Recoverable Water-soluble Polyethylene Glycol-immobilized N-hydroxyphthalimide Mediated Oxidation of Cellulose in the Presence of NaBr and NaClO

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Abstract

As a highly efficient nitroxide radical catalyst for selective catalytic oxidation of cellulose, N-hydroxyphthalimide (NHPI) has attracted much attention because of its low price and light cellulose degradation. However, NHPI is insoluble in water and is difficult to recycle because of its small molecular weight. To address the above issues, the water-soluble polyethylene glycol (PEG)-immobilized NHPI catalyst (PEG-NHPI) was designed and prepared in this work. Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC) and UV-vis light spectroscopy were used to characterize PEG-NHPI. The results showed that PEG-NHPI catalysts with good water solubility and adjustable NHPI loading amounts were successfully synthesized. Using NaBr as promoter and NaClO as oxidant, PEG-NHPI mediated oxidation of cellulose was carried out and good catalytic performance was found. The catalytic performance of PEG-NHPI mediated oxidation of cellulose in water was higher than that in acetonitrile-water. The carboxyl content of PEG-NHPI oxidized cellulose could reach the level of free NHPI oxidized cellulose, and was equivalent to 68% of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) oxidized cellulose, while the degradation degree of cellulose was greatly reduced by more than 40%. The catalytic performance did not decrease significantly after six oxidation cycles. The structure of recycled PEG-NHPI was not changed. These results indicated that immobilizing NHPI onto PEG can achieve the unification of high catalytic performance and good recyclability.

Introduction

Oxidized cellulose, as a bio-based material widely used in high-tech fields, can be prepared by selective catalytic oxidation of primary hydroxyl groups in cellulose to carboxyl groups (Isogai et al. 2011; Coseri et al. 2012; Culica M E et al. 2021; Nabar et al. 1970). A variety of catalysts for selective catalytic oxidation of cellulose have been developed. Among them, the nitroxide radical catalysts such as 2, 2, 6, 6-tetramethylpiperidine-N-oxygen radical (TEMPO) (Hoover et al. 2011; De Mico et al. 1997; Isogai et al. 2011; Wu et al. 2019) and N-hydroxyphthalimide (NHPI) (Coseri et al. 2007; Coseri et al. 2009; Coseri et al. 2012; Coseri et al. 2018; Ishii et al. 1997; Yang et al. 2004; Zhang et al. 2014; Hu et al. 2016) have attracted much attention because of their mild reaction conditions and high catalytic performances. TEMPO mediated oxidation of cellulose has a very high oxidation rate and the by-products are water soluble salts. However, this system has several disadvantages such as high price, high toxicity and serious degradation of cellulose. As an alternative, NHPI has the advantages of low toxicity, low price and light degradation of cellulose (Coseri et al. 2018).

In the process of NHPI catalytic oxidation of cellulose, metallic or nonmetallic cocatalysts are required to stimulate NHPI to form phthalimide-N-oxylradical (PINO) through single electron transfer process (Coseri et al. 2008). Later, Coseri et al. (2018) found that in the presence of NaClO and NaBr, the transfer of NHPI to PINO can be realized efficiently in the acetonitrile/water medium. Biliuta et al. (2013) compared the catalytic properties of NHPI and TEMPO for cellulose oxidation in water. It was found that TEMPO oxidized cellulose had a higher carboxyl content, but the degradation was serious. The degradation

degree of NHPI oxidized cellulose was very light. Zhou et al. (2014) studied NHPI mediated oxidation of cellulose in acetic acid with $\text{Co}(\text{OAc})_2$ as cocatalyst and air as oxidant, and found that the prepared oxidized cellulose had very little degradation.

However, free NHPI is difficult to recycle and reuse. In order to address this issue, researchers have immobilized NHPI onto supports such as silica, molecular sieves, metal frameworks and polymer microspheres (Huang et al. 2018; Yu et al. 2014; Li et al. 2021; Dhakshinamoorthy et al. 2012; Tan et al. 2017; Jian et al. 2016; Yang et al. 2015; Huang et al. 2014, 2015; Gao et al. 2018; Yang et al. 2008). These supported NHPI catalysts have shown good catalytic performances in the catalytic oxidation of small molecule substrates (such as toluene, ethylbenzene and benzyl alcohol) and water-soluble polysaccharides, and can be easily recycled. Li et al. (2021) found that carbon microspheres supported NHPI had good catalytic performances on a variety of alcohols in acetic acid and could be recovered through filtration for recycling. Culica et al. (2019) used polystyrene to immobilize NHPI for selective oxidation of pullulan. The oxidized pullulan containing carboxyl groups was obtained, and four oxidation cycles were realized. Since both polystyrene and NHPI are water-insoluble substances, this system is not suitable for the oxidation of water-insoluble polysaccharides such as cellulose.

