

Synthesis and Characterization of Cellulose-graft-poly(*p*-dioxanone) Copolymers *via* Homogeneous Ring-Opening Graft Polymerization in Ionic Liquids

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Cellulose-graft-poly(*p*-dioxanone) copolymers (cellulose-*g*-PPDO) were homogeneously prepared *via* ring-opening graft polymerization (ROP) between *p*-dioxanone (PDO) and hydroxyl groups of cellulose using the catalyst 4-dimethylaminopyridine (DMAP) in the ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl). Chemical structures and physical properties of the cellulose-*g*-PPDO copolymers were characterized by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (¹H, ¹³C, ¹H-¹³C 2D heteronuclear single quantum correlation (HSQC)-NMR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) techniques. By adjusting the reaction conditions, including the molar ratio of PDO to the anhydroglucose unit (AGU), amount of DMAP, and reaction temperature and time, the structure of the graft copolymers could be altered, and a series of copolymers with molar substitutions (MSs) in the range of 1.09 to 6.97 and polymerization degrees (DPs) varying from 1.85 to 2.88 were obtained. The graft copolymers exhibited a noticeably lower thermal stability than cellulose. After the attachment of PPDO groups, the crystalline structure of cellulose was disrupted because of the elimination of the inter- and intra-molecular hydrogen bonds of cellulose chains.

Keywords: Cellulose; Ionic liquids; Poly(*p*-dioxanone); ROP

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INTRODUCTION

Recently, much attention has been given to the utilization and functionalization of biomass resources as a substitute for petroleum-derived products (Yue *et al.* 2014). Cellulose, one of the main components of lignocellulose biomass, is believed to be a promising resource to supply chemicals, materials, and energy, and it has the advantages of being nontoxic, biodegradable, biocompatible, abundant, low-cost, and renewable (Klemm *et al.* 2005). However, wider applications of cellulose in the form of high-value materials have been restricted by its inherent drawbacks, *e.g.*, stiff polymer backbone, poor solubility in common solvents, lack of thermoplasticity, high hydrophilicity, and poor dimensional stability (Roy *et al.* 2009). Chemical modification of cellulose, especially grafting copolymerization, is an attractive and potentially efficient means to overcome such drawbacks and to impart some functional groups or side chains to the polymer (Qiu and Hu 2013). General grafting methods that are used include, but are not limited to, atom transfer radical polymerization (ATRP) (Meng *et al.* 2009), ring-opening graft

polymerization (ROP) (Carlmark *et al.* 2012), and reversible addition-fragmentation chain transfer polymerization (RAFT) (Barsbay *et al.* 2009).

Ring-opening graft polymerization is a well-known technique for preparing aliphatic polyesters from cyclic monomers; this technique has attracted increasing interest from researchers (Peng *et al.* 2015). Aliphatic polyesters are recognized as potential candidates for biomaterials in drug delivery carriers, tissue scaffolds, and surgical sutures. These aliphatic polyesters have excellent biodegradability, biocompatibility, functionality, and permeability, which make them suitable for biomaterial applications (Ikada and Tsuji 2000; Vert 2005; Hillmyer and Tolman 2014). Until now, considerable efforts have focused on the graft polymerization of cellulose or cellulose derivatives with aliphatic polyesters *via* ROP. The commonly studied and reported grafted aliphatic polyesters include poly(L/D/D,L-lactide) (PLA) (Dong *et al.* 2008; Yan *et al.* 2009; Guo *et al.* 2012a, 2013a), poly(ϵ -caprolactone) (PCL) (Jiang *et al.* 2011; Guo *et al.* 2013b) and poly(*p*-dioxanone) (PPDO) (Lai *et al.* 2012; Ge *et al.* 2015). Among them, PPDO is especially attractive for applications in monofilament sutures and bone and tissue fixation devices (Liu *et al.* 2008). Different from other aliphatic polyesters, PPDO has both ether and ester bonds in its main polymer chain, which provides good flexibility and biodegradability, as well as a fast hydrolyzing rate (Zhu *et al.* 2010). Generally, the ROP of *p*-dioxanone can be easily accomplished with covalent multivalent metal alkoxides or carboxylates, which act as catalysts, *e.g.*, stannous octoate (Sn(Oct)₂) (Liu *et al.* 2014). In fact, several attempts have been conducted to graft PPDO onto the backbone of cellulose or ethyl cellulose using Sn(Oct)₂ as a catalyst (Zhu *et al.* 2009, 2010).

