Adjustment of Molecular Weight for a Cellulose-graft-poly(ethylene glycol dimethacrylate) Polymer Brush by Atom Transfer Radical Polymerization in an Ionic Liquid

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ABSTRACT

A cellulose-graft-poly(ethylene glycol dimethacrylate) (cellulose-g-PEGDMA) molecule brush was synthesized by atom transfer radical polymerization in the ionic liquid 1-allyl-3-methylimidazolium chloride. The controlled mechanism of the polymer brush size and polydispersity index (PDI, Mw/Mn) were investigated. The grafting copolymers were characterized by FTIR, ^{1}H-NMR and GPC. The results indicate that the reaction time was the main factor to control the length of the cellulose-g-PEGDMA molecule brush. The ligand was the decisive factor in controlling the PDI of the molecule brush. The PDI of PEGDMA was precisely controlled at 1.1–1.4 by using pentamethyldiethylenetriamine(PMDETA) as the ligand. Moreover, the graft molecule brush length could be varied with the change of PMDETA concentration. The Mn of PEGDMA was 75210 and had a narrow PDI of 1.15 when the PMDETA/CuBr ratio was 20:1. In addition, TEM images show that the cellulose-g-PEGDMA copolymer could aggregate and self-assemble into a sphere-like polymeric structure in solution, indicating that the obtained grafting copolymers have potential applications in biomedical materials.

KEYWORDS: *Cellulose, Ionic liquid, ATRP, Controlled molecular weight, Self-assembly*

1. INTRODUCTION

Natural cellulose, as one of the most abundant biomacromolecules in the world, has attracted considerable attention in recent years due to its biodegradable, inexpensive, biocompatible, renewable and excellent flexible characteristics[1-4].

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As its anhydroglucopyranose unit contains reactive hydroxyl groups, cellulose has potential use in the design of advanced polymeric materials[5–7]. However, cellulose lacks some of the properties that synthetic polymers possess in some applications, although it has many useful properties. Consequently, the modification of cellulose by graft polymerization provides a significant route to combine the advantages of natural and synthetic macromolecules for a wide range of potential applications[8,9]. With the advent of controlled free radical polymerization techniques, it is now helpful to synthesize polymers with predetermined structures and polydispersity for a great variety of monomers. Among them, atom transfer radical polymerization (ATRP) is one of the techniques used to accurately control the chain length and PDI of the polymer molecular weight, and could be employed to synthesize well-defined copolymers[10-14].

Many efforts have been reported on the grafting modification of cellulose by ATRP[15]. Li and co-workers synthesized EC-g-P(PEGMA) grafting copolymers *via* ATRP. EC-g-P(PEGMA) copolymers can self-assemble into spherical micelles in aqueous solution and present thermosensitive properties, which have potential applications in biomedicine and biotechnology[16]. Afterwards, the MMA was homogeneously grafted on a cellulose-based macro-initiator *via* ATRP and confirmed that the generation of the cellulose-grafted PMMA was a controlled/living ATRP process[17]. Yuan et al. used ATRP to synthesize biocompatible block copolymers with various compositions and the block copolymers were capable of existing as micelles[18]. However, a traditional ATRP reaction was carried out in organic solvents, which are undesirable in the case of strict environmental regulations. Ionic liquids (ILs), as green solvents, have been applied as reaction media in many fields, due to their obvious merits[19–21]. Therefore, syntheses of functional cellulose molecular brushes by ATRP in ionic liquid systems have been investigated[22,23]. Dong et al. designed and synthesized good biocompatibility cellulose-g-PLLA in [AMIM]Cl ILs. The drug loaded micelles formed by the copolymer in aqueous media show sustained drug release, indicating their potential use in drug carrier applications[24].

Cellulose-g-PMMA and cellulose-g-PS copolymers with well-controlled molecular weights and PDI were successfully synthesized by ATRP in ILs. The grafted copolymers in solution could aggregate and self-assembly into sphere-like polymeric structures[25]. Tang et al. prepared a cellulose-g-PDEAEMA of a narrow PDI by ATRP in [AMIM]Cl. The acquired cellulose-g-PDEAEMA could self-assemble into spherical micelles and showed pH sensitivity, implying its potential application in biomedical materials[26]. Subsequently, a pH-responsive cellulose-g-P4VP copolymer was synthesized by ATRP in IL, which has potential as a carrier for released drug delivery[27]. Significant research has been devoted to the grafting of a variety of functional monomers to obtain grafting copolymers. However, the length of the grafted molecule brush and their homogeneities play an important role in the performance of graft copolymers, especially on the application of drug released delivery polymer carriers. Currently, reports on how to control precisely the adjustment of molecular weight size and its PDI on the cellulose graft polymer

brush by ATRP in ILs to meet the requirements of special applications are rare.

