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PAPER

CO₂-responsive diethylaminoethyl-modified lignin nanoparticles and their application as surfactant for CO₂/N₂-switchable Pickering emulsions

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Water-insoluble lignin is modified via atom transfer radical polymerization (ATRP) grafting of 2-(diethylamino)ethyl methacrylate (DEAEMA). These lignin-*g*-DEAEMA samples can be easily dispersed in water upon CO₂ bubbling. They can also be quickly precipitated out by N₂ bubbling. The CO₂/N₂-switchability of dispersion/precipitation is correlated to the graft density and chain length of DEAEMA units. This gas-switchable feature renders the lignin materials a wide range of potential applications. Demonstrated in this work is the use of lignin-*g*-DEAEMA as surfactant for Pickering emulsion. An emulsion of decane is prepared with the lignin nanoparticles and it can be demulsified and re-emulsified by bubbling of the two gases. The emulsification/demulsification processes are highly reversible and easily repeatable. This work represents an innovative approach in developing value-added lignin materials.

Introduction

Exhaustion and environment impact of fossil feedstock call to develop alternative and sustainable resources.¹ Biomass such as lignocellulose is an attractive candidate.²⁻⁵ Lignin is abundant and it is also the by-product of pulping and papermaking industry. As the only biomass containing aromatic structures, it counts for 15 to 36 weight percent of lignified plants.⁶ Conversion of lignin into useful materials helps reduce our dependence on petroleum feedstock. Original lignin, connected to the carbohydrate in plant, cannot be dissolved in any solvent until it is processed through some separation and purification procedures.⁷ Basic hydrophobic phenylpropane units together with some hydrophilic groups can be introduced in separation processes. These functional groups render lignin potential uses in such areas as nature amphiphilic surfactant.⁸ However, the major type of industrial lignin, i.e. alkali lignin, can only be dissolved in highly basic solution or organic solvents, which are hazardous to environment and facilities. At the same time, the application performance of alkali lignin is usually unsatisfactory when it is used directly and some modification is needed in order to make it more useful.

In improving the industrial lignin's applicability, chemical modifications on both side chains and aromatic rings of the lignin have been attempted. On its side chains, most modifications target the phenylcarbinol groups and the alkyl/aralkyl ether linkages. Sulfonating, hydrosulfiding and phenolating reactions can occur in the delignification stage of pulping processes.⁹⁻¹¹ Sulfonated lignosulfonate and its derivatives resulted from further modification have been used as concrete water reducers, water-coal-slurry dispersants, and pesticide dispersants.¹²⁻¹⁴ On the aromatic rings of lignin, halogenating and nitrating can be easily carried out. For example, the hydrophobicity of lignin can be enhanced when alkyl chain is introduced by reacting with alkyl

halide.¹⁵ Aliphatic amine can be introduced by Mannich reaction, which can significantly improve the surfactivity of lignin.¹⁶ The lignin-amine products are effective in emulsifying cationic asphalt and crude oils.^{17, 18}

Chemical grafting represents another effective approach in lignin modification. It can give lignin some novel properties of the "smart" chemicals. One kind of "smart" chemicals of great interest is stimuli-responsive polymers. The properties of these polymers can be adjusted by thermal, light, pH and other stimuli.¹⁹⁻²¹ For example, poly(*N*-isopropyl acrylamide) is well known to be thermo-responsive. It has been grafted from lignin and the polyNIPAM-grafted lignin is thermal responsive.^{22, 23} However, it should be pointed out that each type of stimuli has its merits and drawbacks. Light is limited to its radiation depth. pH changes by acid/base hurt equipment and facilities and accumulate salts. It is also slow and energy consuming to change temperature for a large volume sample.

The recent advent of gas-responsive chemicals and polymers provides a great opportunity for developing smart materials and processes. Compared to the other stimuli, gas is easy to operate and is not limited to sample volume in operation. Recently, amine-containing polymers such as poly(2-(diethylamino) ethyl methacrylate) (PDEAEMA) and poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) are found to be CO₂ responsive. These polymers and their quaternary derivatives are commercially available and have been widely used in such areas as water treatment, papermaking, oil recovery and biomedicine.²⁴⁻²⁷ PDEAEMA has limited solubility in water. After treated with CO₂, they become more hydrophilic and thus more soluble in water. More interestingly, CO₂ can be washed off by N₂ bubbling. The solubility of the polymers is thus switchable with the CO₂/N₂ treatments.

