ) of lignin, L-Br, L-*g*-PS and L-*g*-PMMA were measured by DSC in the heating runs (Fig. 6). Unmodified lignin exhibited a single  $T_g$  at about 12.6 °C, while the  $T_g$  values of L-Br was observed with a slight increase at about 14.3 °C due to the 2-bromoisobutryl ester moiety. It was found that both the L-*g*-PS and L-*g*-PMMA copolymers exhibited two separated  $T_g$  values. The copolymer L-*g*-PS showed  $T_g$  at 14.8 and 101.7 °C, and L-*g*-PMMA showed  $T_g$  at 31.6 and 126. °C, respectively. The lower values of  $T_g$  can be assigned to lignin, while the higher values of  $T_g$  can be ascribed to the PS or PMMA chains which are grafted on the surface of lignin backbone via Fe(III)-catalyzed AGET ATRP. Moreover, both the two  $T_g$  values of L-*g*-PS and L-*g*-PMMA copolymers are higher than the corresponding  $T_g$  values of lignin and L-Br, respectively.

<Fig. 6.EPS>

**Surface morphology.** The surface morphologies of lignin, L-Br, and L-*g*-PS and L-*g*-PMMA were investigated with FE-SEM and the FE-SEM images are shown in Fig. 7. It can be observed that lignin has a rough surface with the granular crowded together, and there are some microscopic cavities dispersed among the particles (Fig. 7(a)). Compared to original lignin, the apparent structure of lignin-based macroinitiator L-Br became less rough

after modified by BiBB (Fig. 7(b)). As shown in Fig. 7(c), it can be observed that the surface of L-*g*-PS is scattered with a large number of microspheres. After the grafting process, the surface of lignin was homogeneously covered by PMMA and indicating existence of the much more harmonized structure (Fig. 7(d)). The morphologies of L-*g*-PS and L-*g*-PMMA were completely changed after grafting copolymerization via Fe(III)-catalyzed AGET ATRP.

< Fig. 7.TIF >

## Conclusions

In conclusion, we demonstrated a novel Fe(III)-catalyzed AGET ATRP to carry out the grafting copolymerization of lignin with St and MMA in homogeneous medium for the first time. The initiators system using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as catalyst,  $\text{PPh}_3$  as ligand and Vc as a reducing agent. The synthesized lignin-based copolymers, L-*g*-PS and L-*g*-PMMA, were characterized by  $^1\text{H}$  NMR, FTIR, DSC, TGA and FE-SEM.  $^1\text{H}$  NMR showed that the detailed structural conformation of the lignin and its copolymers, L-*g*-PS and L-*g*-PMMA. FTIR analysis of L-*g*-PS and L-*g*-PMMA confirmed that the PS and PMMA chains have been successfully grafted onto lignin backbone. The DSC indicated that the graft copolymer had two  $T_g$  values and both of them are higher than those of the original lignin. The thermal stability of the graft copolymers, L-*g*-PS and L-*g*-PMMA, are very different from original lignin. The copolymer L-*g*-PS showed an increase in thermal stability, as the major degradation temperature increased from approximately 310 to 360 °C, while L-*g*-PMMA showed lower initial decomposition temperature and the degradation occurred in two distinguish steps. More interesting is the fact that the apparent structure of the lignin changed greatly after grafting with PS and PMMA chains, which further confirmed that the grafting copolymerization have been occurred between lignin and both polymers. The GPC results showed the narrow molecular weight distributions of the copolymers, PDI = 1.11 for L-*g*-PS and PDI = 1.06 for L-*g*-PMMA could be obtained, which indicated that Fe(III)-catalyzed AGET ATRP is a "living"/controlled technique for grafting copolymerization of lignin with St and MMA. These results indicated that PS and PMMA chains have been successfully grafted onto the lignin backbone via Fe(III)-catalyzed AGET ATRP using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as catalyst,  $\text{PPh}_3$  as ligand and Vc as a reducing agent. The current Fe(III)-catalyzed AGET ATRP showed more effective and easier to control than conventional ATRP and other LCFRP techniques, provided a novel and environment friendly method to synthesize lignin-based copolymers, and should be contributed to the widespread use of grafting copolymerization of lignin with vinyl monomers.