In this study, ATRP is employed to synthesize the graft copolymer of cellulose with a PEGDMA polymer brush with the IL [AMIM]Cl as a reaction medium. The mechanism of ATRP is explored and how to adjust precisely the molecular weight size and PDI of a graft polymer brush on the ATRP reaction in the IL is researched. The effect factors on the molecular weight and PDI of the graft polymer brush were confirmed on the ATRP reaction in the IL. A preliminary study on the morphology of the graft copolymer in solution is also presented.

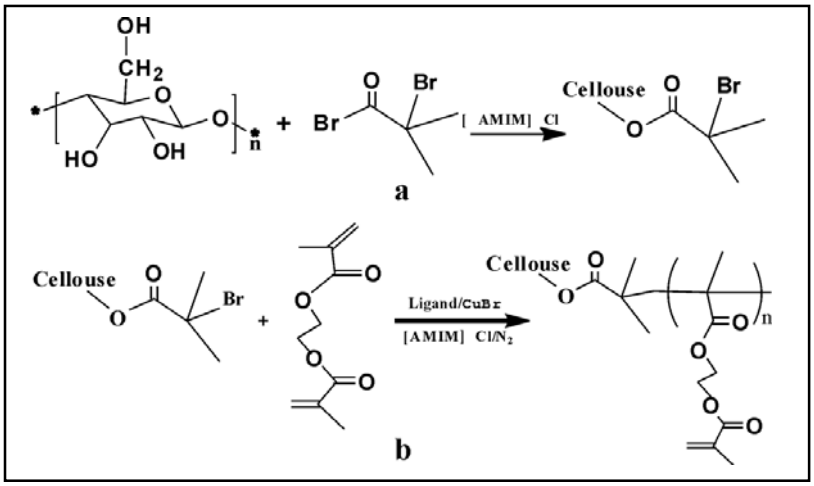
2. EXPERIMENTAL

2.1 Materials

Microcrystalline cellulose (MCC) was obtained from the Tianjin Fuguang Fine Chemical Research Institute and was dried under vacuum before use. The monomer ethylene glycol dimethacrylate (EGDMA, >99%, Aladdin) was distilled under reduced pressure before use. Copper(I) bromide (CuBr, Tianjin Guangfu Fine Chemical Research Institute) was stirred in glacial acetic acid to remove any soluble oxidized species, washed with acetone and then dried under vacuum at 25°C. 2-Bromoisobutyryl bromide (BrBiB), pentamethyldiethylenetriamine (PMDETA), ethylenediamine, diethylenetriamine (DETA) ligand (98%, Aladdin) and [AMIM]Cl (>99%, Shanghai ChengJie Chemical Co) were used as received. Dimethylformamide (DMF), tetrahydrofuran (THF) and acetone dimethyl sulfoxide were distilled prior to use. All other chemicals were of analytical grade and were used without further purification.

2.2 Controllable synthesis of cellulose-g-PEGDMA in IL system

The synthesis route of cellulose-g-PEGDMA is shown in Scheme 1. Graft copolymerization to produce cellulose-g-PEGDMA was performed through a two-step reaction in an IL. The first step was esterification of cellulose with BrBiB to obtain the macroinitiator cellulose-BiB. 0.50 g cellulose was dissolved in 12.00 g, then a mixture of BrBiB and toluene was added dropwise into the solution. The reaction mixture was kept at 30°C for 12h. An excess of deionized water was added to the solution, and the resulting cellulose-BiB flocculent precipitate was washed and freeze-dried. Thus, cellulose-BiB was generated with a degree



Scheme 1. Synthesis procedure of MCC-BiB (a) and MCC-g-PEGDMA (b).

of substitution (DS) of 0.98. In the second step, 0.060 g cellulose-BiB was dissolved in [AMIM]Cl. 0.032g CuBr, 0.12ml PMDETA, 3ml EGDMA were added to the solution, and the reaction mixture was held at 50°C for 8h under nitrogen[28]. An excess of deionized water was added to the solution, and obtained the cellulose-g-PEGDMA copolymer. The copolymer was diluted with distilled water and then transferred to a soxhlet extraction reactor using acetone as the solvent. After 12 h, the sample was repeatedly washed with distilled water and freeze-dried to obtain the graft copolymer.

2.3 Characterization

Fourier transform infrared (FT-IR) spectra of samples were recorded on an FTS-13 spectrometer (Bio-Rad, USA) equipped with a diamond ATR device. ^{1}H-NMR spectra were obtained on an Avance 500 MHz spectrometer (Bruker, Switzerland), with deuterated dimethylsulfoxide used as a solvent. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) employing a SHIMADZU pump (LC-10ADVP) and a detector (RID-10A) using THF as an eluent at a flow rate of 1 ml/min. TEM was carried out on a JEM-2100 transmission electron microscope (JEOL Co., Japan) at an accelerating voltage of 120 kV. The micelle solutions were prepared by dissolving cellulose-g-PEGDMA (50 mg) in DMF (20 mL). Monomer conversion was determined gravimetrically.

