Accepted Manuscript

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PII: S1001-8417(17)30244-9
DOI: http://dx.doi.org/doi:10.1016/j.cclet.2017.07.008
Reference: CCLET 4126

To appear in: *Chinese Chemical Letters*

Received date: 24-4-2017
Revised date: 15-5-2017
Accepted date: 5-7-2017

Please cite this article as: Jilei Wang, Shang Li, Ruiqi Liang, Bing Wu, Yaning He, Synthesis and characterization of water-soluble PEGylated lignin-based polymers by macromolecular azo coupling reaction, Chinese Chemical Lettershttp://dx.doi.org/10.1016/j.cclet.2017.07.008

<DOCHEAD>Communication

<AT>Synthesis and characterization of water-soluble PEGylated lignin-based polymers by macromolecular azo coupling reaction

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<ABS-Head><ABS-HEAD>Graphical abstract

<ABS-P>► Water-soluble PEGylated lignin polymers were efficiently synthesized by macromolecular azo coupling reaction between alkali lignin and PEG based macromolecular diazonium salts in alkaline water.

<ABS-HEAD>ABSTRACT

<ABS-P>Water-soluble PEG grafted lignin-based polymers (AL-*azo*-PEG) were efficiently synthesized by macromolecular azo coupling reaction between alkali lignin and PEG based macromolecular diazonium salts in alkaline water. This one-step PEGylation method showed many advantages such as high efficiency, controllable grafting radio, extremely mild conditions and without organic solvents. The prepared AL-*azo*-PEG polymers were well characterized by using various spectroscopic methods including UV-vis, FTIR and ^{1}H NMR spectra.
<ABS-P><ST>Experimental</ST> results showed that the synthesized polymers had good solubility both in water over a wide pH range (pH 2-12) and in the majority of organic solvents, which helped to easily fabricate self-assembly colloidal particles and nanofibers by vapor diffusion method and electrospinning method, respectively. The azobenzene linkages generated by the macromolecular azo coupling reaction also brought photo-responsive properties to the prepared polymers.

<KWD>*Keywords:*
Lignin-based polymers
Water-soluble
Macromolecular azo coupling reaction
Colloid particles
Nanofibers

Natural polymers with great advantages of eco-friendliness, low cost, abundance, and biocompatibility have attracted more and more attention in recent years [1]. Lignin is one of the major natural biopolymers commonly found in cell walls of wood and annual plants, and is also the second most abundant bioresource after cellulose on earth, which represents up to 40% of the dry biomass weight [2-4]. Large quantities of industrial lignin are produced annually as a by-product in pulping industries and biorefineries [5,6]. The adequate reactive groups existed in lignin such as phenolic hydroxyl, aliphatic hydroxyl and carbonyl groups can be functionalized with the installment of desirable properties. Despite the huge possibilities, lignin technologies are still in the stage of initial development. Lignin-based materials are not often utilized as high value products or even to be discarded as waste. How to selectively convert the lignin into useful chemicals is a burning question due to its practically insoluble and highly complex three-dimensional structure. Additionally, the brittle nature of lignin and its incompatibility with some nonpolar polymeric systems have confined its progress in developing new lignin-based materials with high performance [7,8]. Up to date, great efforts have been devoted to obtain valuable lignin-based materials [9-16]. Chemical grafting by using free radical polymerization, condensation polymerization and even a chemo-enzymatic approach has been applied to adjust the hydrophilic-hydrophobic balance, which will further improve the compatibility with other polymer systems especially the synthetic materials [17-20]. Poly(ethylene glycol) (PEG) with the advantage of low toxicity, good biocompatibility and biodegradability also has been used to functionalize lignin in order to improve the water solubility of lignin [21-23]. However, the functionalized lignin-PEG copolymers were obtained in organic solvents or complicated procedure, which is not environment-friendly.

Azo coupling reaction was an efficiently reaction to prepare organic azobenzene molecules or side chain azo polymers with high degree of functionalization [24-27]. Recently, we reported that well-defined block copolymers can be easily prepared by azo coupling reaction between macromolecular diazonium salt and polymeric block with terminal anilino functionality in organic solvent such as DMF [28-30]. The prepared polymers also showed many interesting properties [31-34]. Besides the anilines, aromatic diazonium salts can also react with phenols to give the azobenzene products. Anyway, up to date, the efficient azo coupling