

# Polyamidoamine Immobilized TEMPO Mediated Oxidation of Cellulose: Effect of Macromolecular Catalyst Structure on the Reaction Rate, Oxidation Degree and Degradation Degree

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**Abstract:** A series of polyamidoamine (PAMAM) immobilized TEMPO macromolecular catalysts were prepared by condensation reduction reactions between carbonyl groups in 4-O-TEMPO and primary amines in PAMAM. The macromolecular catalyst and NaBr/NaClO were used as catalytic system for selective oxidation of cellulose in aqueous medium. Effects of various factors, such as TEMPO loading ratios and PAMAM generations, were studied on the catalytic performances. Compared with free TEMPO, the macromolecular catalyst with less than 50 % TEMPO loading ratio had a higher reaction rate in the initial stage of the reaction. Especially, the reaction rate of G1.0 PAMAM with 30 % TEMPO loading ratio was comparable to free TEMPO in the whole reaction process. Its cellulose oxidation degree (or catalytic activity) was also equivalent to the level of free TEMPO. Interestingly, the cellulose depolymerization degree of macromolecular catalyst was not affected by the cellulose oxidation degree and was lower than that of free TEMPO. The macromolecular catalyst could be recycled efficiently by the combination of supernatant circulation and salting-out extraction, and the recycling performance was excellent.

**Keywords:** Polyamidoamine, Macromolecular nitroxyl radical catalyst, Cellulose oxidation, Recycling

## Introduction

The oxidized cellulose, which is produced by the selective oxidation of C6 primary hydroxyl groups on the cellulose surface to carboxylic groups, has been applied in many aspects, such as absorbable hemostatic agents, sutures, tissue engineering and nano-materials [1-6]. The oxidizing reagents for selective oxidation of cellulose included nitrogen oxides, periodates and nitroxyl radicals [2]. As a stable nitroxyl radical, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) system is considered to be a highly efficient catalytic system for natural cellulose oxidation due to its advantages of mild reaction conditions, high catalytic activity, high selectivity and no change in fiber morphology [7,8]. However, this system generally undergoes conspicuous depolymerization side reactions under alkaline conditions [9]. To overcome depolymerization issues, several modifications have been reported, such as the bromide-free catalytic oxidation by sodium chlorite under slightly acidic or neutral conditions [10-12], TEMPO electro-mediated oxidation of cellulose [13], post-reduced TEMPO oxidized cellulose with NaBH<sub>4</sub> [14], using other chlorine reagents instead of NaClO [15] and N-hydroxyphthalimide/co-catalyst/NaClO oxidation [16,17].

Besides, TEMPO also has the problems such as high cost and difficult post-treatment [18,19]. To simplify the post-treatment of TEMPO catalytic system, the common method is to immobilize it on carrier to realize its recycling. The commonly used carriers include silica [20], mesoporous

molecular sieves [21], carbon nanotubes [22], magnetic spheres [23,24], and water-insoluble polymers [25-31]. These systems have shown excellent catalytic properties and good recycling performances in the catalytic oxidation of low-molecular alcohols. However, these immobilized TEMPO catalysts are generally ineffective when used for selective oxidation of cellulose, since these water-insoluble supported catalysts are difficult to effectively contact with hydroxyl groups of cellulose in the aqueous medium. For example, Patankar and Renneckar [24] prepared an immobilized TEMPO catalyst with magnetic nanoparticle as carrier to oxidize cellulose. Although the catalyst was easily separated by applying a magnetic field, the oxidation effect was only equivalent to about 55 % of free TEMPO at 65 °C. Recently, we prepared a nitroxide amphiphilic block copolymer for selective oxidation of cellulose. When a mixture of acetonitrile and water was used as the reaction medium, the resulting carboxyl content of oxidized cellulose was equivalent to 73.2 % of free TEMPO. However, the carboxyl content decreased obviously when water was used as reaction medium [31].

The preparation of water-soluble supported catalytic system is essential for improving the catalytic performance of cellulose oxidation in water. Araki [32] first immobilized TEMPO on monomethoxy poly ethylene glycol (mPEG2000) to prepare mPEG2000-TEMPO for oxidation of cellulose to prepare carboxylated nanocellulose. The macromolecular catalyst of mPEG2000-TEMPO was recovered by extraction with dichloromethane and reused for further oxidation cycles. It was found that the catalytic performance in the first oxidation cycle could reach 60 % of free TEMPO, but

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was greatly reduced after recycling. Our group [33] used partially acylated water-soluble polyacrylic acid as immobilized segment and synthesized a water-soluble immobilized-TEMPO copolymer for catalytic oxidation of cellulose in aqueous medium. The carboxyl content of oxidized cellulose using this copolymer as catalyst was up to 0.864 mmol/g, equivalently to 60 % of the free TEMPO level. Moreover, the pH sensitivity was utilized to achieve its recycling, and the catalytic activity did not decrease after 4 cycles.