Polyethylene glycol (PEG) with good water-solubility can be used as carrier to prepare the water-soluble immobilized catalyst. Wan et al. (2007) used polyethylene glycol monomethyl ether (mPEG) as carrier to support TEMPO to prepare water-soluble macromolecular TEMPO catalyst. It can catalyze oxidation of various allyl alcohols and aromatic primary alcohols in the acetonitrile/water medium, showing excellent catalytic performances. Araki et al. (2016) loaded TEMPO onto mPEG 2000 to prepare a water-soluble macromolecular catalyst called mPEG 2000-TEMPO for oxidizing cellulose to prepare carboxylated nanocellulose. After the oxidation is completed, the macromolecular catalyst in the reaction medium can be recovered for the next oxidation cycle. However, because TEMPO itself has good water solubility, loading it on water-soluble macromolecules such as PEG cannot further increase its water solubility. Its large molecular weight tends to reduce its catalytic activity when used to oxidize cellulose (Liu et al. 2017, 2018a).

The loading of water-insoluble NHPI on water-soluble PEG is expected to greatly increase the water solubility and catalytic oxidation cellulose properties of the macromolecular NHPI catalyst. In this paper, NHPI was loaded on PEG via ester bonds to prepare recoverable water soluble immobilized NHPI catalyst (PEG-NHPI) for cellulose oxidation in water. Using NaBr as promoter and NaClO as oxidant, the influence of the molecular weight and NHPI loading amount of PEG-NHPI on its catalytic performance was discussed and the recycling performance was studied.

Experimental Section

Materials

Polyethylene glycol (PEG, Mw = 600, 1000, 2000, 4000, 6000, 8000), polyethylene glycol monomethyl ether (mPEG, Mw = 2000, 4000, 5000), trimellitic anhydride acid chloride (TAC, 99%), N-hydroxyphthalimide (NHPI, 99.7%), hydroxylamine hydrochloride (99%), wood derived microcrystalline cellulose powders (particle size: 25 μ m, degree of polymerization: 154), aqueous NaClO solution (8%), NaOH (96%), hydrochloric acid (36%-38%), NaBr (99%), acetonitrile (99%), 1,2-dichloroethane (99%), n-hexane (98%) and diethyl ether (99%) were purchased from Aladdin Industrial Corporation (China) without further purification. Pyridine (99%) and dichloromethane (99.5%) were purchased from Tianjin Damao Chemical Preparation Factory (China) and dried with molecular sieve before use.

Preparation of PEG-NHPI

Under nitrogen atmosphere, PEG containing 10 mmol hydroxyl groups was dissolved in dichloromethane (1 g PEG/8 mL dichloromethane). At 0 °C, 1.03 g pyridine and 20 mL dichloromethane were added. A mixture of 2.10 g of TAC and 40 mL of dichloromethane was slowly dripped. After 1 h, the temperature of reaction mixture was raised to room temperature and stirred for 12 h. The reaction solution was poured into n-hexane for precipitation to obtain the product of PEG-TAC. Then, PEG-TAC and a mixture of pyridine and 1,2-dichloroethane with a volume ratio of 3:1 (80 mL) were added into another reactor. After heating up to 80 °C, 0.69 g hydroxylamine hydrochloride and a mixture of pyridine and 1,2-dichloroethane with a volume ratio of 3:1 (20 mL) were slowly added. After dripping, the reaction mixture was stirred for 24 h. After filtering, the supernatant was poured into n-hexane for precipitation. The precipitate was freeze-dried to obtain PEG-NHPI.

By fixing the molar ratio of PEG and TAC to 1:2 and changing the molecular weight of PEG (Mw = 600, 1000, 2000, 4000, 6000, 8000), PEG-NHPI catalysts with different molecular weights were obtained, which were respectively denoted as PEG600-NHPI, PEG1000-NHPI, PEG2000-NHPI, PEG4000-NHPI, PEG6000-NHPI and PEG8000-NHPI. Similarly, by fixing the molar ratio of mPEG and TAC to 1:1 and changing the molecular weight of mPEG (Mw = 2000, 4000, 5000), mPEG-NHPI catalysts with different molecular weights were obtained, which were recorded as mPEG2000-NHPI, mPEG4000-NHPI and mPEG5000-NHPI, respectively.