3. RESULTS AND DISCUSSION

3.1 Effect of different ligands on cellulose-g-PEGDMA copolymer molecule brush

According to the polymerization mechanism of ATRP, the well-defined cellulose-g-PEGDMA with different PDIs was obtained. To investigate the influence of different ligands on the molecular weight and PDI of the polymer, a series of polymerizations were conducted using CuBr/bpy, CuBr/PEGDMA and CuBr/DETA as the catalyst system, respectively, and ionic liquid [AMIM]Cl as the reaction medium. Table 1 shows the experimental results obtained by changing the reaction catalyst system. It is clear that the PMDETA/CuBr catalytic system had a narrower PDI of cellulose-g-PEGDMA, which showed a better controllability of the reaction. The possible reason might be the controllability of the reaction being enhanced with growing the length of the C chain and increasing the substituent group in amine ligand[29].

TABLE 1. Effect of ligand species on molecular weight and PDI of MCC-g-PEGDMA.

[EGDMA]/[BiB]/CuBr/Ligand	Ligand	Conversion/%	Mn	PDI(Mw/Mn)
100:1:1:10	Ethylenediamine	58.3	29325	2.13
100:2:1:10	Ethylenediamine	82.7	24671	2.37
100:1:1:10	DETA	54.9	112892	1.83
100:2:1:10	DETA	78.5	107630	1.89
100:1:1:10	PMDETA	53.8	83574	1.14
100:2:1:10	PMDETA	74.0	75210	1.15

To understand the variation of PDI and reaction mechanisms with different ligands for the prepared cellulose-g-PEGDMA, the mechanisms of the ATRP reaction system using ethylenediamine and PMDETA as the ligand in [AMIM]Cl were compared. Fig. 1a

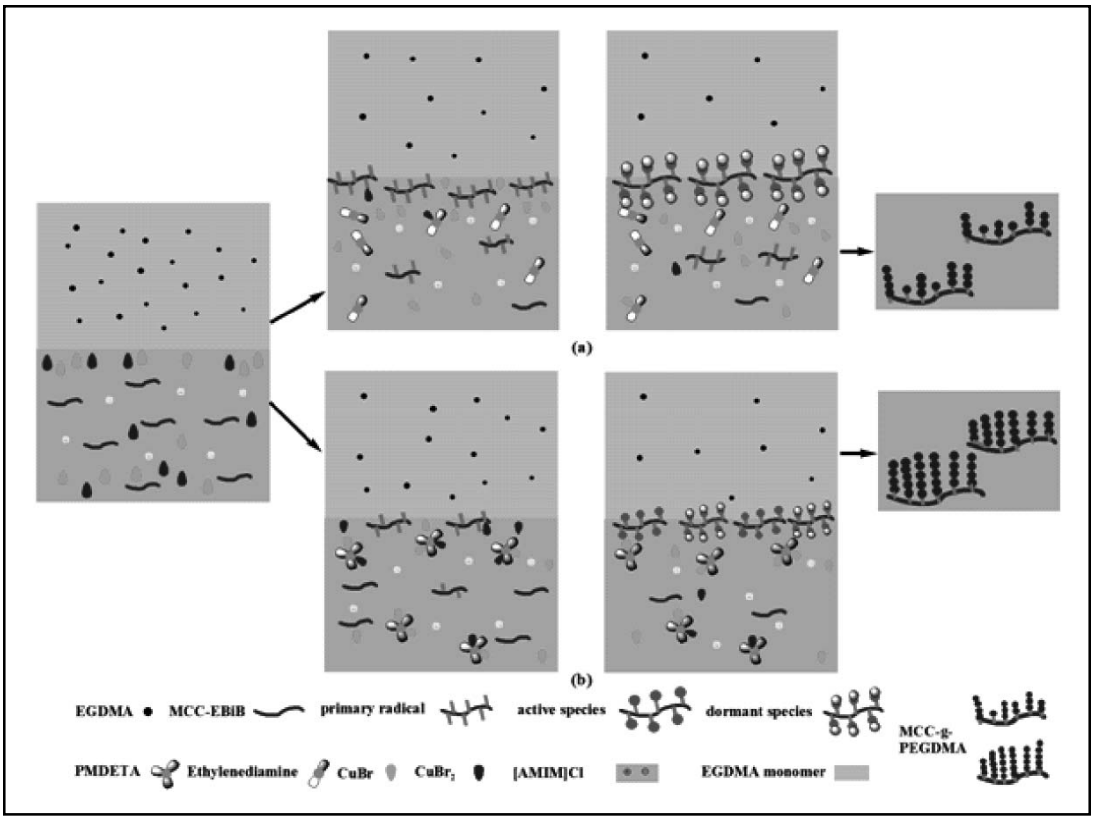


Fig. 1. Reaction mechanism diagram with different ligands (PMDETA and ethylenediamine).