The objective of this work is to modify alkali lignin by grafting small amount of CO₂-responsive 2-(diethylamino) ethyl

methacrylate (DEAEMA) and to demonstrate CO₂/N₂ switchable dispersion/precipitation of the modified lignin nanoparticles in water. We used atom transfer radical polymerization (ATRP) for its good control over the chain length of DEAEMA units. Alkali lignin was partially or fully functionalized with an ATRP initiator and used as a macroinitiator for grafting of DEAEMA from lignin. The dispersion of the DEAEMA-grafted lignin was investigated and correlated to the graft density and chain length of DEAEMA units. We also demonstrated the applicability of the lignin-*g*-DEAEMA nanoparticles as surfactant for preparation of Pickering emulsions and tested the CO₂/N₂-triggered emulsification/demulsification of the emulsion system. It should be pointed out that previous lignin modifications employed highly basic/acidic conditions, while nearly neutral conditions were used in the present work.

Experimental section

Materials

N, N-diethylaminoethyl methacrylate (DEAEMA) (containing 1500 ppm MEHQ as inhibitor, 99%) was purchased from Sigma-Aldrich, and was passed through an inhibitor remover and stored at -4 °C prior to use. N, N, N', N'', N'''-pentamethylenediethylenetriamine (PMDETA) (Aldrich, 99%), α -bromoisobutyryl bromide (BiBB) (Aldrich, 98%), and copper (I) bromide (CuBr) (Aldrich, 99.999%), decane (Aldrich, anhydrous, $\geq 99\%$) were used as received. Alkali lignin was supplied by Shuntai Technology Corp (Huaihua, Hunan, China), and was purified by "alkali-acid" treating for three cycles and continuous washing by DI water. The number-average molecular weight of purified lignin was 2500 g/mol as determined by gel permeation chromatography (GPC). The amounts of phenolic and aliphatic hydroxyl groups of lignin were 4.252 and 4.313 mmol/g, estimated from the titration and ¹H NMR results.^{23, 28} Other chemicals were also used as received without further purification.

Synthesis of lignin-based macroinitiator (lignin-Br)

Fully and partially substituted lignin-based macroinitiators were prepared according to the procedures reported in literature.²⁸ Specifically, the partially substituted macroinitiator was prepared by reacting lignin (200 mg, 0.85 mmol) with BiBB (293 mg, 1.27 mmol) in ethylacetate (2 mL) in the presence of triethylamine (129 mg, 1.27 mmol) at room temperature for 1.5 hours. Fully substituted macroinitiator was prepared by reacting lignin (200 mg, 0.85 mmol) with BiBB (1.564 g, 6.8 mmol) in THF (2 mL) in the presence of pyridine at room temperature for 24 hours. The purification process was the same as in the literature.

¹H NMR (200 MHz, DMSO-*d*₆, δ (ppm)): 1.87 (3H, s, (CH₃)₂-BrCCOO-lignin), 2.0 (3H, s, (CH₃)₂-BrCCOO-Ph-lignin).

Synthesis of lignin-*g*-DEAEMA by ATRP grafting

Five lignin-*g*-DEAEMA samples were synthesized from the partially and fully substituted lignin-Br. Take F5 as an example, macroinitiator (60 mg, 0.227 mmol) was dissolved in DMF (2 mL) in the first flask, monomer DEAEMA (210 mg, 1.133 mmol) was dissolved in DMF (1 mL) in the second flask, and catalyst CuBr (32.534 mg, 0.227 mmol) was charged in the third flask. Nitrogen was continuously bubbled into the flasks for >30 min to remove oxygen. The monomer was transferred into the third flask via a

