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# Green synthesis of a novel biodegradable copolymer base on cellulose and poly(*p*-dioxanone) in ionic liquid

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ABSTRACT

A new cellulose graft copolymer was synthesized in 1-*N*-butyl-3-methylimidazolium chloride ([Bmim]Cl) by the ring opening graft polymerization (ROGP) of *p*-dioxanone (PDO) onto cellulose. The structure of the copolymer was characterized by $^{13}C$ and $^{1}H$ NMR, WAXD, DSC as well as SEM. Cellulose graft copolymers with a molar substitution (MS) in the range of 2.08–4.60 were obtained with 24 h at 80 °C in a completely homogeneous procedure. The obtained copolymers exhibited the clear glass transition temperatures ($T_g$) indicating the inter-molecular and intra-molecular hydrogen bonds in cellulose molecules had been destroyed. The reaction media applied can be easily recycled and reused.



## 1. Introduction

As an important polysaccharide, cellulose is a promising substitute for the limited petroleum resource, because of its renewability, biodegradability, biocompatibility and abundance in nature. However, due to the stiff molecular chain and numerous strong inter-molecular and intra-molecular hydrogen bonds between the hydroxyl groups of glucose unites, cellulose is neither dissolved in common solvents nor thermally processed through the extrusion or the compressed molding, which restricted its wider applications.

Recently, room-temperature ionic liquids (ILs) were found having excellent dissolution ability for cellulose (Welton, 1999). Swatloski et al. investigated the dissolution of cellulose in various ILs, and the results were shown that 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) is an efficient solvent for cellulose isolated from plants (Swatloski, Spear, Holbery, & Rogers, 2002). Zhang et al. reported that 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) was also a excellent solvent for native cellulose (Zhang, Wu, Zhang, & He, 2005). Owing to no formation of covalent bonds and no significant depolymerization of cellulose chains in the dissolving process, it is considered as a good non-derivative solvent for the functionalization of cellulose. The carboxymethylation and acetylation of cellulose with high degree of substitution (DS) can be obtained using [Bmim]Cl as reaction media (Heinze, Schwikal, & Barthel, 2005; Schlufter, Schmauder, Dorn, & Heinze, 2006; Barthel & Heinze, 2006). These studies proved that the ILs containing chloride ion, which can be developed into a strong hydrogen bond connection with cellulose, appear to be the most appropriate media for the chemical modifications of cellulose (Holbrey et al., 2003).

Modification of cellulose by graft copolymerization can provide a significant method to alter its physical and chemical properties (Yuan, Yuan, Zhang, & Xie, 2007). Recently, much consideration had been paid to graft copolymerization between cellulose derivatives and aliphatic polyesters such as poly(lactic acid), poly(ε-caprolactone), etc. due to their excellent biodegradability, biocompatibility (Teramoto & Nishio, 2003; Teramoto, Yoshioka, Shiraishi, & Nishio, 2002; Li, Xie, Cheng, Nickol, & Wang, 1999). However, in contrast to those active studies that have been directed to cellulose derivatives, there is no information about the graft polymerization of biodegradable aliphatic polyesters onto native cellulose in ILs.

Poly(1,4-dioxan-2-one), PPDO, is one of aliphatic polyesters, which has been used widely as a biodegradable suture material and has the potential application in eco-material fields (Yang, Wang, & Wang, 2002; Nishida, Yamashita, Hattori, Endo, & Tokiwa, 2000). In this paper, ring opening graft copolymerization (ROGP) of *p*-dioxanone onto cellulose was carried out homogeneously for the

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first time in [Bmim]Cl as a reaction media. It was IL expected the introduction of PPDO into cellulose molecular chains, which made cellulose not only have the thermal plasticization but also have the good solubility and biodegradability. The novel cellulose-g-PPDO copolymer (CGP) was characterized by NMR, DSC, WAXD, and SEM.

## 2. Experimental

### 2.1. Materials

The IL, 1-*N*-butyl-3-methylimidazolium chloride ([Bmim]Cl) with a yield of 96% was synthesized according to a known procedure (Alexandra & Andreas, 2005). The structure of [Bmim]Cl was confirmed by $^1$H NMR: $\delta$H (400 MHz; $D_2O$; DSS) 8.70 (1H, s, N–CH═N), 7.47 and 7.42 (2H, s, N–CH═CH–N), 4.19 (2H, t, N–$CH_2$), 3.88 (3H, s, N–$CH_3$), 1.84 (2H, m, N–$CH_2CH_2$), 1.32 (2H, m, N–$CH_2CH_2CH_2$), 0.92 (3H, t, N–$CH_2CH_2CH_2CH_3$).