NHPI mediated oxidation of cellulose

NHPI mediated oxidation of cellulose in acetonitrile/water was similar to the process reported by Coseri et al. (2018): Cellulose (2 g), NHPI (0.163 g, 1 mmol), NaBr (1.65 g, 16 mmol), and a mixture of acetonitrile/water with a volume ratio of 5:1 (250 mL) were added into the flask at 25 °C. Then, 8% NaClO solution (9.31 g, 10 mmol) was added dropwise. After dripping, the mixture was stirred for 24 h and 0.5M NaOH solution was used to adjust the pH of the reaction system to about 10. After reaction, the reaction mixture was centrifuged and the obtained solid was washed with water and then freeze-dried to obtain the oxidized cellulose.

NHPI mediated oxidation of cellulose in water was similar to the above process except that the reaction medium was changed to water.

PEG-NHPI mediated oxidation of cellulose

Except that PEG-NHPI was used instead of free NHPI as catalyst, other conditions were the same as the above-mentioned NHPI mediated oxidation of cellulose.

Recycling of PEG-NHPI

Recycling of the supernatant obtained by centrifuging the reaction mixture: After the first cellulose oxidation cycle, the supernatant obtained by centrifugation was concentrated to 250 mL and used as the reaction medium for the next oxidation cycle.

Recycling of PEG-NHPI recovered by dichloromethane extraction: The supernatant obtained by centrifuging the reaction mixture was extracted three times with dichloromethane, and the three extracts were combined and precipitated in n-hexane to obtain the recovered PEG-NHPI for the next oxidation cycle.

Characterization

Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Nicolet) and nuclear magnetic resonance spectroscopy (NMR, Avance500MHz, Bruker) were used to characterize the structure of PEG-NHPI. Gel permeation chromatography curves were recorded by a Waters 1515 instrument with a refractive index detector using a calibration curve from PEG standards in water (containing 0.02% NaN₃) at 35 °C. A UV-vis light spectrophotometer (UV-5800, China) was used to test the NHPI loading amount of PEG-NHPI with free NHPI as standard sample and acetonitrile as solvent.

Conductometric titration was used to determine the carboxyl content of oxidized cellulose (Liu et al. 2017; Li et al. 2019; Sun et al. 2021).

X-ray diffraction (XRD, D/MAX-2500, Rigaku) was used to determine the crystallinity indice (Crl) of cellulose before and after oxidation (Coseri et al. 2008; Segal et al. 2004) using the following formula:

$$Crl = (I_{200} - I_{am}) / I_{200} \times 100\%$$

where I_{200} is the normalized intensity of diffraction at about $2\theta = 22.6^\circ$ and I_{am} is the normalized intensity of diffraction at about $2\theta = 18.6^\circ$.

The viscosity degree of polymerization (DPv) of oxidized cellulose was determined by the reported method (Saito and Isogai 2004; Sun et al. 2021).

The degradation degree of cellulose was estimated by the following formula (Sun et al. 2021):

$$Degradation\ rate = \frac{DPv\ of\ raw\ cellulose - DPv\ of\ oxidized\ cellulose}{DPv\ of\ raw\ cellulose}$$

Results And Discussion

Preparation of macromolecular NHPI catalyst

The synthesis of water-soluble macromolecular NHPI catalyst mainly includes two steps (Fig. 1): Firstly, the intermediate product of PEG-TAC is generated through the esterification reaction between the terminal hydroxyl group of PEG and the acid chloride group on the TAC. Then, hydroxylamine hydrochloride is added to make the PEG-TAC undergo hydroxylation reaction to obtain the macromolecular catalyst of PEG-NHPI.

Figure 2 shows the FT-IR spectra of the main raw material, intermediate product and final product for the synthesis of PEG4000-NHPI. It can be seen that TAC has the carbonyl peak of acid chloride at 1762 cm^{-1} , and PEG4000 has a characteristic peak of fatty ether at 1111 cm^{-1} , a C-H peak at 2883 cm^{-1} and a hydroxyl peak at 3476 cm^{-1} . The above-mentioned characteristic peaks exist in the mixture of PEG4000 and TAC (PEG4000 + TAC). The carbonyl peak of the acid chloride at 1762 cm^{-1} disappears in the spectrum of PEG4000-TAC, indicating the formation of the intermediate product. Compared with PEG4000-TAC, PEG4000-NHPI has characteristic absorption peaks of amide at 1543 cm^{-1} and 1793 cm^{-1} , indicating that PEG4000-NHPI is successfully synthesized.