In order to further improve the catalytic performance of supported catalytic system, we designed and prepared a water-soluble polyamidoamine (PAMAM) supported TEMPO catalyst. Because PAMAM developed by Tomalia et al in 1985 [34] was a classical water-soluble dendrimer possessing highly branched three-dimensional architecture and abundant terminated primary amines, which provided sufficient TEMPO loading sites. Furthermore, the good water solubility would reduce the diffusion resistance in the selective catalytic oxidation of cellulose in water and improve the catalytic activity. This catalytic system with NaBr/NaClO was used for the selective oxidation of cellulose and showed excellent catalytic performance [35]. This positive result prompted us to prepare a series of PAMAM immobilized TEMPO (PAMAM-TEMPO) catalysts with diverse structures, including catalysts having different TEMPO loading ratios (from 10 % to 90 %) with G1.0 PAMAM as carrier and catalysts supported on PAMAM with different generations (from G1.0 to G5.0) at a fixed TEMPO loading ratio (about 30 %). The effect of the macromolecular catalyst structure on the rate of cellulose oxidation, catalytic activity and degree of cellulose depolymerization, was systematically investigated. In addition, in order to reduce the inorganic salt and organic solvent consumption in the cyclic process, the recycling process by the combination of supernatant circulation and salting-out extraction was developed and studied.

## Experimental

### Materials

NaBH<sub>3</sub>CN (95 %) was provided by Shanghai Macklin Biochemical Co., Ltd. (China) and 2,2,6,6-tetramethylpiperidone (99 %) was provided by J&K Scientific Ltd. (China). Cellulose powders (white powders with particle size of 25 µm and viscosimetric average degree of polymerization of 154), NaBr (99 %), aqueous NaClO solution (5 %), sodium tungstate dihydrate (99.5 %), ethylene diamine tetraacetic acid (EDTA, 98 %), aqueous H<sub>2</sub>O<sub>2</sub> solution (30 wt.%), methyl acrylate (99 %), ethylenediamine (99 %), methanol (99.5 %), NaHCO<sub>3</sub> (99.5 %), NaOH (96 %), N,N-dimethylformamide (DMF, 99.5 %), n-hexane (98 %) and other reagents were provided by Aladdin Industrial Corporation (China). Ethylenediamine and methyl acrylate were distilled prior to use. Other reagents were used as received.

### Preparation of PAMAM-TEMPO

#### Preparation of PAMAM

40 ml solution of 50 % (v/v) methylacrylate mixed with methanol was added to a 100 ml three-necked flask, and 12 ml of 21 % (v/v) ethylenediamine-methanol solution was then dropwise added at 0 °C with magnetic stirring. After dripping, the reaction mixture was continuously stirred for 24 h at room temperature. After reaction, the reaction solution was evaporated to remove methanol and residual methylacrylate, and then further purified by column chromatography to obtain the product of G0.5 PAMAM.

Under a nitrogen atmosphere, 50 ml solution of 50 % (v/v) ethylenediamine mixed with methanol was added to a 250 ml three-necked flask, and then the solution of G0.5 PAMAM (12.13 g, 0.03 mol) diluted to 48.6 ml by methanol was slowly added at 0 °C under magnetic stirring. After dripping, the reaction mixture was continuously stirred for 24 h at room temperature. After reaction, the reaction solution was evaporated to remove methanol and residual ethylenediamine. The obtained viscous liquid was re-dissolved in methanol and evaporated to obtain the product of G1.0 PAMAM.

G2.0, G3.0, G4.0, and G5.0 PAMAM were obtained by repeating the above two steps in sequence, respectively.

#### Preparation of 4-O-TEMPO

The synthesis of 4-O-TEMPO was carried out as the following method. Typically, 2,2,6,6-tetramethylpiperidone (10 g), sodium tungstate (160 mg) and EDTA (160 mg) were added to the mixture of methanol (20 ml) and water (10 ml). Then, H<sub>2</sub>O<sub>2</sub> solution (16 ml, 30 wt. %) was slowly added within 10 h at 18-22 °C and continuously stirred for 13 h. The resulting solution was evaporated to remove methanol and water, and the residue was saturated with anhydrous potassium carbonate. The upper brown oil layer was separated and lyophilized. After recrystallized with n-hexane, the orange needle-like 4-O-TEMPO was obtained.