The cellulose substrate, bamboo sulfite pulp consisted of 96.5% α-cellulose (Browning, 1967) (degree of polymerization 650) was purchased from Leshan Beiya Yasong Paper Company (Chengdu, China) and was used after washing with distilling water, milled, and remained in vacuum at 80 °C for 72 h. PDO was provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China), and was dried over $CaH_2$ for 48 h, twice distilled under reduced pressure immediately before use. $Sn(Oct)_2$ was purchased from Sigma Chemical and was used without any further purification. After dilution with dry toluene, the $Sn(Oct)_2$ solution was stored in a glass ampule under argon. Toluene was received from the Hehong Chemical Reagent Factory (Chengdu, China) and was dried by refluxing over a sodium/benzophenone complex and distilled just before use. All other solvents with AR grade were used as received.

### 2.2. Measurement

$^{13}$C and $^1$H NMR spectra of the samples were measured by a 400 MHz NMR spectrometer (Bruker AV II-400, Bruke) with a standard probe at room temperature. All data of the obtained products were acquired in DMSO-d6. The pulse width was 3.0 μs for 16 ($^1$H) and about 10,000 ($^{13}$C) scans. Differential scanning calorimetry (DSC) investigation was carried out with a DSC instrument (DSC Q100, TA) at a heating rate of 10 °C/min under nitrogen atmosphere. The samples first remained at 150 °C for 5 min to remove the thermal history, and then immediately quenched to −20 °C. All data of the second heating scans were recorded from −20 to 250 °C. Wide-angle X-ray diffraction (WAXD) patterns of the powder samples were obtained on a DX-1000 CSC X-ray diffractometer with a Cu Kα radiation source (40 kV, 25 mA). Samples were exposed at a scanning rate of $2\theta = 5°–70°$. Morphology of the surface of the original cellulose, regenerated cellulose and cellulose-g-PPDO copolymer were observed on gold sputter-coated samples, using a Philips Quanta 200 under an accelerating voltage of 10 kV.

### 2.3. Preparation of cellulose substrate in [Bmim]Cl

[Bmim]Cl ILs were heated to 80 °C, and then a certain amount of cellulose substrate was added with strongly stirring. Under a nitrogen atmosphere the mixture was agitated at 80 °C for 6 h to form a transparent solution. The concentration of cellulose in IL was 10% or 6%.

### 2.4. In situ reaction of p-dioxanone with cellulose

Freshly distilled PDO was added into the as-prepared cellulose solution, and then $Sn(Oct)_2$ (0.2 mol/L) as catalyst was syringed with the desired amount. The reaction was performed at 80 °C for 24 h under nitrogen atmosphere. Then the mixture was precipitated in excess anhydrous methanol and the obtained products were purified by the Soxhlet extraction with acetone for 72 h. Finally, the obtained copolymers were dried at 40 °C in vacuum until constant weight.

## 3. Results and discussion

Bamboo fibers with *DP* = 650 could be dissolved in [Bmim]Cl IL as easily as cotton or wood. Because both 1,4-dioxane-2-one (PDO) monomer and cellulose-g-PPDO can be dissolved in [Bmim]Cl IL, the ring opening grafting copolymerization can be carried out homogeneously. It is well known that the living-like polymerization of cyclic esters can be initiated in the presence of $Sn(Oct)_2$ by the hydroxyl-initiator (Kricheldorf, Kreiser-Saunders, & Boettcher, 1995; Schwach, Coudane, Engel, & Vert, 1997). Namely, $Sn(Oct)_2$ may act as an assistant catalyst that co-initiated the ring opening polymerization (ROGP) of PDO with the hydroxyl groups of cellulose in the copolymerization. The expected structure of cellulose-g-PPDO is shown in Fig. 1.