$^1\text{H-NMR}$ analysis of PEG4000-TAC and PEG4000-NHPI is carried out in Fig. 3. In the $^1\text{H-NMR}$ spectrum of PEG4000-TAC, the characteristic shift peak of PEG main chain H appears at 3.5 ppm, and the characteristic shift of benzene ring H appears at 7.7–8.5 ppm. The main difference between PEG4000-NHPI and PEG4000-TAC is the conversion of anhydride groups to hydroxylamine groups. In the spectrum of PEG-NHPI, the characteristic shift peak of N-OH does appear at 11 ppm, further confirming the successful synthesis of PEG-NHPI.

GPC curves of PEG4000, PEG4000-TAC and PEG4000-NHPI shown in Fig. 4 are used to evaluate their hydrodynamic volumes. It can be seen that PEG4000-TAC has two peaks at the retention time below that of PEG4000, which may correspond to PEG4000-TAC with one terminal TAC group and two TAC groups, respectively. It shows that after TAC is bonded to PEG, the hydrodynamic volume increases accordingly. However, when the anhydride group of PEG-TAC is hydroxylated to give PEG-NHPI, the retention time is slightly increased. It may be due to that the hydrogen bonds formed between the hydroxylamine groups and the PEG backbone decrease its hydrodynamic volume slightly.

UV-vis light spectroscopy is used to determine the NHPI loading amount of PEG-NHPI using free NHPI as the standard substance and acetonitrile as the reference solution. Table 1 lists the NHPI loading amounts of water-soluble macromolecular NHPI catalysts with different molecular weights. For PEG-NHPI and mPEG-NHPI, both show a trend of increasing NHPI loading amount as the molecular weight of the carrier decreasing. When both the molecular weight and other reaction conditions are the same, mPEG containing one terminal hydroxyl group has a lower loading capacity comparing with PEG having two terminal hydroxyl groups.

Table 1
The NHPI loading amounts of water-soluble
macromolecular NHPI catalysts with different molecular
weights

Catalysts	OH:TAC	NHPI loading amount (mmol/g)
PEG600-NHPI	1:1	0.93
PEG1000-NHPI	1:1	0.83
PEG2000-NHPI	1:1	0.43
PEG4000-NHPI	1:1	0.33
PEG6000-NHPI	1:1	0.25
PEG8000-NHPI	1:1	0.21
mPEG1000-NHPI	1:1	0.44
mPEG2000-NHPI	1:1	0.39
mPEG5000-NHPI	1:1	0.08

PEG-NHPI mediated oxidation of cellulose

It can be found from Table 2 that the carboxyl content of NHPI oxidized cellulose obtained in the acetonitrile/water medium is 1.04 mmol/g, equivalent to 71% of TEMPO oxidized cellulose. Because NHPI is insoluble in water, the carboxyl content of NHPI oxidized cellulose obtained in water (0.99 mmol/g) is slightly lower than that in the acetonitrile/water system. Interestingly, the DPv of NHPI oxidized cellulose is much higher than that of TEMPO oxidized cellulose, indicating that the degradation of cellulose for NHPI is much less than that of TEMPO. To clarify the relationship between carboxyl content and DPv of NHPI oxidized cellulose, samples with different carboxyl contents are prepared by changing the reaction time and the oxidant dosage. As shown in Fig. 5, the carboxyl content of NHPI oxidized cellulose is in inverse proportion to DPv, similar to that of TEMPO oxidized cellulose. However, when the carboxyl content is the same, the DPv of NHPI oxidized cellulose is much higher than that of TEMPO oxidized cellulose, further confirming the superiority of the NHPI system in inhibiting cellulose degradation.

The macromolecular catalyst of PEG-NHPI has good water solubility, so it shows a better catalytic performance in water than in acetonitrile/water, which proves the hypothesis that loading NHPI on a water-soluble carrier is beneficial to improve its catalytic performance in water. Besides, the DPv of PEG-NHPI oxidized cellulose is also at a high level.