#### Preparation of PAMAM-TEMPO

An anhydrous methanol (30 ml) solution containing G1.0 PAMAM (1.03 g, 2 mmol) and 4-O-TEMPO (1.34 mmol) was prepared under a nitrogen atmosphere, and then NaBH<sub>3</sub>CN (equivalent molar amount as 4-O-TEMPO) was added with three equal parts (3 h, 24 h, 48 h after the start of the reaction, respectively) at 40 °C for 4 days. Saturated aqueous solution of sodium bicarbonate (70 ml) was added to quench excess NaBH<sub>3</sub>CN, and the white solid salt was removed by filtration. The filtrate was evaporated to remove methanol and water, then re-dissolved with anhydrous ethanol and the solution was filtered to remove the insoluble salt. After the filtrate was evaporated to remove ethanol, the residue was dissolved with water, and then extracted with ethyl acetate. After extraction, the organic layer was evaporated to get unloaded 4-oxo-TEMPO, which was used to estimate the TEMPO loading on PAMAM. The aqueous phase was separated and lyophilized to obtain the G1.0

PAMAM-TEMPO with loading ratio about 10 %, which was named G1.0 P-T-10. Then, the stoichiometric ratio of 4-O-TEMPO to the amino group in G1.0 PAMAM was changed to prepare G1.0 PAMAM-TEMPO with loading ratio of about 20 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 % and 90 %, respectively: G1.0 P-T-20, G1.0 P-T-30, G1.0 P-T-40, G1.0 P-T-50, G1.0 P-T-60, G1.0 P-T-70, G1.0 P-T-80 and G1.0 P-T-90. By fixing the stoichiometric ratio of 4-O-TEMPO and the amino group in PAMAM, G1.0 PAMAM was replaced by G2.0, G3.0, G4.0 and G5.0 PAMAM respectively, and G2.0, G3.0, G4.0 and G5.0 macromolecular catalysts with loading rate about 30 % were prepared: G2.0 P-T-30, G3.0 P-T-30, G4.0 P-T-30 and G5.0 P-T-30.

### Selective Oxidation of Cellulose

Cellulose powder (2.5 g), sodium bromide (0.063 g), macromolecular catalyst (containing 0.59 mmol nitroxide radicals) and water (188 mL) were added to a 500 mL three-necked flask. Then, the sodium hypochlorite solution (18.62 g) was dropwise added at 30 °C. The pH was maintained at 10.5 by addition of 0.5 M NaOH. The reaction was finished when no obvious NaOH consumption was observed. The reaction time was about 6 hours. After reaction, the oxidized cellulose was centrifuged and washed twice with water, and then lyophilized to obtain oxidized cellulose.

### Characterization

The structures of PAMAM, PAMAM-TEMPO and oxidized cellulose were characterized by Fourier transform

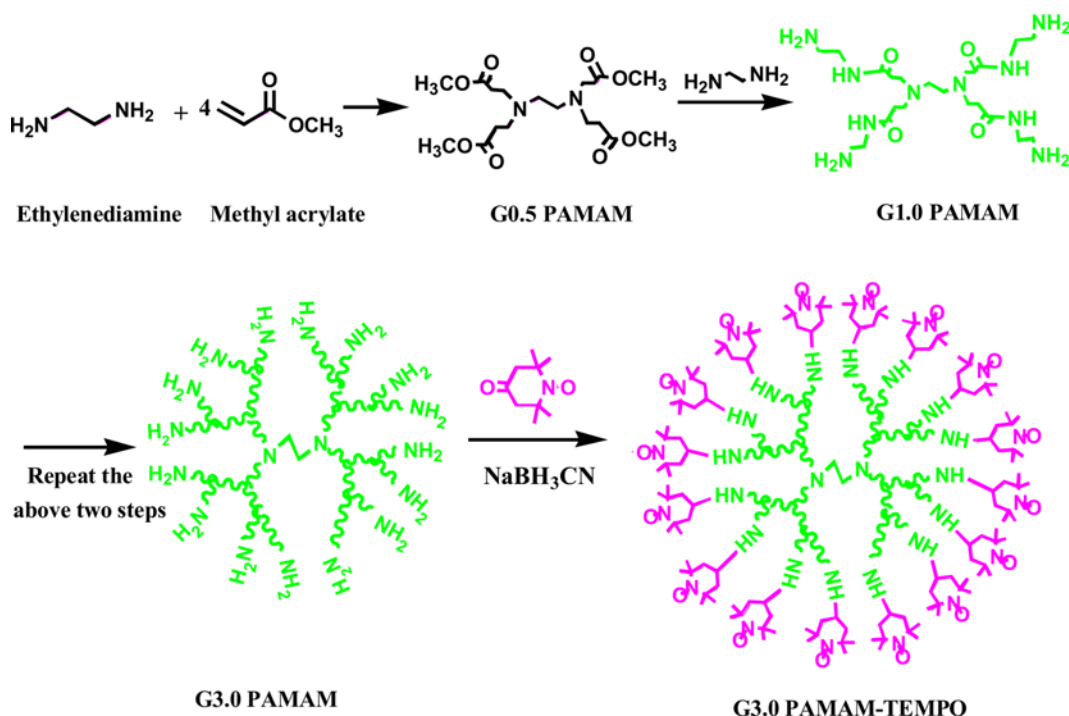
infrared spectroscopy (FT-IR, Nicolet 6700). The TEMPO density of PAMAM-TEMPO was tested by the UV-vis light spectrophotometer (UV-5800). The carboxyl content of oxidized cellulose was determined by conductometric titration [35]. The cellulose and oxidized cellulose samples were dissolved in the prepared copper ethylenediamine solution, and then the intrinsic viscosities of samples were measured by a capillary viscometer. The degree of polymerization (DP<sub>v</sub>) was calculated according to the formula given in the literature [36].