The chemical structure of cellulose grafted PPDO was determined by $^{13}$C NMR and $^1$H NMR spectrum (shown in Figs. 2 and 3, respectively). From Fig. 2, distinctly, the chemical shifts of C1 (100.60 ppm) and C1′ (103.28 ppm) are ascribed to C-1 carbons adjacent to C-2 bearing unsubstituted and substituted hydroxyl groups, accordingly, C4 (80.75 ppm) and C4′ (75.23 ppm) are due to the adjacent C-3 carbons bearing unsubstituted and substituted hydroxyl groups, respectively. This means that the hydroxyl groups of anhydrous glucose units (AGU) in native cellulose were partly substituted through grafting PPDO onto the backbones of cellulose. In addition, the cellulose-g-PPDO gives a series of extra peaks from 62.32 to 69.00 ppm corresponding to $^{13}$C species of PPDO side chains and nearby 170 ppm ascribed to the carbonyl carbon of the repeating and ending unit in PPDO side chains, respectively.

It can be found from Fig. 3 that the chemical shifts of glucose unit of original cellulose appeared from 3.2 to 5.6 ppm. The new peaks at 4.22 ppm and 3.71 ppm are corresponded to the internal methylene group ($H_c$, $H_b$ and $H_{b'}$) of PPDO, respectively. The chemical shift at 4.17 ppm was assigned to $H_a$ and $H_{a'}$ (Chen, Zhou,