Table 2
Catalytic performances of PEG-NHPI, NHPI and TEMPO for oxidation of cellulose

Catalyst	Reaction medium	Reaction time (h)	Carboxyl content of oxidized cellulose (mmol/g)	DPv of oxidized cellulose
TEMPO	water	4	1.46	55
NHPI	acetonitrile/water	10	1.04	120
	water	10	0.99	114
PEG4000-NHPI	acetonitrile/water	10	0.80	125
	water	10	0.91	120

Effects of the molecular weight of PEG-NHPI on its catalytic oxidation performances have been studied (Table 3). Large molecular weight of PEG-NHPI can increase the steric hindrance and limit its mobility, thereby reducing its catalytic performance. When the molecular weight of PEG is 600, the prepared macromolecular catalyst can achieve an oxidation performance equivalent to that of free NHPI. In general, the DPv of PEG-NHPI oxidized cellulose is slightly higher than that of NHPI oxidized cellulose. By comparing the catalytic performances of PEG2000-NHPI and mPEG2000-NHPI, it can be concluded that PEG2000-NHPI gives a higher cellulose oxidation degree, indicating that high NHPI loading is beneficial to the improvement of the catalytic oxidation performance.

Table 3
Effects of the molecular weight of the macromolecular NHPI catalyst on its catalytic oxidation performances

Catalysts	The molecular weight of carrier	Carboxyl content of oxidized cellulose (mmol/g)	DPv of oxidized cellulose
PEG600-NHPI	600	0.99	131
PEG1000-NHPI	1000	0.96	127
PEG2000-NHPI	2000	0.94	126
PEG4000-NHPI	4000	0.91	119
PEG6000-NHPI	6000	0.84	121
PEG8000-NHPI	8000	0.75	124
mPEG1000-NHPI	1000	0.85	126
mPEG2000-NHPI	2000	0.84	120
mPEG5000-NHPI	5000	0.58	135

Figure 6 compares the carboxyl contents and DPv values of oxidized cellulose samples obtained with PEG4000-NHPI, NHPI, TEMPO and polymer-immobilized TEMPO as catalysts. For NHPI oxidized cellulose, the carboxyl content is 0.99 mmol/g (equivalent to 68% of TEMPO oxidized cellulose), and the DPv is as high as 120 (equivalent to 26% degradation rate), which is much higher than that of TEMPO oxidation cellulose (equivalent to 66% degradation rate). The carboxyl content of PEG4000-NHPI oxidized cellulose is 0.94 mmol/g, which reaches 64% of free TEMPO level and 95% of free NHPI level, respectively. The DPv of PEG4000-NHPI oxidized cellulose is 1.1 times higher than that of TEMPO oxidized cellulose, and the degradation degree is only 18%. Compared with the reported macromolecular TEMPO catalysts of P(AA-co-TA) (Liu et al. 2018a) and P(AM-co-VAm)-T (Liu et al. 2018b), the oxidation performance of PEG4000-NHPI is higher than P(AA-co-TA) and can reach 84% of P(AM-co-VAm)-T level. The cellulose degradation rates of these two macromolecular TEMPO catalysts (41% and 21%, respectively) are higher than that of PEG4000-NHPI (18%). These results show that loading water-insoluble NHPI on a water-soluble macromolecular carrier not only has a good oxidation performance but also significantly inhibits the degradation of cellulose.

Recycling of PEG-NHPI

Considering the good water solubility of PEG-NHPI, it should remain in the supernatant after the oxidation is completed. The aqueous supernatant also contains a certain amount of inorganic salts such as NaCl. Inorganic salts within a certain concentration range gave little affect on the oxidation of cellulose (Liu et al. 2018a, b). Therefore, the concentrated supernatant can be directly used for the next oxidation. After 6 cycles, the supernatant can be extracted with dichloromethane to obtain recovered PEG-NHPI (Fig. 7).

It can be seen from Fig. 8 that the carboxyl contents of the oxidized cellulose samples obtained both in water and in acetonitrile/water, can still be maintained at high levels after recycling the supernatant 5 times. After 3 recycles, the DPv of oxidized cellulose decreases slightly (Fig. 9). This may be due to that, the accumulation of inorganic salts increases the concentration of reactive ions in the system, which may cause a certain degree of cellulose degradation.