## Results and Discussion

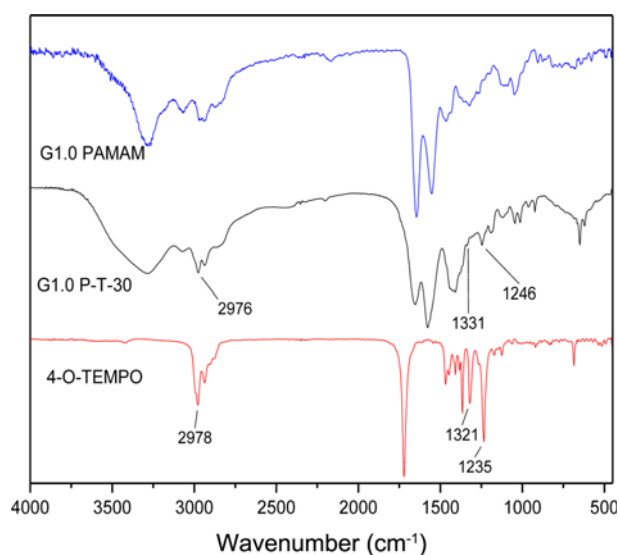
### Preparation of PAMAM-TEMPO

Due to the three-dimensional structure, a large number of surface primary amino groups and good water solubility [37–39], PAMAM is an ideal carrier for preparing a water-soluble nitroxyl radical macromolecular catalyst. The previous research of our group has proved that it can efficiently oxidize cellulose in water and can be recovered by salting-out extraction [35]. In order to systematically study effects of the structures of PAMAM immobilized TEMPO (PAMAM-TEMPO) on the performances of selective catalytic oxidation of cellulose including reaction rate, cellulose oxidation degree and depolymerization degree, a series of PAMAM-TEMPO catalysts with different structures were designed and synthesized (Table 1). Figure 1 showed the synthesis process of G3.0 PAMAM-TEMPO.

The infrared spectra of G1.0 PAMAM, G1.0 P-T-30 and 4-



**Figure 1.** Synthetic route of G3.0 PAMAM-TEMPO.



**Figure 2.** FT-IR spectra of G1.0 PAMAM, G1.0 P-T-30 and 4-O-TEMPO.

O-TEMPO were shown in Figure 2. Compared with G1.0 PAMAM, the spectrum of G1.0 P-T-30 still had asymmetric and symmetric stretching vibration and bending vibration of  $-\text{CH}_2-$  at  $2936\text{ cm}^{-1}$ ,  $2849\text{ cm}^{-1}$  and  $1409\text{ cm}^{-1}$ . The stretching vibration and asymmetric deformation vibration of  $-\text{CH}_3$  of

TEMPO appeared at  $2975\text{ cm}^{-1}$  and  $1190\text{ cm}^{-1}$ , respectively. The characteristic absorption peak of nitroxyl radical appeared at  $1363\text{ cm}^{-1}$  [40], and the stretching vibration absorption peak of C-N appeared at  $1246\text{ cm}^{-1}$ . Furthermore, the characteristic absorption peak of C=O in 4-O-TEMPO at  $1721\text{ cm}^{-1}$  disappeared. These results proved that TEMPO was successfully immobilized onto PAMAM.

Taking TEMPO as the standard substance, a standard UV-vis absorption curve for nitroxide was obtained. According to this standard absorption curve of TEMPO, the loading degree and loading amount of a series of PAMAM-TEMPO catalysts prepared in this work were determined and listed in Table 1. The surface morphology, surface properties and size of these PAMAM-TEMPO catalysts should be mainly determined by the support of PAMAM. The size, shape, and surface chemistry of PAMAM are closely related to its generation, which have been described in detail in the literature [41]. The molecular weight and the number of the peripheral functional groups of PAMAM increase exponentially with the increase of the generation, but the diameter increases almost linearly with the increase of the generation. PAMAM dendrimers of G1.0 and G2.0 are planar open structures with 1-2 nm in size, but G3.0, G4.0 and G5.0 are spherical structures with diameter of 3-5 nm. The characteristics of PAMAM dendrimers used in this work were listed in Table 2.