## Acknowledgements

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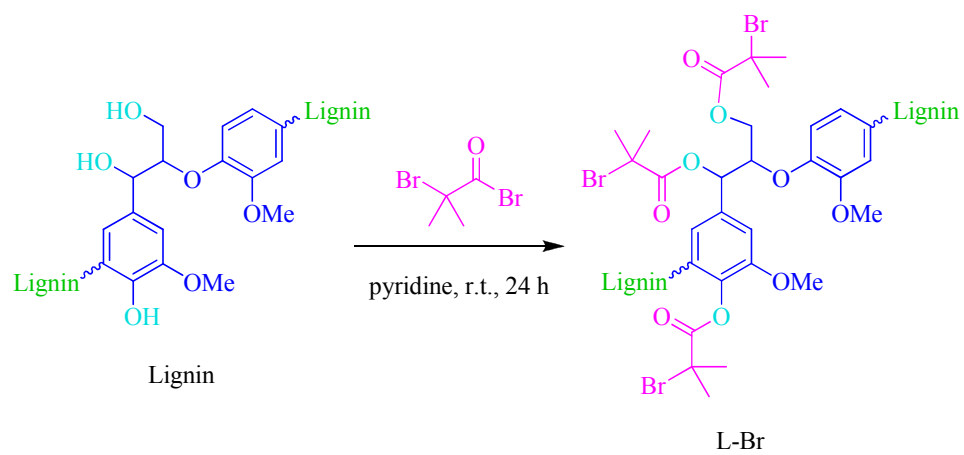
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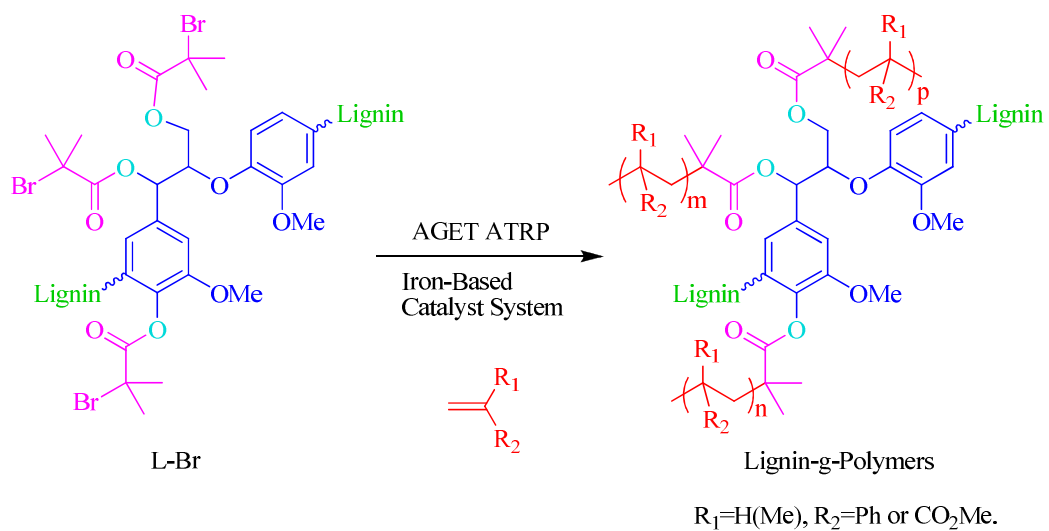
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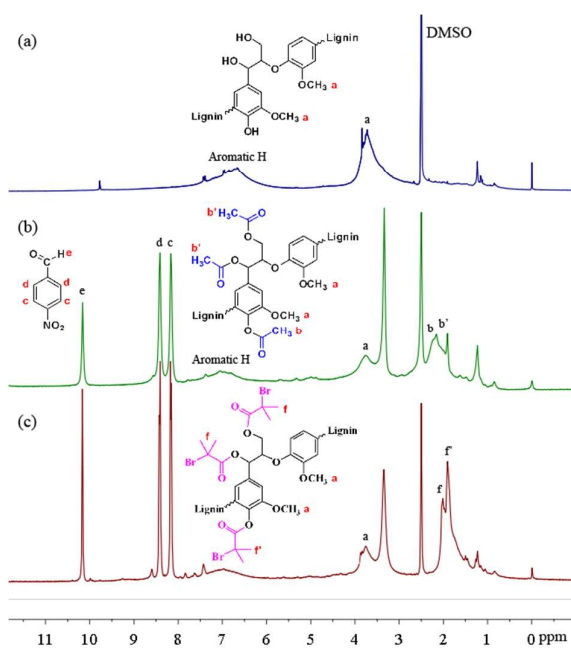
&lt; Scheme 1 &gt;



&lt; Scheme 2 &gt;



&lt;Fig. 1.TIF&gt;



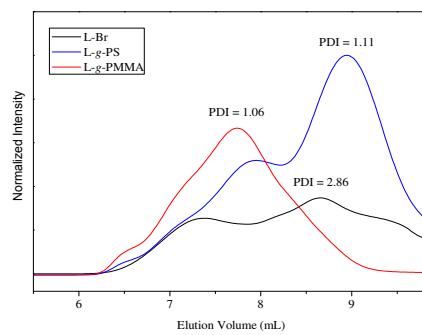
&lt; Table 1 &gt;