shows the reaction mechanism using ethylenediamine as the ligand. It could be seen that significant Cu(I) was obtained by the reduction of Cu(a!) due to the active H in the ATRP reaction system, which resulted in the increase of concentration of free radicals in the system, even leading to an irreversible termination reaction and the generation of numerous dormant species[30,31]. Consequently, the PDI of cellulose-g-PEGDMA molecular brushes obtained was wide, which implied the poor controllability of the ATRP reaction. Correspondingly, the reaction mechanism using PMDETA as the ligand is shown in Fig. 1b. The Cu(I) and Cu(II) are presented in the reaction system. The tendency of self-polymerization is reduced in the reaction system, achieving a reversible dynamic equilibrium of active species and dormant species. Therefore, the obtained copolymers had grafted a polymer brush with well-controlled molecular weight and PDI, which indicates that the ATRP reaction was controlled and PEGDMA molecular brushes were uniformly grafted from the cellulose backbone[32,33]. The reason is due to the fact that the effect of PMDETA is only coordinated with Cu ions and has no strong ability of reduction. Therefore, PMDETA was used as a ligand to only increase

the solubility of CuBr in the [AMIM]Cl. This result indicated that the ligand was the main factor in controlling molecular brush length and PDI. The cellulose-g-PEGDMA copolymer molecular brush with a narrow PDI and precise molecular weight was synthesized using PMDETA as a ligand.

3.3 Effect of amount of ligand on cellulose-g-PEGDMA

CuBr was used with PMDETA as the complexing ligand of the ATRP reaction. ATRP experiments were carried out with PMDETA in various concentrations. Fig. 2 shows kinetic plots of $\ln[M_0]/[M_t]$ versus time. It is clear that the polymerization was approximately first-order with respect to the monomer concentration. The reaction rate improved with increasing ligand concentration (Fig. 2). The effect of the amount of ligand on the molecular weight and PDI of cellulose-g-PEGDMA was studied. The results are shown in Table 2. It is shown that the PEGDMA had a molecular weight of 15473 and a PDI of 2.21 when the ratio of ligand to catalyst was 1:1. As the ratio of ligand to catalyst (PMDETA: CuBr) increased, the molecular weight change of PEGDMA was small and uneven. Moreover, the PDI of cellulose-g-PEGDMA is gradually narrowed. Additionally, the PDI of the polymer was 1.15

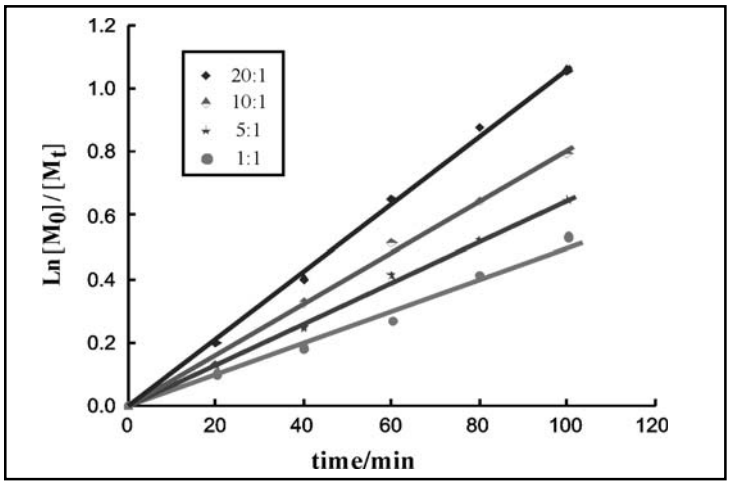


Fig. 2. Kinetic plots of MCC-g-PEGDMA prepared by ATRP with different amounts of ligand.

TABLE 2. Effects of the amount of ligand on polymerization by ATRP.

Sample	t/h	n(PMDETA)/n(CuBr)	T/°C	Conversion/%	Mn	PDI(Mw/Mn)
1	8	1:1	65	54.2	15473	2.21
2	8	5:1	65	59.3	40840	1.36
3	8	10:1	65	65.4	61542	1.27
4	8	20:1	65	74.0	75210	1.15
5	8	25:1	65	75.2	68465	1.92

when the ratio of the amount of ligand to catalyst substance was 20:1. However, when PMDETA:CuBr was greater than 20:1, with the amount of ligand increasing, the conversion rate was slowly increasing and the PDI was suddenly widened, which presented poor controllability. The increase of ligand could promote solubility of the catalyst complex and increase reactivity sites in the system, which would enhance the reaction rate. As the ligand concentration continued to increase, the rate of polymerization reaction was improved. However, the conversion rate did not obviously increase, which led to a reduction in the controllability of the reaction and a wide PDI[34, 35]. The molecular weight size and width of the PDI of MCC-g-PEGDMA can be controlled by adjusting the ratio of PMDETA to CuBr to obtain the cellulose-g-PEGDMA copolymer with the determined molecular weight.