**Table 1.** Prepared nitroxide dendrimers in this work

Nitroxide dendrimers	Dendrimer support	4-O-TEMPO/ $\text{NH}_2$ in PAMAM	TEMPO loading degree	TEMPO density ( $\text{mmol g}^{-1}$ )
G1.0 P-T-10	G1.0 PAMAM	0.67/4	9.7 %	0.75
G1.0 P-T-20	G1.0 PAMAM	1.33/4	22.4 %	1.73
G1.0 P-T-30	G1.0 PAMAM	2/4	30.8 %	2.38
G1.0 P-T-40	G1.0 PAMAM	2.67/4	42.7 %	3.31
G1.0 P-T-50	G1.0 PAMAM	3.33/4	52.8 %	4.08
G1.0 P-T-60	G1.0 PAMAM	4/4	63.6 %	4.92
G1.0 P-T-70	G1.0 PAMAM	4.67/4	73.5 %	5.69
G1.0 P-T-80	G1.0 PAMAM	5.33/4	80.6 %	6.24
G1.0 P-T-90	G1.0 PAMAM	6/4	91.8 %	7.10
G2.0 P-T-30	G2.0 PAMAM	4/8	33.3 %	1.87
G3.0 P-T-30	G3.0 PAMAM	8/16	27.6 %	1.36
G4.0 P-T-30	G4.0 PAMAM	16/32	28.0 %	1.30
G5.0 P-T-30	G5.0 PAMAM	32/64	27.9 %	1.26

**Table 2.** Characteristics of PAMAM dendrimers [41]

Dendrimer	Molecular formula	Molecular weight	Diameter (nm)	No. of surface $-\text{NH}_2$
G1.0 PAMAM	$\text{C}_{22}\text{H}_{48}\text{O}_4\text{N}_{10}$	516	1.1	4
G2.0 PAMAM	$\text{C}_{62}\text{H}_{128}\text{O}_{12}\text{N}_{26}$	1428	1.6	8
G3.0 PAMAM	$\text{C}_{142}\text{H}_{288}\text{O}_{28}\text{N}_{58}$	3252	2.4	16
G4.0 PAMAM	$\text{C}_{302}\text{H}_{608}\text{O}_{60}\text{N}_{122}$	6900	3.1	32
G5.0 PAMAM	$\text{C}_{622}\text{H}_{1248}\text{O}_{124}\text{N}_{250}$	14196	4.0	64

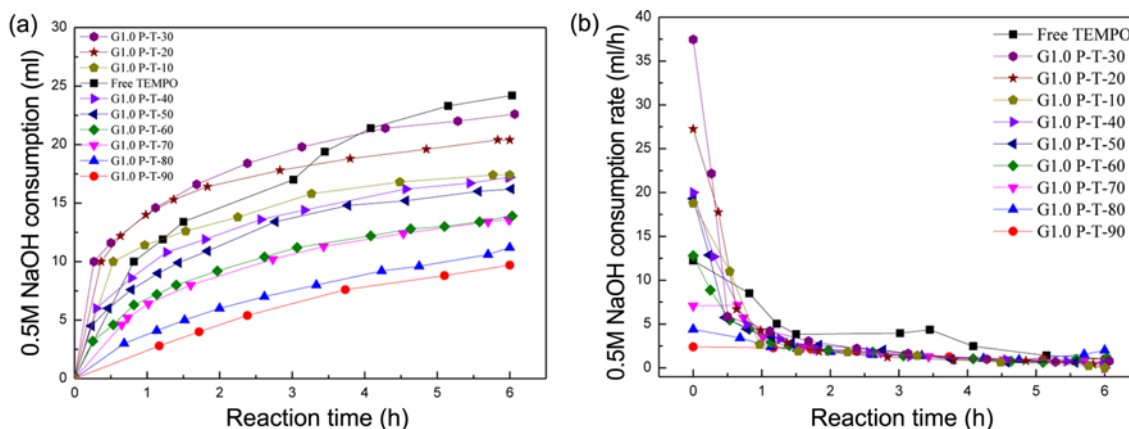
## PAMAM-TEMPO Mediated Oxidation of Cellulose

### Reaction Rate

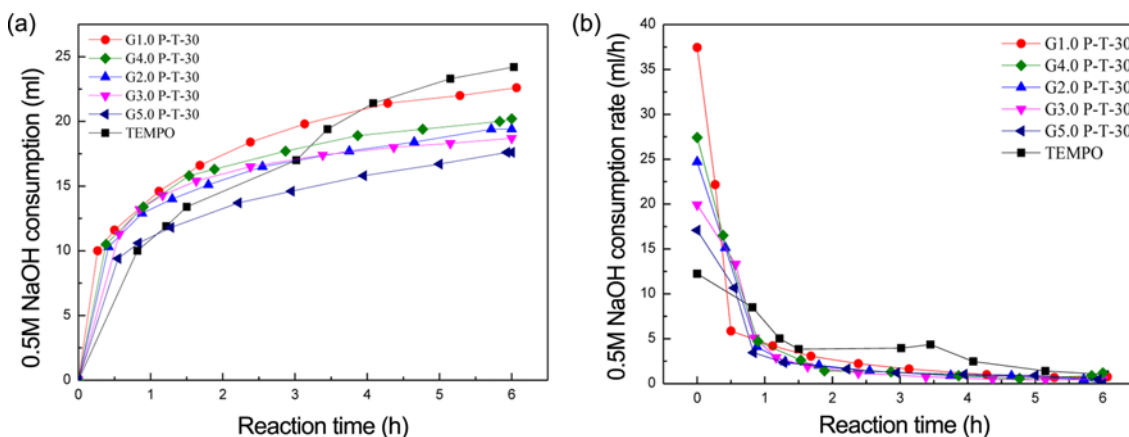
A series of PAMAM-TEMPO catalysts prepared above were used to catalytic oxidation of cellulose in water with NaBr as cocatalyst and NaClO as oxidant. All reactions were carried out for 6 hours at 30 °C. The oxidation reaction rate was characterized by the NaOH consumption rate.