Organic nucleophilic catalysts, including 4-dimethylaminopyridine (DMAP) (Coulembier and Dubois 2012), *N*-heterocyclic carbenes (NHCs) (Connor *et al.* 2002), 1,8-diazabicyclo-undec-7-ene (DBU) (Zhang *et al.* 2015), citric acid (Labet and Thielemans 2012), and amino acids (such as serine and proline) (Casas *et al.* 2004), are alternative catalysts for ROP. These catalysts are promising because of their availability and favorable selectivity. In our previous work, the catalytic activity of DMAP was found to be higher than that of Sn(Oct)₂ (Guo *et al.* 2013b). In the present study, DMAP was explored as the catalyst for the ROP reaction between *p*-dioxanone and cellulose. The ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl) was employed as the reaction medium. The obtained copolymers were characterized by Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (¹H-, ¹³C-, and ¹H-¹³C 2D HSQC-NMR), X-ray diffraction (XRD), and thermal analysis. The effects of reaction conditions, including the molar ratio of cyclic monomer to anhydroglucose units, the amount of DMAP, and the reaction temperature and time, on the compositions of copolymers were comparatively studied.

EXPERIMENTAL

Materials

BmimCl (99.0% purity) was purchased from Chengjie Chemical Co., Ltd. (Shanghai, China) and dried under vacuum at 60 °C for 72 h. *p*-Dioxanone (99.0% purity) was obtained from Jiaxing Light Chemical Co., Ltd. (Zhejiang, China); it was initially dried over calcium hydride for 48 h and then twice distilled before use. Microcrystalline cellulose with a degree of polymerization (DP) of 200 was obtained from Sinopharm Chemical Reagent Co., Ltd. (Tianjin, China) and vacuum dried at 45 °C for 48 h before use. DMAP (99.0% purity) was procured from Saien Chemical Technic Co., Ltd. (Xuzhou, China). All

other chemicals used in this study were of analytical reagent grade and used without further purification.

Methods

Synthesis of cellulose-g-PPDO copolymers

BmimCl (16.7 g) was charged into a 100-mL dried three-neck flask, which was placed into an oil bath and heated to 80 °C on a hot plate. Cellulose (1.0 g) was added into the above solution and mixed using magnetic stirring at 80 °C for 3 h under a nitrogen blanket. After the complete dissolution of the cellulose into BmimCl, the solution was heated up to 100 °C. The PDO monomer and the DMAP catalyst (at the desired amounts) were added into the solution. Then, the grafting reaction was performed at 100 °C with magnetic stirring for 12 h under a nitrogen blanket. When the reaction was over, the mixture was cooled to room temperature in an ice-water bath. The crude copolymers were obtained by precipitating the mixture using 200 mL of anhydrous methanol. The precipitate was washed three times with anhydrous methanol to remove BmimCl, PDO, and DMAP. The crude copolymers were purified by Soxhlet extraction with acetone for 48 h to remove the homo PPDO polymers that were possibly formed during grafting polymerization. The final products were vacuum dried at 45 °C for 48 h.

Characterization of cellulose-g-PPDO copolymers

The FT-IR spectra of cellulose-g-PPDO copolymers were collected from KBr discs containing 1% finely ground samples on a Fourier transform infrared spectrometer (TENSOR27, Bruker, Germany); scans were performed over the wave numbers of 400 to 4000 cm^{-1} . The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and HSQC-NMR spectra of cellulose-g-PPDO copolymers were measured using a 400 MHz NMR spectrometer (AV-III 400M, Bruker, Germany) operating at room temperature. The copolymer data were acquired using dimethylsulfoxide (DMSO-d_6) as the solvent. The chemical shifts were calibrated by the signals of trimethylsilane (TMS). The concentration of the copolymer in the solvent was 20 mg/mL for $^1\text{H-NMR}$, 80 mg/mL for $^{13}\text{C-NMR}$, and 60 mg/mL for HSQC-NMR.

The molecular weights of copolymers were determined by gel permeation chromatography (GPC, Waters, USA) using a PL aquagel-OH 50 column (300 \times 7.7 mm, Polymer Laboratories Ltd., USA), a Waters 1515 pump, and a differential refractive index detector (RID, Waters, USA). The phosphate buffer solution (5 mM, pH 7.5) with 0.02 N NaCl was used as the eluent. The flow rate of the eluent was constant at 1.0 mL/min, while the temperature of the column was 30 °C. The concentration of the copolymer was 1 mg/mL. A series of monodispersed pullulan standards (Mw of 783, 12,200, 100,000, and 1,600,000; Polymer Laboratories Ltd., USA) were used for the calibration curve.

The XRD patterns of copolymers were acquired on a D/max-III A X-ray diffractometer (Rigaku, Japan). Monochromatic nickel-filtered Cu-K α radiation with high intensity was generated at 40 kV and 40 mA. Copolymers were scanned in the range of 2θ from 5° to 70° with a speed of 1°/min and a step size of 0.04°.

The thermal stability of copolymers was determined with a thermogravimetric instrument (TGA Q500, TA, USA). Copolymers (5 to 10 mg) were initially placed into an aluminum crucible. The experiments were performed by heating from room temperature to 600 °C with a heating rate of 10 °C $\cdot\text{min}^{-1}$.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on the Grafting of PPDO onto Cellulose

DMAP, an efficient nucleophilic catalyst for ROP of cyclic polyesters, was employed to catalyze the grafting reaction between cellulose and PDO, while the hydroxyl groups of cellulose were used as initiators. BmimCl, an ionic liquid, was used to dissolve the cellulose, while PDO and DMAP were added to the homogeneous medium to synthesize cellulose-*g*-PPDO copolymers.