3.4 Effect of reaction time on PEGDMA copolymer molecule brush

A series of ATRP experiments were carried out in various reaction times in order to research the effect of reaction time on the cellulose graft

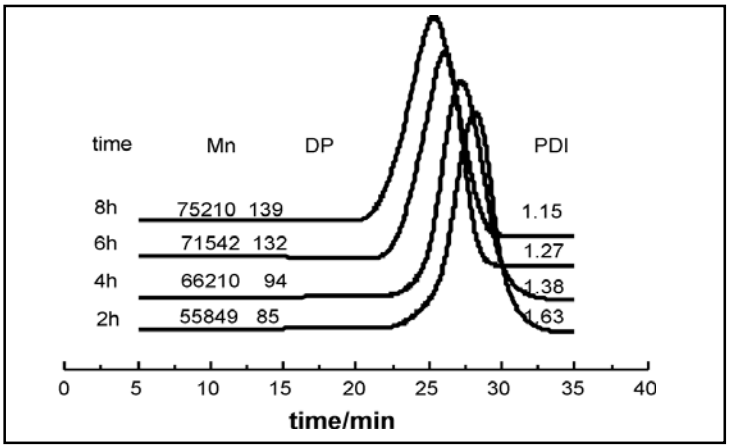


Fig. 3. GPC traces of copolymer PEGDMA polymerized at different reaction times.

TABLE 3. Effects of different reaction times on PEGDMA molecular weight and PDI.

Sample	t/h	T/°C	Conversion/%	DP	Mn	PDI(Mw/Mn)
1	2	65	45.2	85	45849	1.33
2	4	55	53.5	82	59813	1.28
3	4	65	56.3	94	66210	1.22
4	6	65	65.4	132	71542	1.17
5	8	65	74.0	139	75210	1.15
6	8	75	77.1	143	92325	1.92

n(EGDMA)/n(MCC-Br)/n(CuBr)/n(PMDETA)=200/1.5/1/10; DP (Degrees of polymerization=n(EGDMA)/n(MCC-BiB) Concentration of Cu:molar ratio of Cu to monomer.

molecular brush. The molecular weight and PDI of PEGDMA are depicted in Fig. 3 and Table 3. It is shown that the molecular weight of the graft copolymer was increased with the monomer conversion and the PDI was reduced by a factor of 1.6 after the grafting polymerization. It was clear that the PEGDMA had a degree of polymerization of 85 and a molecular weight of 45849 with a PDI of 1.33 after the reaction for 2 h. The degree of polymerization and molecular weight of PEGDMA increased with the prolongation of reaction time, but the PDI decreased. After 8 h of reaction, the degree of polymerization of PEGDMA was 139, Mn increased to 75210 and the PDI reduced to 1.15. The relationships of molecular weight versus conversion and conversion versus time are depicted in Fig. 4 and 5. The linearity of the plot indicated that the polymerization reaction was a first-order reaction with respect to the monomer. The number of active species was constant throughout the polymerization process and the amount of radical termination in the ATRP system was low. The monomer concentration gradually decreased with increasing conversion rate. The whole process presented the active polymerization characteristics. Fig. 5 shows the molecular weight and PDI versus conversion of EGDMA polymerization. The molecular weight of PEGDMA increases with the consumption of the monomer. In the reaction, the PEGDMA had a molecular weight in the range of 1.5×10^4 to 8.0×10^4 and PDI 1.15 to 1.33. While molecular weight increased linearly with conversion, PDI remained relatively narrow, which further confirmed the living/controlled characteristics of the polymerization in ATRP system[36-37]. The ATRP reaction could control the length of the polymer chain by adjusting the reaction time, so the cellulose-g-PEGDMA copolymer molecule brush with precise molecular weight size could be synthesized by controlling the reaction time.

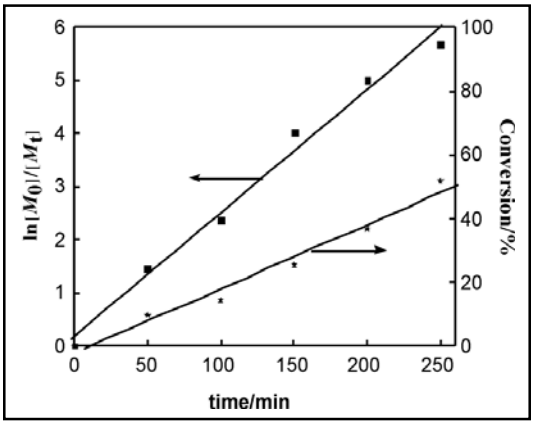


Fig. 4. Kinetic Plots of polymerization prepared by ATRP at different reaction times.