It was seen from Figure 3 that, in the initial stage of the reaction (within 1 h), the reaction rates of PAMAM-TEMPO catalysts with less than 50 % TEMPO loading ratios were faster than free TEMPO. In general, the reaction rate increased with the increase of the TEMPO loading ratio, and then decreased. Among them, G1.0 P-T-30 had the fastest reaction rate, even faster than the free TEMPO. According to the reaction mechanism of TEMPO mediated oxidation of cellulose, the effective contact of TEMPO with the hydroxyl groups of cellulose was a necessary condition for the reaction to be proceeded. Based on this, it could be inferred that when the TEMPO loading ratio was lower than a certain value, the catalyst would have good water solubility, which

was favorable for triggering the oxidation reaction by contacting with hydroxyl groups on the surface of cellulose. Good water solubility was the main factor affecting the performances of supported TEMPO catalysts. Besides, the previous study showed that the high TEMPO loading could accelerate the regeneration speed of TEMPO on supported catalysts through intramolecular synproportionation [30]. However, when the loading ratio exceeded a certain value, the water solubility of catalysts decreased, and the reaction rate was reduced accordingly, so the maximum reaction rate occurred at the loading rate of about 30 %. In the middle and late reaction stages, the reaction rate of free TEMPO was faster than that of the macromolecular catalyst. Probably because the initial oxidation occurred on the cellulose surface, and the diffusion rates of catalysts with different molecular sizes to the cellulose surface were close. The high local nitroxyl radical concentrations of the macromolecular catalysts would facilitate their regeneration. After the reaction proceeded to the middle and late stages, the reaction mainly occurred in the inner pores of cellulose, and the



**Figure 3.** Effects of TEMPO loading ratios of PAMAM-TEMPO on the cellulose oxidation rate; (a) NaOH consumption and (b) NaOH consumption rate.



**Figure 4.** Effects of PAMAM generations of PAMAM-TEMPO on cellulose oxidation rate; (a) NaOH consumption and (b) NaOH consumption rate.

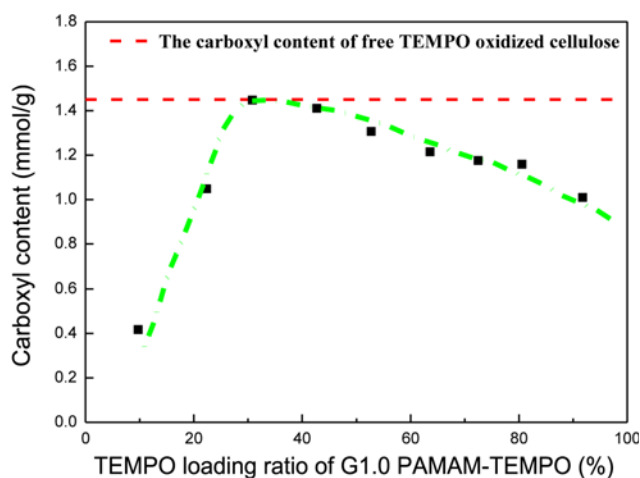


advantage of small size of free TEMPO was revealed. For macromolecular catalysts with different PAMAM generations at about 30 % TEMPO loading ratio (Figure 4), their reaction rates were also higher than that of free TEMPO within 1 h, and then tended to be stable and lower than free TEMPO. G1.0 P-T-30 had the best catalytic performance, probably due to its combination of small molecular size, good water solubility and low steric hindrance. With the increase of PAMAM generation, the reaction rate increased first and then decreased, indicating that the catalytic performances of macromolecular catalysts were related to the loading ratio, loading capacity and spatial size.