two-tipped needle and the ligand PMDETA (47.35 μ L, 0.227 mmol) was added. The mixture in the third flask was then gradually transferred to the first flask. The flask was sealed and placed into an oil bath of 70 °C. After 24 hours, the flask was opened to air to stop the reaction. The reaction mixture was passed through a neutral aluminum oxide column to remove the copper catalyst, and then dropped into excess amount of hexane to precipitate out the lignin-*g*-DEAEMA samples. They were then dried under vacuum for further use. The monomer conversion was determined from the NMR results of the reaction mixtures. Figure 1 shows the functionalization of lignin with an ATRP initiator and the synthesis of lignin-*g*-DEAEMA through atom transfer radical polymerization (ATRP) of DEAEMA.

¹H NMR (200 MHz, DMSO-*d*₆, δ (ppm)): 0.87 (3H, s, CH₂(CH₂)C(CH₃)COO DEAEMA), 1.06 (3H, t, CH₂N(CH₂CH₃)₂ DEAEMA), 2.2 (3H, s, DEAEMA-CH₃-Br), 2.6 (2H, q, CH₂N(CH₂CH₃)₂ DEAEMA), 2.7 (2H, t, CH₂N(CH₂CH₃)₂ DEAEMA), 3.75 (3H, s, OCH₃ lignin methoxy), 4.02 (2H, t, COOCH₂CH₂ DEAEMA).

Preparation of Pickering emulsions

A lignin-*g*-DEAEMA sample (4 mg) and water (4 mL) were charged to a vial, which was bubbled with CO₂ for 4 h until a well-dispersed solution was obtained. The dispersion was then bubbled with N₂ for 0.5 h to remove CO₂. Decane (1 mL) was added to the dispersion and it was homogenized at 20,000 rpm for 1 min. It should be pointed out that the bubbling process was diffusion controlled. Any improvement in gas/liquid contact and mass transfer would significantly shorten the bubbling time. With

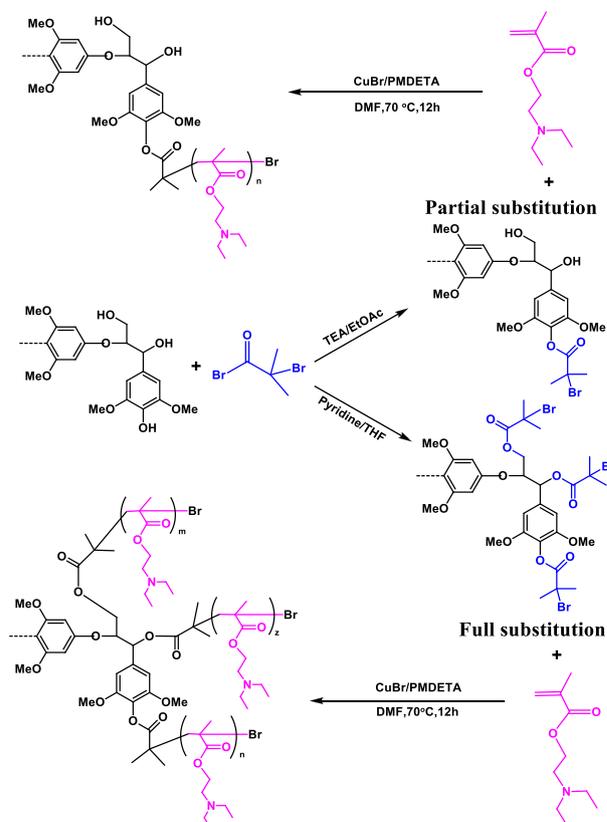


Fig. 1 Synthesis of lignin-*g*-DEAEMA via ATRP of DEAEMA

some help of ultrasonication, it was reduced from 4 h to 1 h.