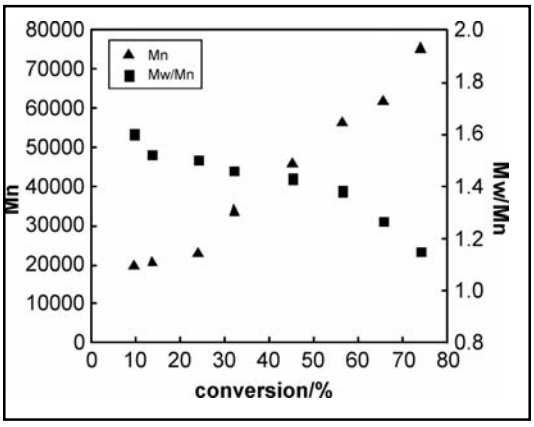


Fig. 5. 0Molecular weights and Mw/Mn vs. monomer conversion in ATRP of [Amim]Cl.

3.5 FT-IR and ^{1}H-NMR analysis of cellulose-g-PEGDMA

The FT-IR spectra of the native microcrystalline cellulose-BiB and cellulose- g-PEGDMA are shown in Fig. 6. The FT-IR spectrum of cellulose-

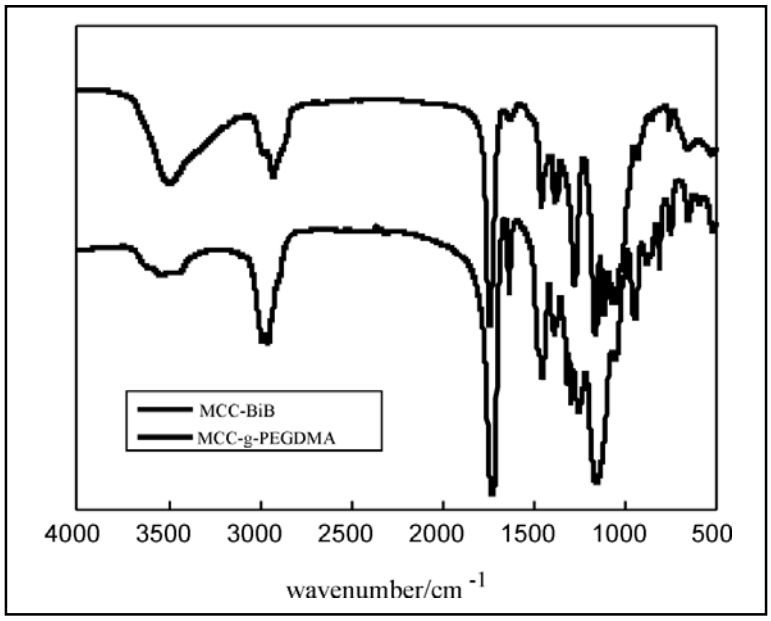
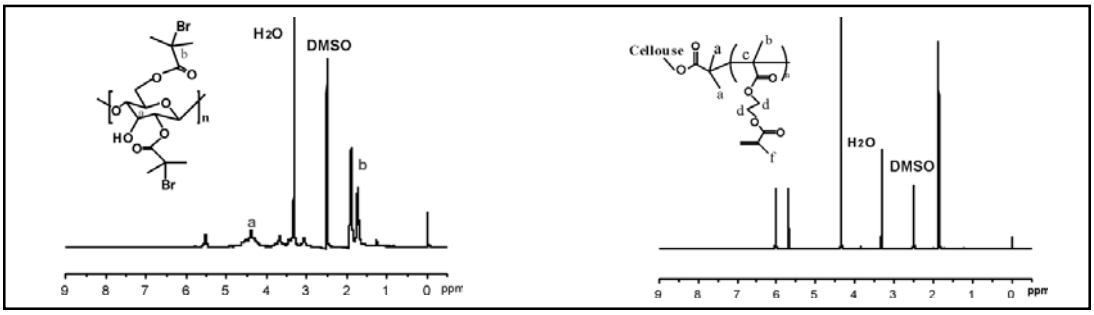


Fig. 6. FT-IR spectra of macro-initiator MCC-BiB (a) and MCC-g-PEGDMA copolymer (b)

g-PEGDMA (Fig. 6b) show a new peak at 1159 cm^{-1}, which arose from fat ether bond C–O–C stretching vibrations. Absorption peaks due to C-H symmetric stretching of -CH_2 and -CH_3 groups appeared at 2863 and 2958 cm^{-1}. The peak corresponded to the saturated esters of C–O of the PEGDMA chains. In addition, the peaks at 1735, 1649 and 1262 cm^{-1} corresponded to the stretching vibration peaks of C=O and C=C of the PEGDMA chains. The weak peak of hydroxyl groups of the cellulose backbones at ~3350 cm^{-1} also indicated the lower amount of hydroxyl groups in the graft copolymers. These results indicated that PEGDMA chains were chemically bonded onto the cellulose substrates.