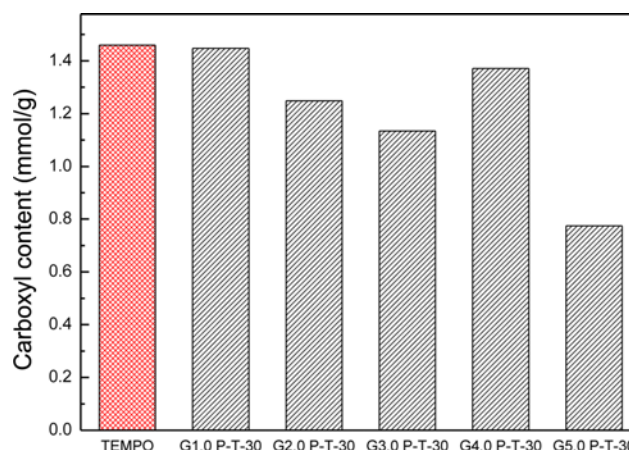
#### Cellulose Oxidation Degree

To evaluate the catalytic performances, the experimental conditions including reaction time were fixed for all cellulose oxidation runs. Thus, the cellulose oxidation degree (the carboxyl content) could be used as the indicator for evaluating catalytic activity. As shown in Figure 5, when G1.0 PAMAM was used as carrier and the TEMPO loading ratio was about 30 % (The molar ratio of PAMAM and TEMPO was about 0.83), the carboxyl content of obtained oxidized cellulose was 1.45 mmol/g, and was equivalent to the level of free TEMPO (1.46 mmol/g). This indicated that the optimal loading ratio was about 30 % when G1.0 PAMAM was used as carrier. Besides, all G1.0 PAMAM-TEMPO catalysts gave more than 70 % cellulose oxidation degree of free TEMPO, higher than other reported immobilized catalysts [24,31-33], indicating that the water-soluble PAMAM-TEMPO was suitable as a highly efficient catalyst for the catalytic oxidation of cellulose in aqueous media.

The effect of PAMAM generation on the catalytic performance of PAMAM-TEMPO was studied at the fixed TEMPO loading ratio of 30 %. As shown in Figure 6, similar to the reaction rate, G1.0 P-T-30 catalyst had the best



**Figure 5.** Effects of TEMPO loading ratios on carboxyl content of oxidized cellulose using G1.0 PAMAM-TEMPO as catalyst.

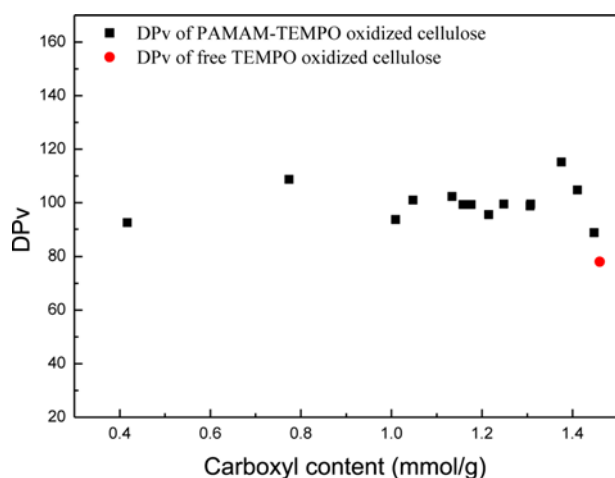


**Figure 6.** Effects of PAMAM generations on carboxyl content of oxidized cellulose obtained by PAMAM-TEMPO.

catalytic performance. Generally, the cellulose oxidation degree decreased slightly with increasing the generation of PAMAM used as TEMPO carrier. Probably, the increased dendrimer size with the increase of generation resulted in a large steric hindrance. In addition, the TEMPO loading density of PAMAM-TEMPO would decrease accordingly at a fixed TEMPO loading ratio (Table 1) when the generation of PAMAM was increased. Therefore, in order to ensure the same molar amount of TEMPO moieties in the reaction system, the added mass of PAMAM-TEMPO would increase accordingly and the diffusion resistance between macromolecular catalyst and cellulose was increased, resulting in the catalytic performances of high generation catalysts were worse than that of G1.0. However, the catalytic activity of G4.0 P-T-30 was higher than that of G2.0 P-T-30, G3.0 P-T-30 and G5.0 P-T-30. This may be due to the fact that PAMAM gradually becomes spherical after G3.0, and the accessibility to cellulose is increased.

#### Polymerization Degree of Oxidized Cellulose

In general, the depolymerization inevitably occurred during TEMPO mediated oxidation of cellulose and the depolymerization degree depended on some factors such as reaction temperature, time, catalyst structure and oxidant type. In this work, depolymerization was also found when PAMAM-TEMPO was instead of free TEMPO to oxidize cellulose. The DP<sub>v</sub> of natural cellulose was 154 and the values of oxidized cellulose samples were reduced to 90-115. However, it was interesting that the DP<sub>v</sub> values of oxidized cellulose samples with different carboxyl contents obtained with different catalysts showed little difference and were higher than that of free TEMPO (DP<sub>v</sub>=78). This was different from the results obtained with free TEMPO. DP<sub>v</sub> was inversely proportional to the carboxyl content of free TEMPO mediated oxidized cellulose [36]. It seemed that the immobilized macromolecular catalyst reduced the occurrence of cellulose depolymerization to a certain extent. Probably