Characterization

^1H NMR measurements were done using a Bruker 200 MHz spectrometer. Specifically, 5 mg lignin-g-DEAEMA samples were dissolved in 0.5 mL of chloroform- d . After 24 hours, the NMR spectra were recorded at 300 K and 64 scans were collected. A delay of 7 s was used to ensure complete relaxation of the aldehyde protons. The determination of phenolic hydroxyl group was performed on the automatic potentiometric titrator (809 Titrando, Metrohm Corp., Switzerland) by non-aqueous conductometric titration. The number-average molecular weight of lignin was determined by Agilent 1100 series gel permeation chromatography (GPC) after acetylation. The mobile phase was THF and the flow rate was 1 mL/min. The acetylating procedure of alkali lignin was the same as that reported.²⁸ Effective diameters of lignin samples were measured by dynamic light scattering (DLS). DLS measurements were performed using a BI-9100 AT digital correlator (Brookhaven, USA) apparatus and 35 mW laser with a wavelength of 632.8 nm at 90°. The temperature was kept at 25 °C. The emulsion droplets were observed using a Zeiss Axiovert 100M microscope and the images were acquired with Zeiss Axio Cam HRc camera (Zeiss, Thornwood, NY, USA). The images of lignin-g-DEAEMA nanoparticles and microstructures of the corresponding Pickering emulsions were obtained using a JEOL JEM 1200EX TEMSCAN transmission electron microscope (TEM) (JEOL, Peabody, MA, USA) with an accelerating voltage of 80 kV.

Results and discussion

Synthesis of lignin-g-DEAEMA

Due to a large number of hydroxyl groups in lignin, 2-bromoisobutyryl ester can be easily introduced as initiating site for ATRP. Phenolic hydroxyl groups can be selectively esterified in the presence of aliphatic hydroxyl groups when TEA is added.²³ Therefore, partially and fully substituted lignin-Br macroinitiators were prepared in this work, aiming at different grafting densities of DEAEMA units. Figure 2 shows the ^1H

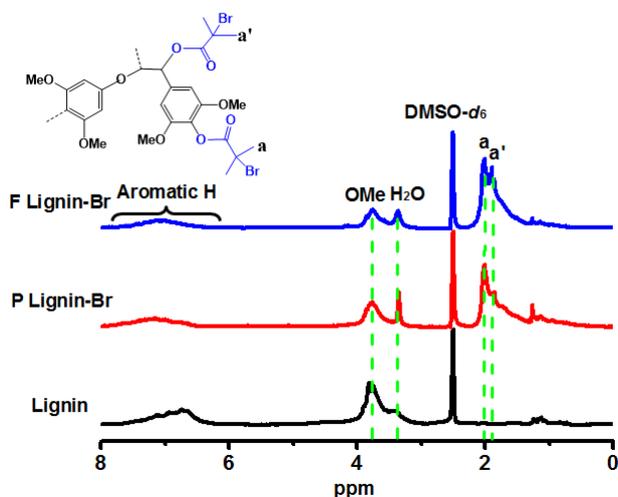


Fig. 2 ^1H NMR spectra of alkali lignin, partially and fully substituted lignin-Br in $\text{DMSO}-d_6$.

NMR spectra. The signals near 2.0 ppm and 1.85 ppm were from the bromoisobutyryl ester moieties substituted at the phenolic and aliphatic hydroxyl groups, respectively. When TEA was added, the signal near 1.85 ppm decreased significantly, confirming the partial substitution of lignin. The average number of initiator functional groups on each lignin molecule was estimated to be about 11 and 21 for partially and fully substituted samples, respectively.

DEAEMA-grafted lignin samples with targeted chain lengths of 1 to 10 DEAEMA repeat units were then synthesized via ATRP, by using the partially and fully substituted lignin-Br. The resulting samples after purification could no longer be dissolved in DMSO and thus their ^1H NMR spectra were recorded in CDCl_3 . As shown in Figure 3, the characteristic chemical shifts of grafted DEAEMA were obvious, with signals at 0.87 ppm, 1.06 ppm, 2.6 ppm, 2.7 ppm and 4.02 ppm referred to $\text{CH}_2(\text{CH}_2)\text{C}(\text{CH}_3)\text{COO}$, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$ and $\text{COOCH}_2\text{CH}_2$ of DEAEMA units. The characteristic shift of H in DEAEMA's methyl group closest to bromide was at 2.2 ppm. At the same time, the peak area ratios of these signals ($A_{0.87+1.06+2.2}$: $A_{2.6+2.7}$: $A_{4.02}$) were very close to their stoichiometric ratios (9: 6: 2), where $A_{0.87+1.06+2.2}$ is the peak area at 0.87, 1.06 and 2.2 ppm, $A_{2.6+2.7}$ is the peak area at 2.6 and 2.7 ppm, and $A_{4.02}$ is that at 4.02 ppm. However, there was no obvious signal of lignin, except for the very weak signal of methoxyl group near 3.75 ppm, which could be found in the insert spectrum of Figure 3. This might be caused by the limited solubility of lignin in CDCl_3 .