The procedure used to synthesize cellulose-*g*-PPDO copolymer is illustrated in Fig. 1. The degree of substitution (DS), the molar substitution (MS), the degree of polymerization (DP), and the weight content of PPDO (W_{PPDO}) of the grafted copolymers derived under various reaction conditions are listed in Table 1. The composition of grafted copolymers was affected by the molar ratio of PDO to AGU, the amount of catalyst, and the reaction temperature and time.

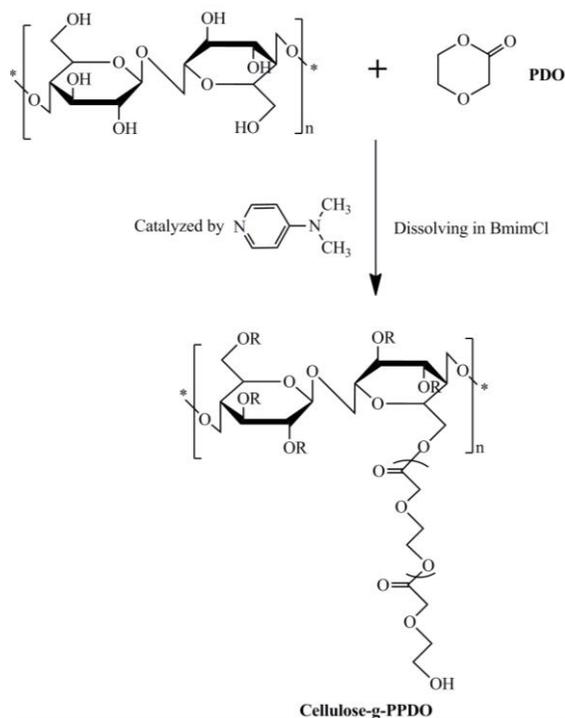


Fig. 1. The route for preparing cellulose-*g*-PPDO copolymers

Generally, as the molar ratio of DMAP to AGU was adjusted from 1:20 to 1:2, the DS, DP, MS, and W_{PPDO} of graft copolymers were enhanced from 0.57 to 1.89, 1.89 to 2.25, 1.09 to 4.25, and 40.7% to 72.8%, respectively. The molecular weights of graft copolymers also increased, from 32,500 to 66,200 g/mol. The GPC curves of typical prepared copolymers are shown in Fig. 2. It is known that an increase in the amount of DMAP used can accelerate polymer grafting between hydroxyl groups and PDO. However, the molecular weight, DS, MS, DP, and W_{PPDO} of graft copolymers were reduced when further increasing the amount of DMAP from 1:1 to 2:1; this was probably caused by the inducement of some side reactions, *e.g.*, the homopolymerization of PPDO. Therefore, excessive addition of DMAP (molar ratios > 1.0) was not beneficial for the synthesis of cellulose-*g*-PPDO copolymers.

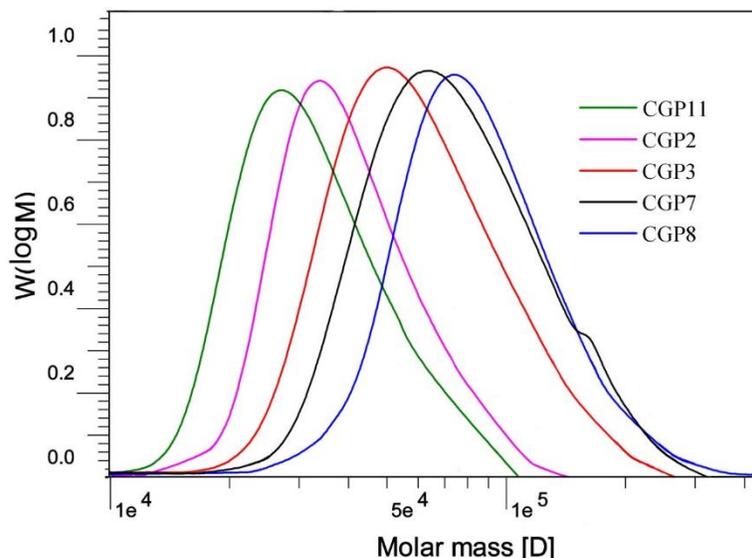


Fig. 2. The GPC curves of typical prepared copolymers

As expected, the amount of PDO used also affected the preparation of cellulose-*g*-PPDO copolymers. Increasing the molar ratio of PDO to AGU from 5:1 to 20:1 enhanced the DS, MS, DP, and W_{PPDO} of copolymers from 0.58 to 2.42, 1.10 to 6.97, 1.90 to 2.88, and 40.9% to 81.4%, respectively. The results of the GPC analysis also demonstrated that the M_w of copolymers progressively increased from 33,200 to 83,900 g/mol, accompanied by the continuous increment of PPDO groups onto the cellulose. Additionally, the elevation of reaction temperature from 80 to 100 °C led to an increase in DS, DP, and W_{PPDO} from 0.70 to 1.89, 2.19 to 2.25, and 49.1% to 72.8%, respectively. However, further increases in the reaction temperature from 100 to 120 °C yielded copolymers that had slightly lower DS, DP, and W_{PPDO} values. This observation was primarily attributed to the depolymerization of copolymers at high reaction temperature. It was also found that prolonging the reaction time from 12 to 24 h decreased the ROP grafting efficiency, primarily caused by the degradation of the grafted copolymers.