The structure of cellulose-BiB (Fig. 7a) and



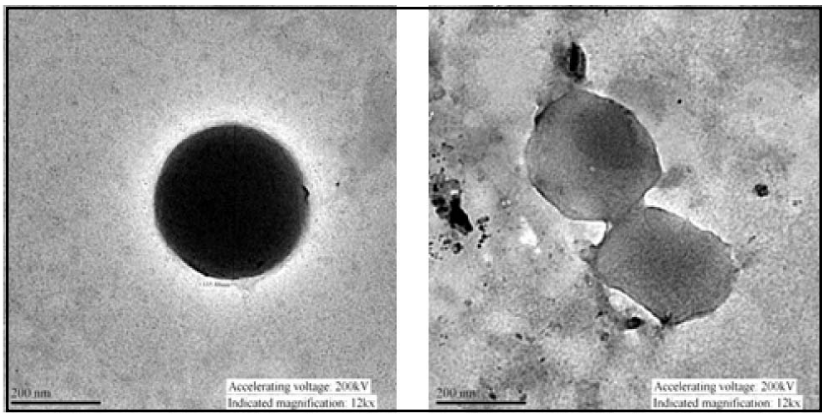
(a) MCC-BiB (b) MCC-g-PEGDMA

Fig. 7. ^{1}HNMR spectra of macro-initiator MCC-BiB and MCC-g-PEGDMA copolymer

cellulose-g-PEGDMA (Fig. 7b) were characterized through ^{1}H-NMR spectroscopy. It was found that the chemical shift corresponding to each peak was δ_1 = 6.020 ppm, δ_2 = 5.695 ppm, δ_3 = 4.352 ppm and δ_4 =1.867 ppm, among the main chain peak of PEG at 3.500~4.352 ppm (Fig. 7b). These characteristic peaks were due to protons of the PEGDMA side chains, indicating the successful synthesis of cellulose-*g*-PEGDMA.

3.6 Self-assembly of different cellulose-g-PEGDMA in DMF

Herein, cellulose-g-PEGDMA, with different PDIs, was tested for self-assembly in the organic solvent DMF. The cellulose graft copolymer tends to form micelles through the aggregation of the cellulose backbone or polymer side chain. The hydrophilic PEGDMA chains reside mainly in the corona of the micelles, whereas the hydrophobic backbone of cellulose was mainly in the core of the micelles[38]. The morphology of aggregation produced changes with the different PDIs of PEGDMA. Fig. 8 shows images of the micelle solutions at different PDIs. It showed that the cellulose-g-PEGDMA with a PDI of 1.83 was self-assembled in DMF solution to form an irregular shape. However, the cellulose-g-PEGDMA with a PDI of 1.15 could be self-assembled to a regular spherical structure in DMF solution. The results indicated that the morphological characteristics of aggregates depended on the PDI of PEGMDA chains, which is beneficial to their application in drug delivery systems.



(PDI=1.15) (PDI=2.13)

Fig. 8. Self-assembled morphology the different PDI of MCC-g-PEGDMA in DMF

4. CONCLUSIONS

The controlled mechanism of adjusting precisely the molecular weight size and PDI of the graft polymer brush were investigated and their effects were discussed. The molecular weight and PDI were mainly adjusted by the

reaction time and ligand. The main factor of controlling the PEGDMA chains is the reaction time. However, the ligand is the key factor to adjust the PDI of PEGDMA chains. Moreover, the concentration of ligand also regulates the length of PEGDMA chains. Furthermore, cellulose-g-PEGDMA of narrow PDI can be self-assembled in DMF solution to form a regular, stable spherical nanoscale micelles. These cellulose-g-PEGDMA polymeric micelles could be applied to biomedical carrier materials.