When bromide initiator sites were activated and DEAEMA grafted from lignin, the characteristic chemical shift of H in the bromoisobutyryl ester moiety (position a^* in Figure 3) moved from the original 2 ppm around to 1.24 ppm. Therefore, the chain length (n) of the grafted DEAEMA units and the initiator efficiency (f) of the lignin-Br could be calculated. The chain length (n) could be estimated from the relative areas characteristic of DEAEMA units to the bromoisobutyryl ester connected to DEAEMA ($A_{1.24}$). For example, $A_{4.02}/A_{1.24} = 2n/6$ and then n could be calculated from the ratio $A_{4.02}/A_{1.24}$. At least, three n values could be estimated from the areas of different H's in

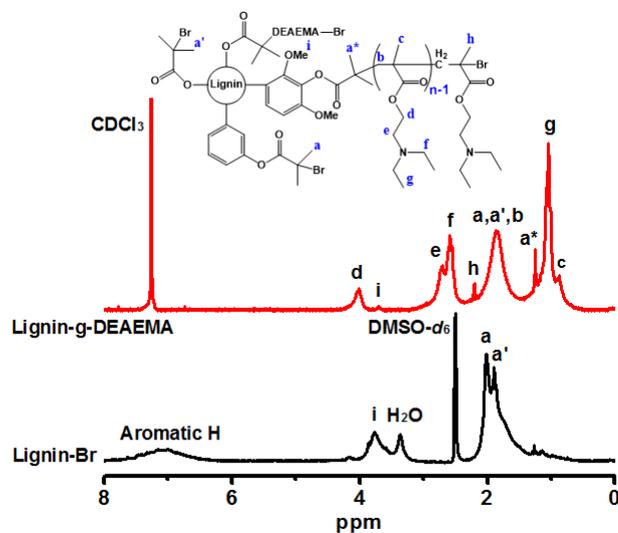


Fig. 3 Typical ^1H NMR spectra of fully substituted lignin-Br in $\text{DMSO}-d_6$ and its corresponding lignin-g-DEAEMA sample in CDCl_3 .

grafted DEAEMA and Table 1 listed the average values of the three estimated chain lengths (n_{ave}).

The initiator efficiency (f) could be estimated according to $f = n_d/n_{ave} = n_d \cdot \alpha / n_{ave}$, where α is the conversion of DEAEMA, n_d and n_a are the designed and the theoretical chain lengths. Please note that the designed chain length is the targeted value at a complete monomer conversion, while the theoretical chain length is the value at the present monomer conversion assuming all the initiating sites effectively activated for the growth of DEAEMA. As shown in Table 1, all the theoretical chain lengths were shorter than the experimental ones estimated from the NMR data, suggesting that not all the bromide sites were activated. As the amount of monomer increased, the initiator efficiency increased, regardless of partial or full substitution. This was because the initiating sites had a better access to monomer molecules to trigger the grafting reaction. The initiator efficiency in F1 was therefore the lowest. It could also be observed that the initiator efficiency of the fully substituted lignin-Br was a little higher than that of the partially substituted lignin-Br, suggesting that the -Br substituted from aliphatic hydroxyl was more efficient than that from aromatic hydroxyl in initiating ATRP.

Switchability of lignin-g-DEAEMA nanoparticles

All the five DEAEMA-grafted lignin samples were hydrophobic, none of them could be dispersed in water even with the help of ultrasonication. However, after treated with CO₂, light yellow transparent solutions were obtained, as shown in Figure 4. DLS results showed that the dispersed particles had their sizes in the range of 237–404 nm.