Table 1. Results of the Graft Copolymerization of PDO onto Cellulose in BmimCl

Samples	PDO/AGU (mol ratio)	T (°C)	t (h)	Catalyst (mol ratio)	DP	MS	DS	W_{PPDO} (%)	M_w 10 ⁴	M_w/M_n
CGP1	10:1	100	12	20:1	1.89	1.09	0.57	40.7	3.25	1.77
CGP2	10:1	100	12	10:1	1.93	2.22	1.15	58.3	4.04	1.43
CGP3	10:1	100	12	2:1	2.25	4.25	1.89	72.8	6.62	1.92
CGP4	10:1	100	12	1:1	2.05	1.68	0.83	51.4	3.56	1.54
CGP5	5:1	100	12	2:1	1.90	1.10	0.58	40.9	3.32	1.89
CGP6	8:1	100	12	2:1	1.97	2.21	1.12	58.2	5.46	1.71
CGP7	15:1	100	12	2:1	2.38	5.07	2.13	76.1	7.86	1.98
CGP8	20:1	100	12	2:1	2.88	6.97	2.42	81.4	8.39	1.61
CGP9	10:1	100	24	2:1	2.40	4.27	1.78	72.9	5.25	1.32
CGP10	10:1	120	12	2:1	1.85	4.07	2.20	71.9	5.77	1.40
CGP11	10:1	80	12	2:1	2.19	1.53	0.70	49.1	3.24	1.62

As shown in Table 1, the DP value of PPDO grafted onto cellulose polymer ranged from 1.85 to 2.88, which was too low for a typical PPDO side chain. The limited length of PPDO segment was attributed mainly to side-reactions, especially the homo-polymerization reaction of monomer PDO in ILs. It was well known that there is a trace amount of water in ILs, even after vacuum drying or freeze drying. The water in ILs could easily initiate the homo-polymerization reaction of PDO. The produced by-products homo PPDO polymers were also the initiators. The 1,3-dialkylimidazolium salt of BmimCl solvent acted as the catalyst for homo-polymerization reaction of PDO. Due to the high contents of ILs in the reaction system, relatively large amounts of PDO monomer could take part in the homo-polymerization reaction and form into the homo PPDO polymers. Such a reaction should decrease the chance of side-chain polymerization between cellulose and PDO, thus reducing the DP values of poly(p-dioxanone) (PPDO) of prepared copolymers. The proposed mechanism for homo-polymerization reaction of PDO catalyzed by 1,3-dialkylimidazolium salt is illustrated in Fig. 3 (A). As shown, the hydrogen at the C-2 position of the 1,3-dialkylimidazolium salt functioned as an acid catalyst by coordinating the carbonyl group of PDO and forming into the PDO-BmimCl complex. Meanwhile, the positive charge shifted to the nitrogen atom. The initiation reaction occurred when the nucleophile hydroxyl groups in water or homo PPDO polymers attacked the complex and resulted into adducts by ROP of PDO. After the ROP reaction, these adducts were dissociated with the complex to give the homo PPDO polymers and the free BmimCl catalyst. Except for catalyzing the ROP reaction between PDO and cellulose, the added catalyst of DMAP could also catalyze the homo-polymerization reaction of PDO. And the possible scheme for the homo-polymerization reaction of PDO catalyzed by DMAP is depicted in Fig. 3 (B).