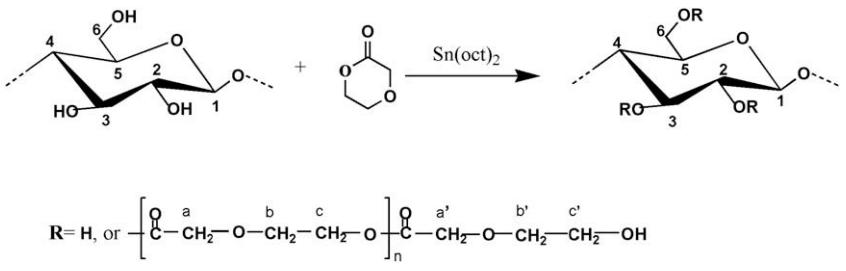


**Fig. 1.** Proposed reaction between cellulose and PDO.

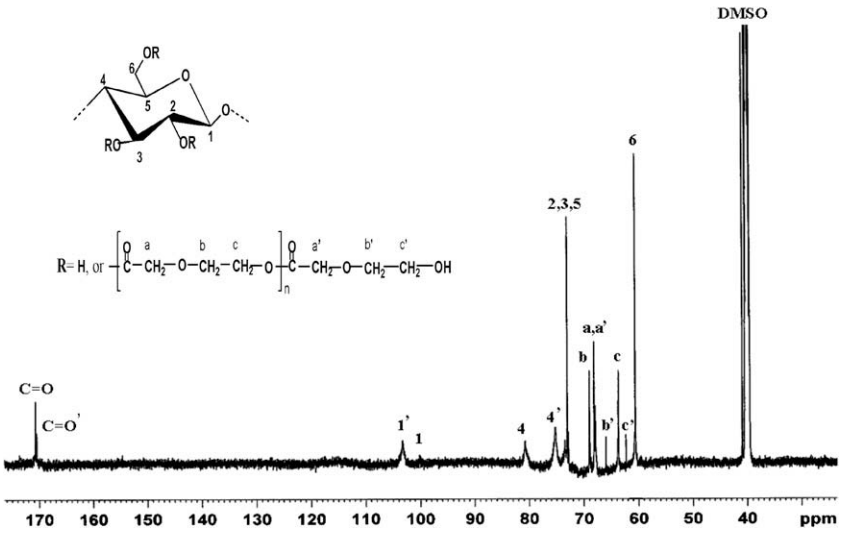


**Fig. 2.** The typical $^{13}C$ NMR spectrum of CGP.

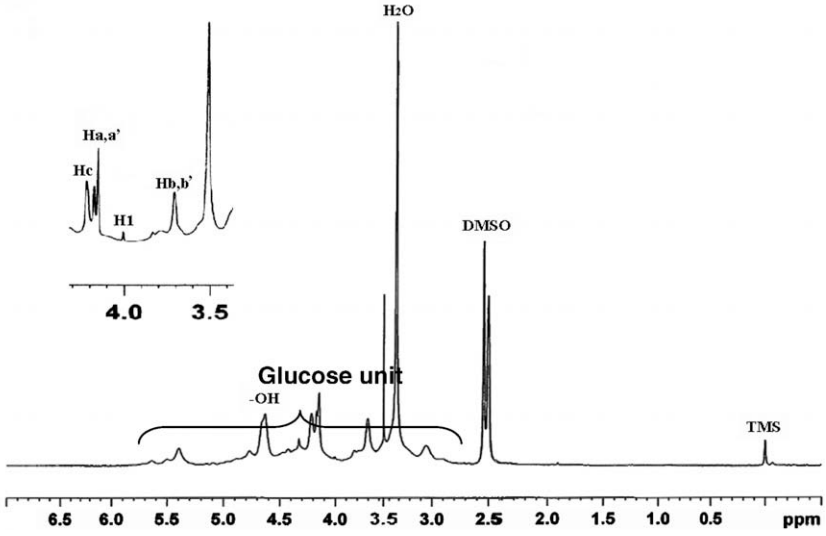


**Fig. 3.** The typical $^{1}H$ NMR spectrum of CGP.

Wang, Wang, & Yang, 2006). However, the peaks of the terminal methylene group ($H_{c'}$) were not found.

As we know, during cellulose dissolving in [Bmim]Cl, free $Cl^-$ ions of [Bmim]Cl associated with the hydroxyl proton of cellulose, and the free cations were in complex with the hydroxyl oxygen of cellulose, which disrupted hydrogen bonds in cellulose and led to the dissolution of cellulose (Zhang et al., 2005). This may deteriorate the initiating activity of hydroxyl groups and make PPDO side chains were not so long. Therefore, the peaks of the terminal methylene group could not be observed. To clearly understand the initiating activity of hydroxyl groups during cellulose dissolving in [Bmim]Cl, reaction kinetics investigated by NMR spectroscopy and some more effective characterization techniques, is still needed.

The signal at 4.02 ppm involved the proton of $H_1$ on the cellulose unit (Hiroyuki, Tomoki, & Mitsuo, 2003; Hiroyuki, Yukari, Tomoki, & Mitsuo, 2004), and it was clearly differentiated from the methylene proton of the PDO unit. Therefore, the molar substitution (MS) and the content of PPDO ($W_{PPDO}$) can be estimated by the following equation:

$$MS = \frac{I_a + I_{a'}}{2I_{H1}}$$

$$W_{PPDO} = \frac{M_{PDO} \times MS}{M_{AGU} + M_{PDO} \times MS} \times 100$$

where $I_{H1}$ is the integral peak area of $H_1$ of cellulose, $M_{PDO}$ (102 g/mol) is the molecular weight of PDO monomer, and $M_{AGU}$ (162 g/mol) is the molecular weight of an anhydrous glucose unit.

In order to investigate the influence of reaction conditions on the copolymerization, *MS* and $W_{PPDO}$ values of the copolymer obtained under different reaction conditions were listed in Table 1. Trials 1–4 were carried out with different amounts of catalyst and fixed concentration of cellulose in IL, molar ratio of cellulose to PDO, reaction time and temperature. It is found that both *MS* and $W_{PPDO}$ values were enhanced when $Sn(Oct)_2$ content was increased from 0.05 to 0.1 wt% (based on PDO). When the content of $Sn(Oct)_2$ was increased to 0.3 wt%, both the values decreased. However, further increase of catalyst content, *MS* and $W_{PPDO}$ values were almost invariant. The increase of $Sn(Oct)_2$ content provided more living centers, more PPDO side chains were connected onto the cellulose backbone indicating by the high *MS* value. However, further increase of catalyst content would cause some side reac-