CO₂ could be easily washed off with N₂ bubbling. When N₂ was bubbled into the well dispersed lignin-g-DEAEMA aqueous solutions, the five lignin-g-DEAEMA samples were all flocculated. F1 was almost instantaneously flocculated and precipitated out because of its shortest DEAEMA chain length. In comparison, it took much longer time for F10. Due to its longest chain length, F10 was flocculated and suspended in water after N₂ bubbling. The samples prepared from the partially substituted lignin-Br (P5 and P10) were easier to flocculate due to their lower amount of DEAEMA units. All the five samples could be precipitated out if N₂ bubbling was remained for a sufficiently long time. The flocculated suspensions could be easily re-dispersed into water with CO₂ bubbling. This CO₂/N₂-triggered switchability between dispersion and flocculation of the lignin-g-DEAEMA nanoparticles was repeatable.

Table 1 Designed, theoretical, actual chain lengths (n_d , n_a , n_{ave}), monomer conversion (α) and initiator efficiency (f) of lignin-g-DEAEMA materials.

Samples*	n_d	α	n_a	n_{ave}	f
F1	1	0.74	0.74	1.8	0.42
F5	5	0.44	2.2	3.3	0.68
F10	10	0.39	3.9	5.0	0.78
P5	5	0.25	1.25	1.9	0.65
P10	10	0.27	2.7	3.8	0.70

*F and P stand for lignin-g-DEAEMA prepared from fully and partially substituted lignin macroinitiators respectively, with the number (1, 5 and 10) standing for the designed chain length of grafted polyDEAEMA.

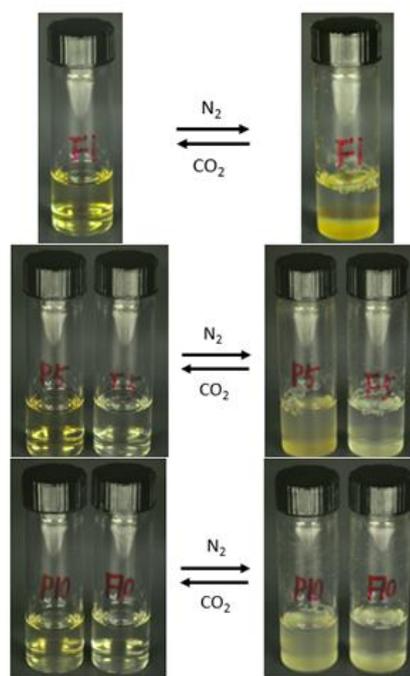


Fig. 4 Switching between dispersion and flocculation/precipitation of the lignin-g-DEAEMA nanoparticles in water with CO₂ and N₂ bubbling.

CO₂/N₂-switchable Pickering emulsions

We employed the above gas-switchable lignin-g-DEAEMA nanoparticles as surfactant for the preparation of Pickering emulsions. Decane was used as the oil phase. Stable Pickering emulsions were obtained by homogenizing decane in water with the added lignin samples. The morphology and microstructure of the Pickering emulsion droplets were visualized by microscope and TEM. Figure 5a shows the Pickering emulsion, formed from homogenizing the oil at 20 000 rpm for 1 min in an aqueous phase containing suspended F5. This emulsion was still stable after stored for one month. These emulsion droplets were all spherical and micrometer scale, as shown in Figure 5b. To analyze the droplet structure, the emulsion was frozen on a grid for TEM observation. It is evident in Figure 5c and 5d that there was an obvious boundary after evaporation of the oil phase and that the boundary contained the lignin nanoparticles. The size of the F5 particles observed here was smaller than the DLS measurement because of breaking down of the particles during the homogenization.