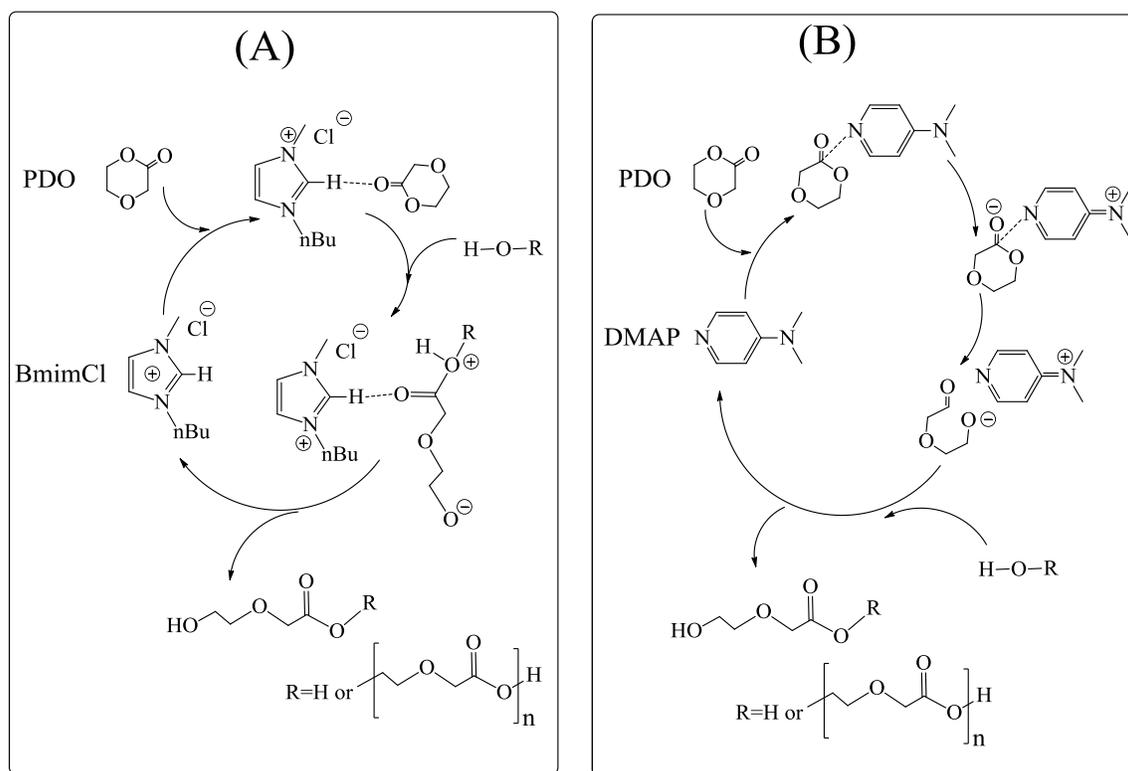


Fig. 3. The proposed mechanisms for homo-polymerization reaction of PDO catalyzed by BmimCl (A) or DMAP (B)

FT-IR Spectra

The FT-IR spectra of cellulose and cellulose-*g*-PPDO copolymers are shown in Fig. 4. In the spectra of cellulose, the assignments for the characteristic peaks at 3402, 2917, 1635, 1432, 1160, 1112, and 1057 cm^{-1} have been previously reported (Guo *et al.* 2012b). Three new peaks, at 1750 cm^{-1} for C=O stretching in ester, 1210 cm^{-1} for C-O-C stretching in the PPDO side chain, and 720 cm^{-1} for CH₂ rocking, were observed in the spectra of the graft copolymers. To verify that these peaks were derived from the PPDO grafted onto the cellulose but not from the homo-PPDO polymer that did not react with the cellulose, a sample of regenerated cellulose (reg-cellulose) was obtained by stirring a mixture of cellulose and PDO in BmimCl at 100 °C for 12 h without DMAP catalyst, followed by acetone extraction of the mixture. Comparatively, the typical peaks for the PPDO polymer chain were not found in the spectra of regenerated cellulose, which confirmed the successful ROP of PDO with cellulose.

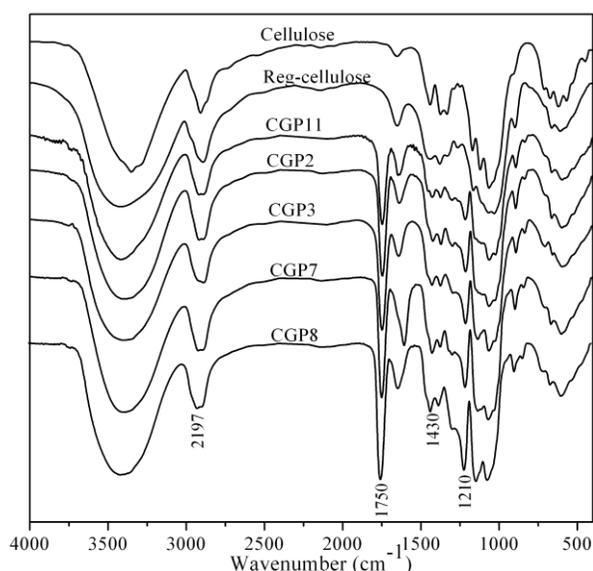


Fig. 4. The FT-IR spectra of cellulose, reg-cellulose, and graft copolymers

¹H-NMR, ¹³C-NMR, and ¹H-¹³C HSQC NMR

The chemical structures of cellulose-*g*-PPDO copolymers were elucidated using ¹H-NMR, ¹³C-NMR, and HSQC NMR techniques. In the ¹H-NMR spectra of cellulose-*g*-PPDO copolymers (Fig. 5), the signals in the range of 3.2 ppm to 5.6 ppm were assigned to the protons in glucose units of cellulose. The signals of methylene protons in the attached PPDO side chains were observed at δ of 3.39 ppm (-CH₂OH, c', PPDO terminal end), 3.70 ppm (-OCH₂-, b and b', repeating and terminal end), 4.15 ppm (-COCH₂-, a', terminal end), 4.17 ppm (-COCH₂-, a, repeating unit) and 4.22 ppm (-CH₂O-, c, repeating unit). The signal at δ of 3.06 ppm, corresponding to the proton of the H₄ position on the glucose units of cellulose, was clearly differentiated from the methylene protons of the PPDO chains. Therefore, the structure of graft copolymers, including DS, DP, MS, and *W*_{PPDO} of the PPDO side chains, were calculated based on the following equations,