**Table 1**
Results of the graft polymerization of PDO on cellulose in IL [Bmim]Cl.

| Sample | Concentration of cellulose (wt %) | Cellulose:PDO (mol:mol) | Temp. (°C) | Time (h) | Catalyst (wt %) | *MS*[a] | $W_{PPDO}$[a] | Solubility | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $CHCl_3$ | DMSO | DMF |
| CGP1 | 6 | 1:5 | 80 | 24 | 0.05 | 3.50 | 68.8 | ○ | ● | ● |
| CGP2 | 6 | 1:5 | 80 | 24 | 0.1 | 3.90 | 71.1 | ○ | ● | ● |
| CGP3 | 6 | 1:5 | 80 | 24 | 0.3 | 2.66 | 62.6 | ○ | ● | ● |
| CGP4 | 6 | 1:5 | 80 | 24 | 0.5 | 2.58 | 61.9 | ○ | ● | ● |
| CGP5 | 6 | 1:10 | 80 | 24 | 0.3 | 2.08 | 56.7 | ○ | ● | ● |
| CGP6 | 10 | 1:10 | 80 | 24 | 0.3 | 4.60 | 74.3 | ○ | ● | ● |
| CGP7 | 6 | 1:10 | 80 | 12 | 0.3 | 1.72 | 52.0 | ○ | ● | ● |
| CGP8 | 10 | 1:10 | 80 | 12 | 0.3 | 2.20 | 58.1 | ○ | ● | ● |

○: Swelling.
●: Soluble.
[a] Determined by H NMR spectra.

tions, for example, the homopolymerization of PPDO, which made *MS* and $W_{PPDO}$ values decrease.

Beside this, reaction time and cellulose concentration in [Bmim]Cl had great effect on the *MS* and $W_{PPDO}$ values. From trial 5 to 7, it can be seen that the prolongation of reaction time would benefit the copolymerization, and both *MS* and $W_{PPDO}$ values were enhanced. When the cellulose concentration in [Bmim]Cl was increased to 10 wt%, this trend was clearer. *MS* and $W_{PPDO}$ values were 4.6 and 74.3, respectively, when the reaction time was 24 h. When the reaction time exceeded 24 h, very little products were obtained and it was found that PPDO grafted chains were pulled off cellulose backbones (determined by IR spectrum). This may be ascribed to the poor thermal stability of PPDO in ILs, and would be investigated later. It also can be found that the higher concentration of cellulose would avail the enhancement of *MS* and $W_{PPDO}$ values. For the same reaction time, *MS* and $W_{PPDO}$ values were higher for cellulose concentration in [Bmim]Cl of 10 wt% (seen trials 5 and 6, trials 7 and 8). However, we found that if the concentration in [Bmim]Cl exceeded 10 wt%, the solution was too viscous to make PDO and $Sn(Oct)_2$ conglomerate easily. This was disadvantage to the copolymerization.

It was found that all the obtained copolymer had good solubility in DMSO, DMF. When chloroform was used as solvent even heating they can barely swell in it, which may be ascribed to the poor solubility of PPDO in chloroform. The good solubility of the copolymers in DMSO and DMF indicated the copolymerization modification on cellulose was successful and the inter- and intra-hydrogen bonds between the cellulose was disrupted.

The thermal transition behaviors of CGPs were investigated by DSC. The second heating scans of CGPs were shown in Fig. 4. As we know, the native cellulose has no glass transition temperature ($T_g$) and melting temperature ($T_m$) due to the strong inter- and intra- hydrogen bonds (Hatakeyama & Nakamura, 1982). From the DSC curves of CGPs, a slight base-line deviation was observed in each DSC curves, indicating these copolymers have a glass transition temperature. We found that $T_g$ of CGPs had a closed relationship with $W_{PPDO}$. CGP2 ($W_{PPDO}$ = 71.1%) and CGP6 ($W_{PPDO}$ = 74.3%) with high PPDO content had low $T_g$ values corresponding to 192.4 and 191.7 °C, respectively. Whereas, CGP1 ($W_{PPDO}$ = 68.6%) and CGP4 ($W_{PPDO}$ = 61.9%) with low $W_{PPDO}$ values had high glass transition temperatures corresponding to 203.1 and 214.9 °C, respectively. However, we still cannot find the melting point of CGPs, meaning that although the introduction of PPDO side chains destroyed the inter- and intra-molecular hydrogen bonds of cellulose, the regularity of cellulose was also demolished, which made it be unable to crystallize. Additionally, PPDO side chains were too short to crystallize. Therefore, only the glass transition temperature could be found.

