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Graft copolymerization of N,N-Dimethylacrylamide to cellulose in homogeneous media using atom transfer radical polymerization for hemocompatibility

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ABSTRACT

In homogeneous media, N,N -Dimethylacrylamide (DMA) was grafted copolymerization to cellulose by a metal-catalyzed atom transfer radical polymerization (ATRP) process. First, cellulose was dissolved in DMAc/LiCl system, and it reacted with 2-bromoisobutyloyl bromide (BiBBr) to produce macroinitiator (cell-BiB). Then DMA was polymerized to the cellulose backbone in a homogeneous DMSO solution in presence of the cell-BiB. Characterization with FT-IR, NMR, and GPC measurements showed that there obtained a graft copolymer with cellulose backbone and PDMA side chains (cell-PDMA) in well-defined structure. The proteins adsorption studies showed that the cellulose membranes modified by the as-prepared cell-PDMA copolymer own good protein adsorption resistancet.

Keywords: Cellulose; Atom transfer radical polymerization (ATRP); Homogeneous; Graft copolymerization; Hemocompatibility

1. INTRODUCTION

Cellulose is the most fluent feedstock in the world that could be used to prepare new kinds of materials, and cellulose derivatives have potential application as functional polymers. Graft copolymers are the important topic for their novel properties. Today, "grafting from" method has been widely used to prepare cellulose copolymers. Ceric ion initiation, Fenton's reagent and ɣ -radiation are the widely used methods to graft monomers to cellulose [1,2]. However, there are some drawbacks of these methods, such as the production of unwanted homopolymer together with the graft copolymer, chain degradation of the cellulose backbone during the formation of free radical grafting sites, and the presence of a considerable amount of ungrafted cellulose in the product. In addition, these techniques usually results in the graft copolymer with poor control over the composition, such as molecular weight and the polydispersity of the grafted chains [3]. Recently, controlled/"living" radical polymerization methods have been developed [4], which is able to minimize chain transfer and to control the molecular weight and polydispersity. Among them atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer polymerization (RAFT) are the two convenient methods to prepare well-defined polymers. Using living free radical polymerization methods to prepare cellulose graft copolymer is an attractive topic and some investigations had been carried out. Perrier, *et al.* reported a preparation of polystyrene graft cellulose by a RAFT process [5]. Carlmark and Malmstrom synthesized a poly(2-hydroxyethyl methacrylate) graft cellulose using an ATRP process [6]. However, in both the studies, the graft copolymerization occurs only on the surface of cellulose fiber due to the heterogeneous process. Huang, *et al.* reported a homogeneous ATRP process to prepare cellulose graft copolymers with different monomers; the reason why ethyl cellulose was selected as the feedstock is its easily dissolving ability in many solvents[8, 9, 25, 26, 27]. By now there are still less reports to synthesize cellulose graft copolymer through a living radical polymerization directly from cellulose in its homogeneous solution, and it is important to prepare well-defined structures of the graft copolymer.

Poly(N,N-dimethylacrylamide) (PDMA) is well-known for its remarkable water solubility and biocompatibility [10]. Recently, well-defined PDMA has been prepared by both RAFT [11] and ATRP pro-

cesses [12]. Also PDMA has been grafting polymerization to polystyrene colloid by ATRP method [13].

Hemodialysis is one of the most important methods for blood purification [14], and cellulose membranes, especial cellulose acetate (CA) membranes, are still the major materials for hemodialysis [15]. The cellulose membranes could take the porous and asymmetrical structure and have both good permeability and mechanical strength. However thrombus formation on the blood-contact surface could not suppressed by the membrane. Thus, its hemocompatibility must be further improved for better hemodialysis [16]. Several efforts had been carried out to solve these problems, such as modification of the surface of the membrane with low-molecular-weight compounds, hydrophilic polymers and biologically active heparin [17,18].