$$MS = \frac{I_{(a+a')}}{I_{H4}} / 2 \quad (1)$$

$$DS = \frac{I_{a'}}{I_{H4}} \quad (2)$$

$$DP = \frac{MS}{DS} = \frac{I_a}{I_{a'}} + 1 \quad (3)$$

$$W_{PPDO} = \frac{102 \cdot MS}{162 + 102 \cdot MS} \cdot 100\% \quad (4)$$

where I_a , $I_{a'}$, and I_{H4} are the integral areas for the corresponding methylene proton signal at the a, a', and H₄ positions, respectively; 102 and 162 are the molecular weights of PPDO and glucose, respectively (in g·mol⁻¹).

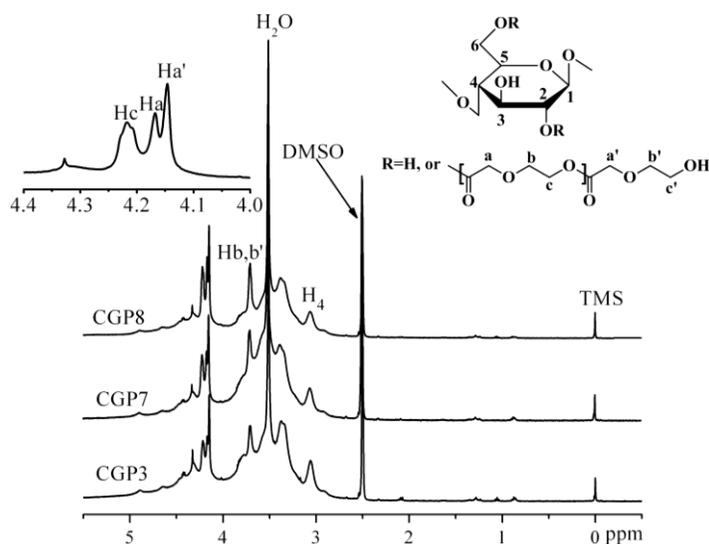


Fig. 5. Typical ¹H NMR spectra of cellulose-*g*-PPDO copolymers

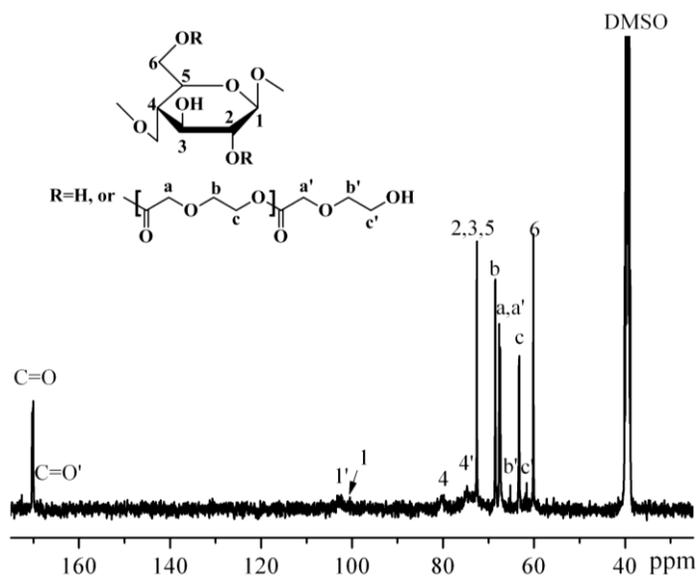


Fig. 6. Typical ¹³C-NMR spectra of CGP8 sample

The ^{13}C -NMR spectra of CGP8 in DMSO- d_6 are depicted in Fig. 6. The signals of the methylene carbons in the PPDO side chains were found at δ of 61.7, 63.2, 65.2, 67.6, and 68.5 ppm, ascribed to the carbons at the c' , c , b' , a (a') and b positions, respectively. The signal at δ of 170.3 ppm was assigned to the carbonyl carbons in the PPDO segment, which suggests the successful attachment of PPDO groups onto the cellulose polymer backbone. The four signals at δ of 100.2, 80.1, 72.6, and 60.0 ppm were attributed to C_1 , C_4 , C_2 , C_3 , C_5 , and C_6 in the glucose unit of cellulose, respectively. Moreover, the C_4' signal at δ of 74.8 ppm that belonged to the C_4 adjacent to the C_3 with a hydroxyl group substituted by PPDO appeared, while the signal at δ of 102.7 ppm that corresponded to the C_1 adjacent to C_2 bearing a substituted hydroxyl group also appeared. These observations indicated that the PPDO side chains were grafted onto the hydroxyl groups at multiple sites along the glucose unit of the cellulose polymer.