The crystalline structures of the copolymer and original cellulose were investigated by WAXD measurements (shown in Fig. 5). The native cellulose shows two diffraction peaks at $2\theta$ = 15.7° and 22.5°, as the typical diffraction patterns of cellulose type I (Murakami, Kaneko, & Kadokawa, 2007). However, a conspicuous broad peak was observed in the WAXD patterns of se-

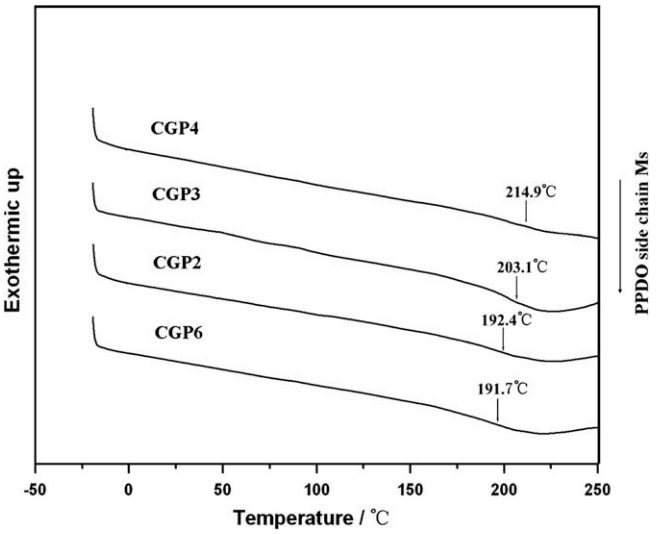


**Fig. 4.** DSC heating scans of CGP.

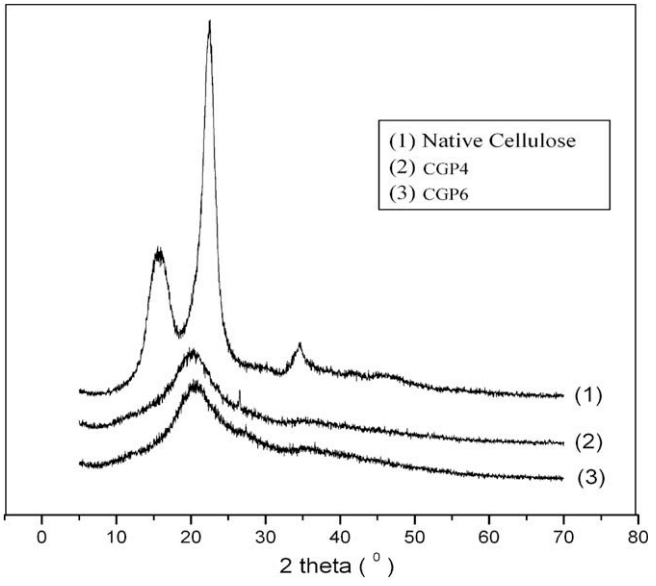


**Fig. 5.** WAXD patterns of native cellulose, CGP4 and CGP6.

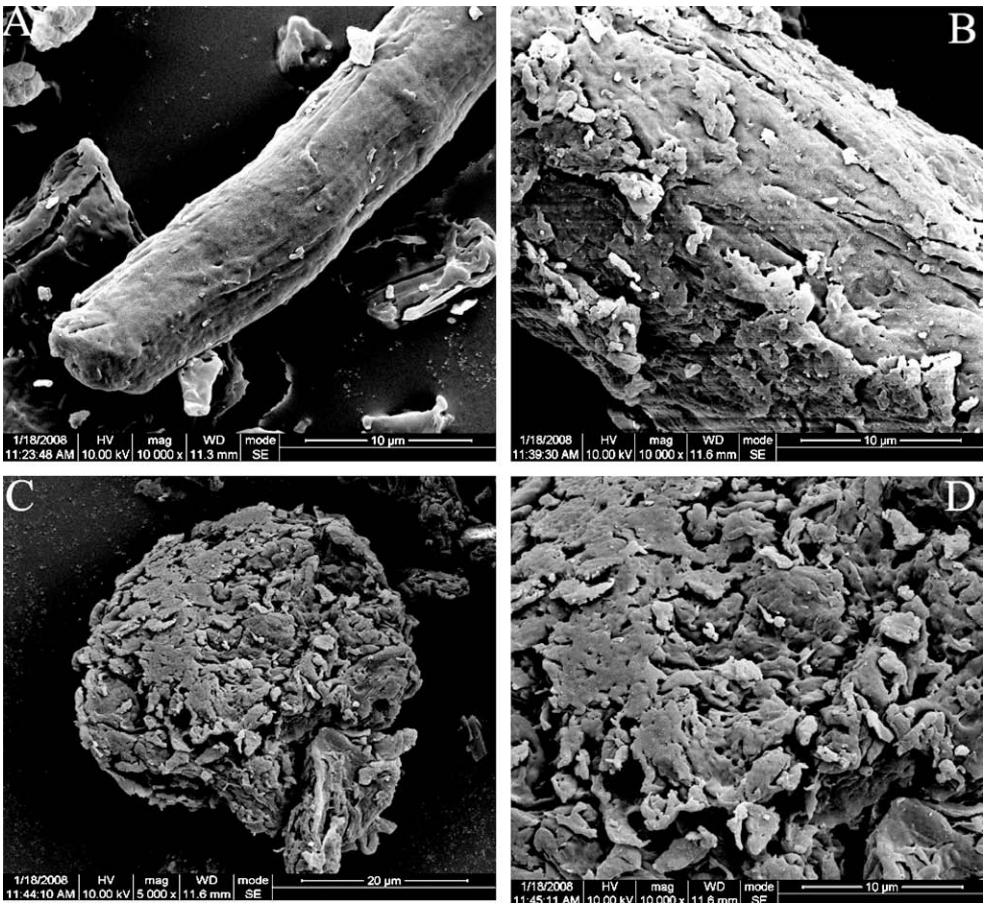


**Fig. 6.** SEM photomicrographs of the native cellulose (A), regenerated cellulose from [Bmim]Cl (B), and CGPs at low-magnification (C), high-magnification (D).

lected products, which were different from that of pure cellulose (cellulose I and cellulose II) (Klemm, Heublein, Fink, & Bohn, 2005) and pure PPDO (Kricheldorf & Damrau, 1998). It was reported by other research team (Zhang et al., 2005) that after cellulose dissolving in ILs and subsequently coagulating with water, the regenerated cellulose exhibits the typical diffraction patterns of cellulose II at $2\theta = 20.3^\circ$ and $21.2^\circ$, accompanying with lower crystallinity. This further demonstrated that the crystallization of cellulose was destroyed not only by the introduction of PPDO side chain but also by the dissolution and precipitation process in [Bmim]Cl. The crystalline pattern of PPDO grafted chains could not be observed due to its lower chain length. In any case, the variety depicted that PPDO was grafted onto cellulose.

The morphology of native cellulose, regenerated cellulose from [Bmim]Cl and cellulose-g-PPDO copolymers were investigated by scanning electron microscopy (shown in Fig. 6). The regenerated cellulose from [Bmim]Cl was chosen for analysis of the morphological variations of the graft copolymers. From Fig. 6, we can