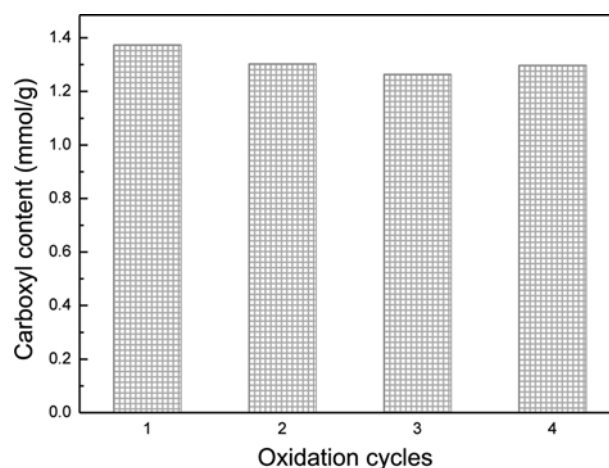
**Figure 7.** Relationship between DPv value and carboxyl content for oxidized cellulose obtained with PAMAM-TEMPO.

due to the large size of the macromolecular catalyst, the oxidation reaction mainly occurred on the cellulose surface.

### The Recycling Performances of PAMAM-TEMPO

After PAMAM-TEMPO mediated oxidation of cellulose, the oxidized cellulose was separated by centrifugation. Since PAMAM-TEMPO was soluble in water, it would remain in the supernatant. The previous reported recycling process [35] consumed a large amount of inorganic salts and organic solvents for salting out and extracting PAMAM-TEMPO. Therefore, we explored the feasibility of directly recycling the supernatant containing the macromolecular catalyst. In the first cellulose oxidation cycle, the added water was 188 mL. In order to ensure similar experimental conditions, the collected supernatant solution was concentrated to 188 mL and used for the next oxidation cycle directly as shown in Figure 8.

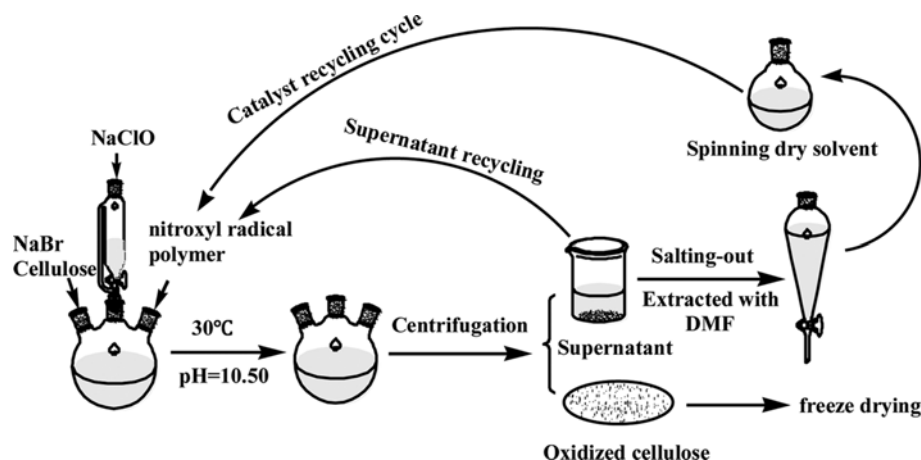
Taking G4.0 P-T-30 as an example, the catalytic



**Figure 9.** Recycling performance of G4.0 P-T-30.

performances of the supernatant containing nitroxyl radical polymers were studied. Figure 9 showed that carboxyl content of oxidized cellulose was still satisfactory after two reused cycles.

However, the content of inorganic salts was gradually accumulated with the reused cycle increasing. When the concentration of inorganic salts in the reaction system was increased to a certain value, the solubility of PAMAM-TEMPO would be reduced, thereby reducing its catalytic performance. Therefore, after two reused cycles, the method of salting-out extraction was adopted again. PAMAM-TEMPO was separated and reused in the cycle 4 as shown in Figure 9. Compared to cycle 3, the carboxyl content of oxidized cellulose of cycle 4 increased slightly, and the recovery level of macromolecular catalyst after four cycles was as high as 90 %. The above results indicated that it was feasible to salt out and extract the supernatant for recovering the macromolecular catalyst after the supernatant was circulated a certain number of times.



**Figure 8.** Schematic diagram of the recycling process of PAMAM-TEMPO.

## Conclusion

The PAMAM immobilized TEMPO catalysts were used for the selective catalytic oxidation of cellulose in water. Effects of TEMPO loading ratios and PAMAM generations of these macromolecular catalysts on the reaction rate, cellulose oxidation degree and depolymerization degree were studied. The results showed that the catalytic activity of G1.0 PAMAM with about 30 % TEMPO loading ratio was equivalent to free TEMPO, and the catalyst could be recovered by salting out and extraction. Besides, the immobilized macromolecular catalyst reduced the cellulose depolymerization degree to some extent in the cellulose oxidation process and the cellulose oxidation degree seemed to have little effect on its depolymerization. The combination of supernatant circulation and salting-out extraction was found to be a suitable method for the macromolecular catalyst recycling. The catalytic performance did not decrease after 4 cycles. This work will provide new ideas for overcoming depolymerization issues and achieving TEMPO recycling for TEMPO-mediated oxidation of cellulose.

## Acknowledgment

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