The 2D HSQC NMR spectra of CGP8 sample are shown in Fig. 7. Obviously, the marked signal correlations at δ_C/δ_H 101.9/4.29, 79.9/3.31, 74.4/3.34, 72.5/3.02, 72.1/3.47, and 59.9/3.52 ppm were assigned to C_1/H_1 , C_4/H_4 , C_3/H_3 , C_2/H_2 , C_5/H_5 , and C_6/H_6 in the glucose unit of cellulose. More importantly, the signal correlations corresponding to the structural elements of PPDO chains were observed at δ_C/δ_H 67.5/4.40, 68.0/3.68, 65.4/4.34, 62.6/4.18, and 61.5/3.79 ppm, attributed to C_a/H_a ($C_{a'}/H_{a'}$), C_b/H_b , C_c/H_c , $C_{c'}/H_{c'}$, and $C_{b'}/H_{b'}$ in the PPDO side chains, respectively. The presence of these correlations confirmed that the PPDO group was successfully grafted onto cellulose.

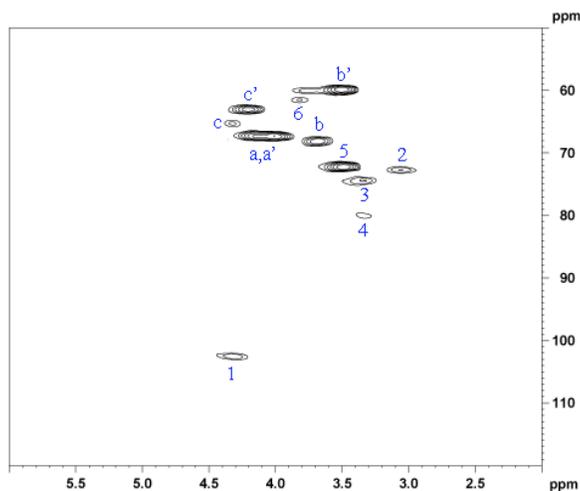


Fig. 7. 2D HSQC spectra of CGP8 sample

Thermal Stability and Crystallization Structure of Graft Copolymers

The TGA and differential thermogravimetric analysis (DTGA) curves of cellulose-*g*-PPDO copolymers are shown in Fig. 8. In the TGA curve, almost all of the weight loss of cellulose took place in the temperature range of 290 to 370 °C. Comparatively, the weight loss of graft copolymers primarily proceeded in the temperature range of 150 to 370 °C. Cellulose started to decompose at approximately 290 °C, whereas the graft samples CGP11 (MS = 1.53), CGP2 (MS = 2.22), CGP7 (MS = 5.07), and CGP8 (MS = 6.97) began to decompose at 201, 173, 160, and 152 °C, respectively. The decomposition temperatures at 50% weight loss were calculated to be 323 °C for CGP11, 320 °C for CGP2, 309 °C for CGP7, and 259 °C for CGP8, which were lower than that for cellulose. These observations indicated that the thermal stability of cellulose-*g*-PPDO copolymers was lower than that of cellulose. In the DTGA curve, cellulose displayed only one peak for the maximum weight

loss rate at 313 °C. However, the graft copolymers exhibited two different peaks for the maximum weight loss rates. The peak at relatively lower temperatures corresponded to the scission of the PPDO segment from the cellulose backbone and the decomposition of the PPDO group, while the peak at higher temperatures was ascribed to the degradation of the cellulose backbone. However, the maximum decomposition temperature of cellulose-*g*-PPDO copolymers was lower than that of cellulose, which also confirmed that the thermal stability of graft copolymers was decreased after the ROP reaction. This observation could be explained by the fact that grafting of PPDO side chains onto the cellulose backbone disrupted the inter-/intra-hydrogen bonds of the original crystalline structure of cellulose to some extent. Furthermore, the thermal stability of graft copolymers was highly affected by their chemical structure, especially the content of the grafted PPDO segment in the copolymers. Clearly, the first peak in the DTGA curve of the graft copolymer was enhanced, while the second peak decreased with increasing PPDO content. Additionally, the CGP11 sample, with a lower PPDO content, had a higher initial decomposition temperature (201 °C) and 50% weight loss temperature (323 °C), whereas the CGP8 sample, with a higher PPDO content, possessed a lower initial decomposition temperature (152 °C) and 50% weight loss temperature (259 °C). Thus, the thermal stabilities of graft copolymers were expected to be reduced gradually with increasing PPDO side chain content.