see clearly that the surface of regenerated cellulose (Fig. 6B) was relatively rough compared with that of native cellulose (Fig. 6A). This may be attributed to the variation of crystalline structure in original cellulose through the dissolution and regeneration in [Bmim]Cl. As the graft copolymer was concerned, its morphology was different from those of cellulose and regenerated cellulose. The graft copolymer lost its fiber shape, an incompact sphere can be seen from its low-magnification SEM photograph (Fig. 6C). From the high-magnification SEM image (Fig. 6D), we cannot see clearly which one is cellulose or PPDO, demonstrated that they had been syncretized together and graft copolymerization was carried out completely.

The residual ILs in the mixture of ILs and ethanol after obtaining the products by precipitation can be recovered by simply process of distillization under reduced pressure to remove ethanol. The purity of [Bmim]Cl was confirmed by NMR spectra.

## 4. Conclusion

As a powerful, non-derivative and green solvent, [Bmim]Cl was first applied for the ring opening graft polymerization of PPDO and cellulose. PPDO with different molar substitution were successfully introduced into cellulose molecular structure and made copolymers have different properties compared with that of original cellulose. The copolymer was amorphous and had clear glass transition temperature. It had good solubility in DMSO, DMF. Beside this, we found by SEM photos that cellulose and PPDO had been syncretized together indicating the reaction carried out completely. In a conclusion, [Bmim]Cl is a good solvent for ROGP of PPDO and cellulose, although the grafted PPDO side chain was not so long. In order to clearly understand the difference of initiating activity of hydroxyl groups during cellulose dissolving in [Bmim]Cl, some detailed investigation were under going.

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