Sample	Yield (g)	Conv. (%)	Mass % lignin <sup>a</sup>	$M_n$ (g mol <sup>-1</sup> )	PDI <sup>b</sup>
L-Br	-	-	-	7200	2.86
L-g-PS	1.9167	35.87	9.55	44800	1.11
L-g-PMMA	3.2312	65.28	6.15	38400	1.06

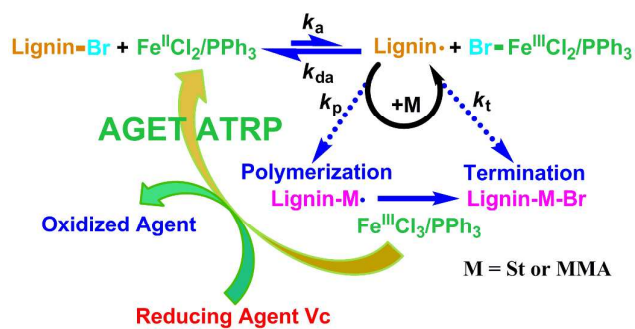
<sup>a</sup> Mass % lignin was calculated according to equation as follows:  $Mass \% lignin = (m_{L-Br} - m_R) / m_T$ . Where  $m_{L-Br}$  is the weight of original L-Br,  $m_R$  is the weight of residual unreacted L-Br,  $m_T$  stands for the total weight of grafted copolymer. <sup>b</sup>  $PDI = M_w / M_n$ ,  $M_w$  stands for the weight-average molecular weight.



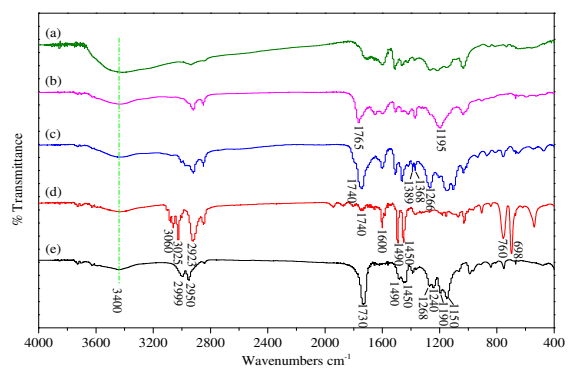
&lt;Fig. 2.EPS&gt;



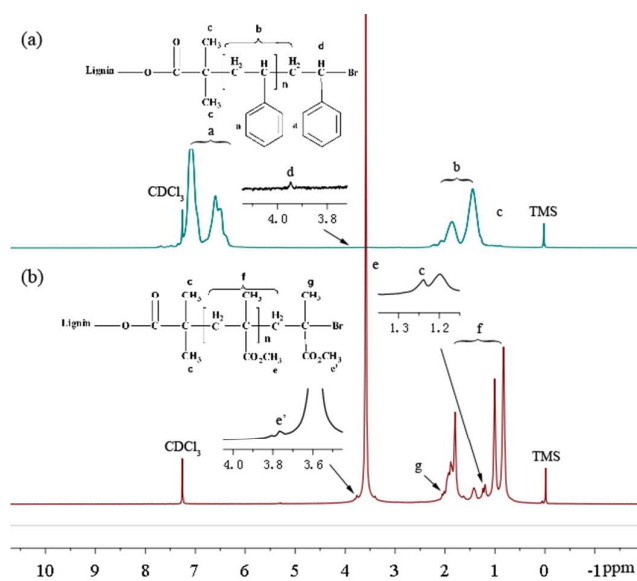
&lt; Scheme 3.TIF &gt;



&lt;Fig. 3. EPS&gt;

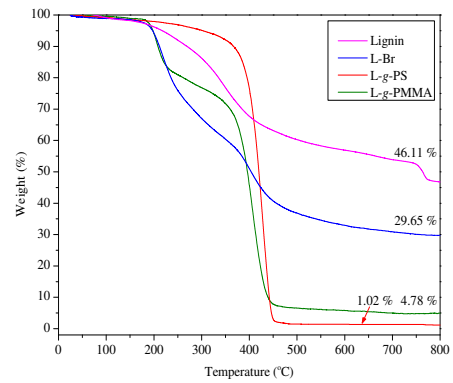


&lt;Fig. 4.TIF&gt;