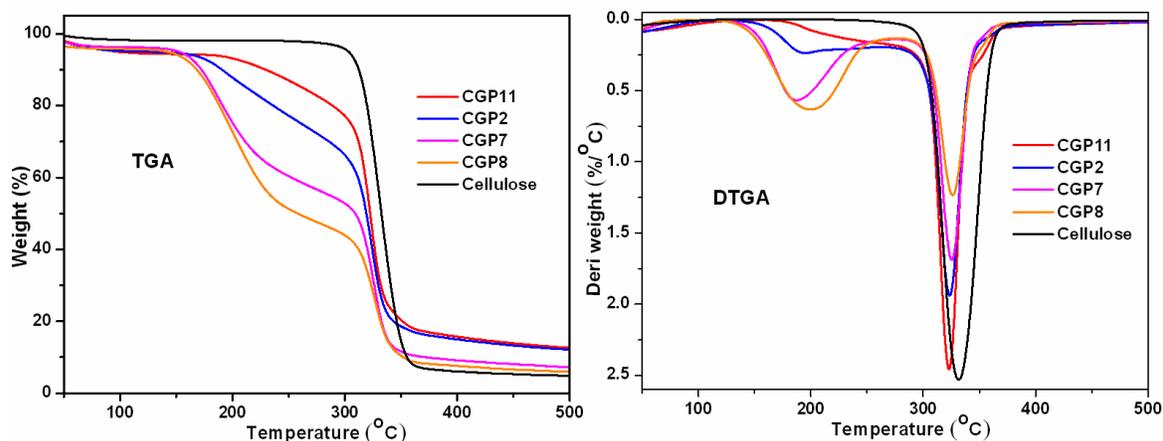


Fig. 8. TGA and DTGA curves of cellulose and cellulose-*g*-PPDO copolymers

The XRD patterns of cellulose-*g*-PPDO copolymers are shown in Fig. 9. In the pattern of cellulose, four characteristics peaks appeared, at 2θ of 14.90°, 16.67°, 22.82°, and 34.67°, which can be attributed to the diffraction patterns of the 101, 10 $\bar{1}$, 002, and 040 planes, respectively. However, the reflection peaks of the 101, 10 $\bar{1}$, and 040 planes were not observed for the graft copolymers, while the reflection peak of the 002 plane gradually disappeared with increasing PPDO content. The broad peak at 2θ of 20.0° was ascribed to the amorphous regions of the cellulose counterparts and was greatly enhanced in the patterns of the copolymers. It was concluded that grafting of the PPDO side chains onto the backbone of cellulose could disrupt its crystallinity by interfering with the inter-/intra-hydrogen bonds of cellulose chains. It should be noted that the crystalline peaks of the PPDO chains were not observed in all of the patterns of graft copolymers, which was attributed to the limited chain length of the PPDO segments.

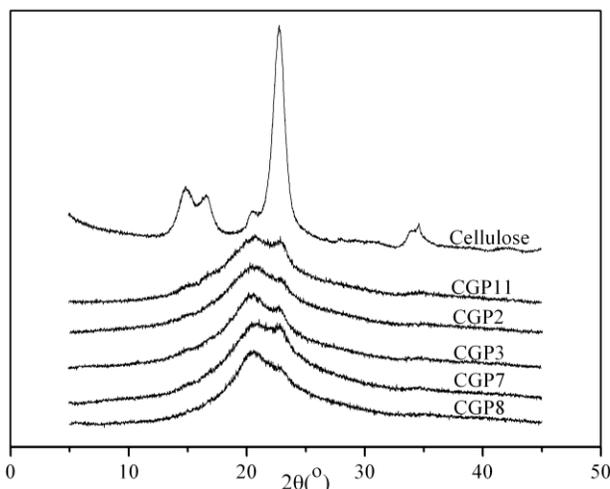


Fig. 9. XRD patterns of cellulose and cellulose-*g*-PPDO copolymers

CONCLUSIONS

1. Poly(*p*-dioxanone) (PPDO) was successfully grafted onto cellulose *via* the ring-opening polymerization (ROP) reaction with 4-dimethylaminopyridine (DMAP) as the catalyst in BmimCl. The effects of reaction conditions, *e.g.*, the molar ratio of PDO or DMAP to anhydroglucose unit and the reaction temperature and time, on the structure of graft copolymers were investigated.
2. FT-IR and NMR (¹H-NMR, ¹³C-NMR, and 2D HSQC-NMR) analyses provided the evidence of the successful grafting of PCL side chains onto the cellulose polymer. The ¹H-NMR analysis suggested that the MS and DP of obtained copolymers were in the range of 1.09 to 6.97 and 1.85 to 2.88, respectively. The ¹³C-NMR analysis indicated that the PPDO groups were grafted onto the hydroxyl groups at multiple sites along the glucose unit of the cellulose polymer.
3. After the attachment of PPDO side chains onto the cellulose polymer, the thermal stability of graft copolymers decreased and the original cellulose crystallinity was diminished.

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