It can be seen from Fig. 10 that the characteristic peaks of the recovered catalyst and the fresh catalyst are the same, indicating that the structure of the recovered catalyst is not changed and can be reused (cycle 7 in Fig. 8 (left)). It can be seen that the carboxyl content of oxidized cellulose obtained in cycle 7 is similar to that of cycle 1. This shows that the recovered macromolecular catalyst by extraction still has a good catalytic effect.

Oxidized cellulose samples obtained by different catalytic systems are characterized by XRD. After the original XRD data is normalized using the software of OriginPro 8, the XRD patterns are plotted as shown in Fig. 11. It can be found that the diffraction angle 2θ peak positions of oxidized cellulose samples and raw cellulose are the same and correspond to the type I crystal structure, indicating that the oxidation modification does not change the crystal type of the cellulose.

As shown in Table 4, comparing with raw cellulose ($I_{am}=0.175$, $I_{200} = 1.000$, $CrI = 82.5\%$), the crystallinity of NHPI oxidized cellulose is decreased. This may be due to that a part of cellulose in the crystalline area is oxidized to soluble oxidized cellulose, so the crystallinity of centrifuged water-insoluble oxidized cellulose is decreased. The crystallinity of PEG4000-NHPI oxidized cellulose is higher than that of NHPI oxidized cellulose. This may be due to that PEG4000-NHPI with large size is difficult to enter the crystalline region of cellulose, and can only oxidize the amorphous region and the surface of the crystalline region. The reason for the improved crystallinity of oxidized cellulose after recycling may be that the accumulation of residual oxidant in the system increases the oxidation degree of cellulose, increasing the amount of water-soluble oxidized cellulose.

Table 4
The crystallinity of NHPI oxidized cellulose and PEG4000-NHPI oxidized cellulose

Samples	acetonitrile/water system			water system		
	I _{am}	I ₂₀₀	CrI	I _{am}	I ₂₀₀	CrI
NHPI oxidized cellulose	0.321	1.000	67.9%	0.323	1.000	67.7%
PEG4000-NHPI oxidized cellulose for cycle 1	0.250	1.000	75.0%	0.226	1.000	77.4%
PEG4000-NHPI oxidized cellulose for cycle 6	0.183	1.000	81.7%	0.188	1.000	81.2%

Conclusions

A water-soluble PEG supported NHPI catalyst called PEG-NHPI is prepared for catalytic oxidation of cellulose with NaBr as cocatalyst and NaClO as oxidant. The results show that PEG-NHPI with good water solubility can give a similar catalytic performance to free NHPI in the water medium and can reach 68% of free TEMPO level. The degradation degree of PEG-NHPI oxidized cellulose is significantly lower than that of TEMPO oxidized cellulose. Furthermore, PEG-NHPI can be recycled easily, and the recycling performance is excellent.

Declarations

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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Figures

Figure 1

Synthetic routes of PEG-NHPI (a) and mPEG-NHPI (b)

Figure 2

FT-IR spectra of the main raw material, intermediate product and final product for the synthesis of PEG4000-NHPI

Figure 3

^1H -NMR spectra of PEG4000-TAC (a) and PEG4000-NHPI (b) in DMSO

Figure 4

GPC curves of PEG4000, PEG4000-TAC and PEG4000-NHPI

Figure 5

The relationship between the carboxyl content and DPv for NHPI oxidized cellulose and TEMPO oxidized cellulose

Figure 6

The carboxyl contents and DPv values of oxidized cellulose samples obtained with PEG4000-NHPI, NHPI, TEMPO and polymer-immobilized TEMPO as catalysts

Figure 7

Schematic recycling process of PEG-NHPI

Figure 8

Effects of oxidation cycle on the carboxyl content of PEG4000-NHPI oxidized cellulose obtained in water (left) and acetonitrile/water (right)

Figure 9

Effects of oxidation cycle on DPv of PEG4000-NHPI oxidized cellulose obtained in water and acetonitrile/water

Figure 10

FT-IR spectra of PEG4000-NHPI before and after recovery

Figure 11

XRD patterns of raw cellulose (a), NHPI oxidized cellulose obtained in acetonitrile/water (b), NHPI oxidized cellulose obtained in water (c), PEG4000-NHPI oxidized cellulose obtained in acetonitrile/water for cycle 1 (d), PEG4000-NHPI oxidized cellulose obtained in water for cycle 1 (e), PEG4000-NHPI oxidized cellulose obtained in acetonitrile/water for cycle 6 (f) and PEG4000-NHPI oxidized cellulose obtained in water for cycle 6 (g)