The prepared Pickering emulsion could be demulsified within ten minutes of CO₂ bubbling. Figure 6 shows three cycles of CO₂/N₂-triggered emulsification and demulsification. At first, the lignin-g-DEAEMA (F5) was dispersed in water by bubbling CO₂

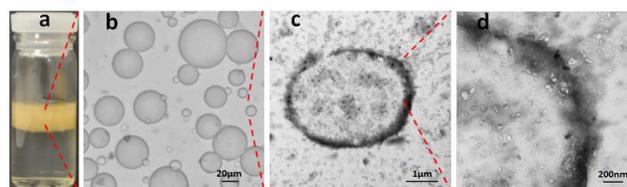


Fig. 5 Pickering emulsion prepared using F5 as emulsifier (a) and its microscope and TEM images (b, c, d). The aqueous/oil volume ratio was 4:1. F5 in the aqueous phase was 0.1 wt%.

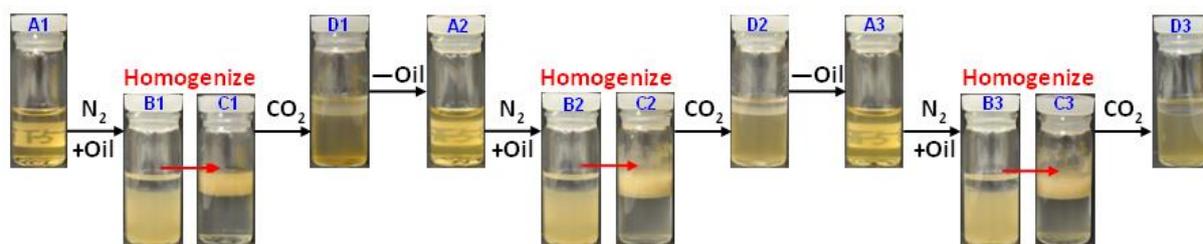


Fig. 6 Three cycles of N_2/CO_2 -triggered emulsified/demulsified process of lignin-g-DEAEMA Pickering emulsion.

(A1). Bubbling N_2 quickly flocculated and precipitated the dispersed particles. When the oil phase was added (B1) and homogenized at 20 000 rpm for 1 minute, the Pickering emulsion was formed (C1). At this time, bubbling CO_2 could demulsify the emulsion within ten minutes (D1). As a result, phase separation happened. After the oil was completely removed, a clear aqueous lignin-g-DEAEMA suspension (A2) was obtained. It could be used again in the preparation of Pickering emulsion. The following two cycles CO_2/N_2 -triggered demulsification/ and re-emulsification processes showed excellent repeatable switchability of the Pickering emulsion prepared by the lignin-g-DEAEMA nanoparticles. In comparison to the existing methods of preparing alkali lignin Pickering emulsions under an extremely acidic condition and recycling alkali lignin under highly basic condition,^{29, 30} preparation of Pickering emulsions with the lignin-g-DEAEMA and recycling of the emulsifier, in this work, were under nearly neutral conditions. This new lignin-based CO_2/N_2 -switchable Pickering emulsion can be used for oil recovery, recyclable polymerization,²⁹ templates for preparation of functional materials.^{30, 31}

Conclusions

In summary, alkali lignin was chemically modified with tertiary amine functionality through atom transfer radical polymerization (ATRP) grafting of N, N-diethylaminoethyl methacrylate (DEAEMA). The modified lignin samples could be easily dispersed in water upon CO_2 bubbling. The dispersed lignin nanoparticles could also be quickly precipitated out by N_2 bubbling. The ability of dispersion and precipitation is determined by the grafting density and chain length of the DEAEMA units. These DEAEMA-grafted lignin nanoparticles were useful in preparation of Pickering emulsions. The lignin-emulsified decane droplets could be demulsified and re-emulsified by CO_2 and N_2 bubbling. The demulsification and re-emulsification processes were highly reversible and easily repeatable. The lignin materials could be easily reclaimed and re-used in this application. Such gas-switchable lignin systems have clear advantages over the existing ones reported in literatures and may provide an innovative approach in commercial exploitation of the green industrial lignin materials.

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Notes and references

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CO₂/N₂-triggered water-dispersible/collectable lignin-g-DEAEMA nanoparticles were successfully synthesized and used to prepare emulsified/demulsified switchable Pickering emulsions by gas processing in nearly neutral condition.