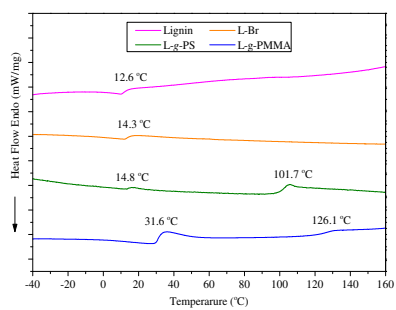




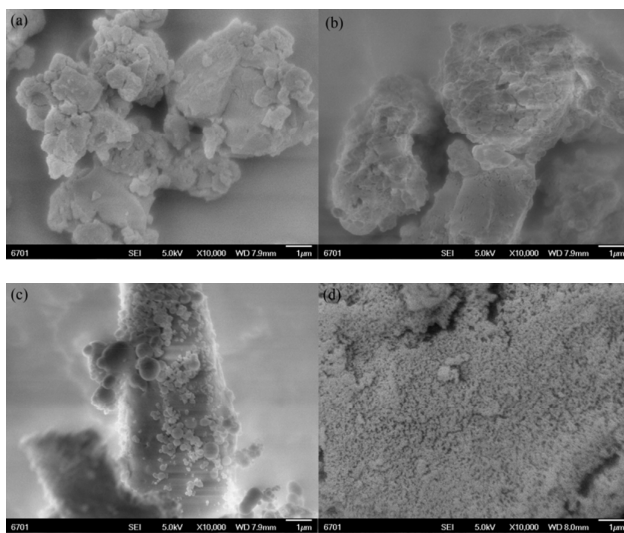
&lt;Fig. 5. EPS&gt;



&lt;Fig. 6. EPS&gt;



&lt;Fig. 7. TIF&gt;



**Figure Caption:**

< **Scheme 1** > Scheme 1 Synthesis of lignin macroinitiator (L-Br)

Scheme 1 showed the synthesis of lignin macroinitiator L-Br.

< **Scheme 2** > Scheme 2 Synthesis strategy of L-*g*-Polymers through Fe(III)-catalyzed AGET ATRP

Scheme 2 showed the strategy toward the copolymers of lignin grafted PS and PMMA via Fe(III)-catalyzed AGET ATRP.

< **Fig. 1.TIF** > Fig. 1 <sup>1</sup>H NMR spectra of (a) lignin, (b) L-Ac, and (c) L-Br in DMSO-*d*<sub>6</sub>

Fig. 1 showed the <sup>1</sup>H NMR spectra of (a) lignin, (b) L-Ac, and (c) L-Br in DMSO-*d*<sub>6</sub>.

< **Table 1** > Table 1 The molecular weights and PDI of L-Br, L-*g*-PS and L-*g*-PMMA copolymers

Table 1 summarized the results of the molecular weights and PDI of L-Br, L-*g*-PS and L-*g*-PMMA copolymers.

< **Fig. 2.EPS** > Fig. 2 GPC traces of L-Br, L-*g*-PS, and L-*g*-PMMA

Fig. 2 showed the GPC traces of L-Br, L-*g*-PS, and L-*g*-PMMA.

< **Scheme 3.TIF** > Scheme 3 Proposed mechanism for AGET ATRP of grafting copolymerization

Scheme 3 showed the proposed reaction mechanism for Fe(III)catalyzed AGET ATRP of grafting copolymerization.

< **Fig. 3.EPS** > Fig. 3 FTIR spectra for (a) Lignin, (b) L-Ac, (c) L-Br, (d) L-*g*-PS, and (e) L-*g*-PMMA

Fig. 3 showed the FTIR spectra for (a) Lignin, (b) L-Ac, (c) L-Br, (d) L-*g*-PS, and (e) L-*g*-PMMA.

< **Fig. 4.TIF** > Fig. 4 <sup>1</sup>H NMR spectra of (a) L-*g*-PS, and (b) L-*g*-PMMA in CDCl<sub>3</sub>

Fig. 4 showed the <sup>1</sup>H NMR spectra of (a) L-*g*-PS, and (b) L-*g*-PMMA in CDCl<sub>3</sub>.

< **Fig. 5.EPS** > Fig. 5 TGA curves of lignin, L-Br, L-*g*-PS, and L-*g*-PMMA

Fig. 5 indicated the thermal degradation behavior of lignin, L-Br, L-*g*-PS, and L-*g*-PMMA.

< **Fig. 6.EPS** > Fig. 6.DSC curves of lignin, L-Br, L-*g*-PS, and L-*g*-PMMA

Fig. 6 illustrated the glass-transition temperatures (*T*<sub>g</sub>) of lignin, L-Br, L-*g*-PS, and L-*g*-PMMA.

< **Fig. 7.TIF** > Fig. 7 FE-SEM images of (a) lignin, (b) L-Br, (c) L-*g*-PS, and (d) L-*g*-PMMA

Fig. 7 showed the morphological characteristics of (a) lignin, (b) L-Br, (c) L-*g*-PS, and (d) L-*g*-PMMA.