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REFERENCES

1. CF Hsu, PA Kilmartin . *React. Funct. Polym.* 2012, 72, 814-22.
2. R Zuluaga, JL Putaux, J Cruz, J Velez, L Mondragon, P Ganan. *Carbohydr. Polym*. 2009, 76, 51-59.
3. M Ishimaru, M Nagatsuka, A Masubuch, J Okazaki, K Kurita. *Polym. Bull.* 2014, 71, 301-313.
4. L Yue, A Maiorana, F Khelifa, A Patel, JM Raquez, L Bonnaud, R Gross, P Dubois, L. Manas-Zloczower *Polym.* 2018, 134, 155-162.
5. AJ Carmichael, DM Haddleton, SAF Bon, KR Seddon. *Chem. Commun*. 2000, 14: 1237-1238.
6. F Bougard, M Jeusette, L Mespouille, P Dubois, R Lazzaroni. *Langmuir.* 2007, 23, 2339-2345.
7. HC Liu, LD Rong , BJ Wang , ZP Mao, RY Xie, H Xu, LP Zhang, Y Zhong, XF Sui. *Carbohydr. Polym.* 2017, 170, 117-123.
8. X Yin, A Koschella, TH Heinze. *React. Funct. Polym.* 2009, 69, 341-346.
9. M Wang, J Yuan, XB Huang, XM Cai, L Li, J .Shen *Colloid. Surf.* 2013, 103: 52-58.
10. JS Wang, K Matyjaszewsli. *J. Am. Chem. Soc*. 1995, 117, 5614-5615.
11. WW Li, K Matyjaszewski. *Rapid. Commun.* 2011, 32, 74-81.
12. G Lu, YM Li, CH Lu, ZZ Xu, H. Zhang *Polym. Bull.* 2010, 65, 227-244.
13. K Mukumoto, MJ Zhong, K.Matyjaszewski *Eur. Polym. J.* 2014, 56, 11-16.
14. A Hajlane, J Roberts. *Ind. Crops. Prod.* 2017, 100, 41-50.
15. EP Timothy, K Matyjaszewski. *Adv. Sci.* 1998, 12, 901-915.
16. YX Li, RG Liu, W Y Liu, HL Kang, M Wu, Y Huang. *J. Polym. Sci. Polym. Chem.* 2008, 46, 6907-6915.
17. JF Zhong , XS Chai , SY Fu. *Carbohydr. Polym.* 2012, 87, 1869-1873.
18. B Yuan, Q Chen, WS Ding, PS Liu, SS Wu, SC Lin, J Shen, Y Gai . *ACS Appl. Mater. Interfaces.* 2012, 4, 4031-4039.
19. P Kubisa. *Polym. Sci.* 2004, 29, 3-12.
20. YF Xiao, JH Jiang, SH Peng, JP He, MM Fan, K Wang. *Polym. Mater. Sci. Eng*. 2017, 33, 56-61.
21. JM Zhang, J Wu, J Yu, XC Zhang, QY Mi, J Zhang. *Acta. Polymerica. Sinica.* 2017, 7, 1058-1072.
22. XF Sui, JY Yuan, M Zhou, J Zhang, HJ Yang, WZ Yuan, Wei Yen, CY Pan. *Biomacromolecules*. 2008, 9, 2615-2620.
23. G Wang, L Mang, W Hu. Polym. 2012, 53, 1093-1097.

24. HQ Dong, Q Xu, YY Li, SB Mo, SJ Cai, LJ Liu . *Colloids and Surfaces B: Biointerfaces.* 2008, 66, 26-33.

25. EJ Tang, KD Du, XY Feng, M Yuan, SJ Liu, DS Zhao. *Eur. Polym. J.* 2015, 66, 228-235.

26. T Meng, X Gao, J Zhang, JY Yuan, YZ Zhang, JS He. *Polym*. 2009, 50, 447-454.

27. H Du, T Xue, EJ Tang, M Yuan, SJ Liu, DS Zhao. *J. Chem. Eng. Chinese Universities.* 2017, 31, 352-360.

28. D Q Wang, J J Tan, H L Kang, L Ma, X Jin, RG Liu, Y Huang. *Carbohydr. Polym.* 2011, 84, 195-202.

29. T Xue, Tang E J, Zhou J, Han RT, Liu SJ. *J. Appl. Polym. Sci.* 2017, 134, 45484.

30. W Tang, K Matyjaszewski. *Macromolecules*. 2006, 39, 4953-4959.

31. HJ Chen, T T Sun, Q Ren. *Polym. Mater. Sci. Eng.* 2012, 28: 17-21.

32. T Ando, M Kamigaito, M Sawamoto. *Macromolecules.* 2000, 33, 5825-5829.

33. A J Clarka, GM Battle, AM Heming, DM Haddleton, A Bridge. *Tetrahedron Lett*. 2001, 42, 2003-2005.

34. AK Nanda, K. Matyjaszewski *Macromolecules.* 2003, 36, 1487-1493.

35. BY. Tian, EJ Tang, M Yuan, RX Hao, CM Li, F Bian, L Li. *Property Adv. Mater. Res.* 2013, 705, 115-119.

36. A Zorvaryan, S Inceoglu. *Polym.* 2010, 52, 617-621.

37. XF Sui, JY Yuan, M Zhou, J Zhang, HJ Yang, WZ Yuan, Y Wei, CY Pan. *Biomacromolecules.* 2008, 9, 2615-2620.

38. NM Ranjha, G Ayub, S Naseem, MT Ansari. *J. Mater. Sci. Mater. M.* 2010, 21, 2805- 2816.

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