In this paper, synthesis of the graft copolymer composed of PDMA chains and cellulose backbone (cell-PDMA) in homogeneous solution have been studied via an ATRP. Moreover, the protein adsorption resistivity on the cellulose membrane surface modified with the cell-PDMA was evaluated to understand hemocompatibility of the cell-PDMA.

2. EXPERIMENTAL SECTION

2.1. Materials

The chemical formula of the DMA is shown in **Scheme 1**. Commercial product of microcrystalline (Sigma, DP = 121) was used without further purification. 2,2'-Bipyridine (bpy) purchased from Aldrich was recrystallized from ethanol to remove impurities. DMA, CuBr with purity of 99.999% and 2-bromoisobutyloyl bromide (Br*Bi*B) were purchased from Aldrich and used without further purification. Other solvents and reagents were extra-pure grade reagents and used without further purification.

2.2. Dissolution of cellulose in N,N-dimethyl acetoamide (DMAc)/LiCl

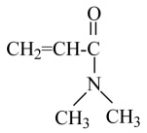
After dried in vacuum at 35°C overnight microcrystalline cellulose (5.167 g) was put into a 250 ml three-necked round-bottom flask, and adding 100 ml of distilled water for 30 min to swell it, then water was removed and fresh water was added again, and the process was repeated for three times. Then removing the water and adding 100 ml of methanol to swell again for 30 min for three times. After removing methanol the cotton was dried in vacuum at 50 °C for 3 h. Then cooling down the solution and adding 120 ml of DMAc and heated at 160 °C for 1.5h, and removing 20 ml of DMAc under reduced press by a rotary evaporator. At the same time, about 10.22 g of LiCl was dried in baker at 60 °C. After the removing process of DMAc finish, adding the dried LiCl into the system, and stirring at 80 °C for 13 h, and the cellulose solution was obtained at the end [19].

2.3. Synthesis macroinitiator for ATRP

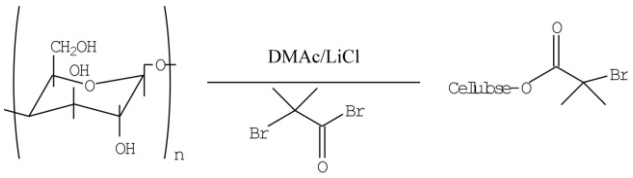
Cellulose was acylated with Br*Bi*B in the presence of pyridine as shown in **Scheme 2** [25, 26, 27]. In a 250 ml three-necked round-bottom flask, 60 ml of the cellulose solution in DMAc/LiCl and 5 ml of pyridine were added and mixed, then 6.3541 g of Br*Bi*B was slowly dropped into the solution at 0 °C in an ice/water bath. The reaction mixture was further stirred at room temperature overnight. Then the mixture was added with de-ionized water and plenty of precipitate appeared, and after washed by plenty of de-ionized water, the precipitate was dried at 50 °C in vacuum overnight. Finally, there obtained white powder product of macroinitiator(cell-B*i*B) with weight of 4.81 g. The cell-B*i*B can be well dissolved in dimetyl sulfoxied (DMSO).

2.4. Grafting copolymerization of DMA by the cell-B*i*B

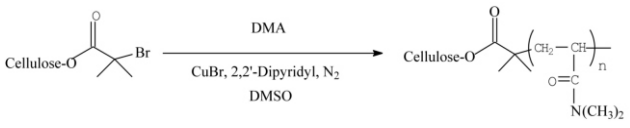
The cell-B*i*B(0.1737 g, 0.9 mmol) was dissolved in 30 ml of DMSO in a 100 ml of flask. Then 7.92 g (0.08 mol) of DMA was added, and the solution was evacuated and flushed with nitrogen for 30 min. Finally, 0.1021 g of bpy (0.7 mmol) and 0.0444 g of CuBr (0.31 mmol) were added, and the polymerization was carried out at room temperature under the protect of nitrogen. A few milliliter of samples were withdrawn from the flask at different reaction time using degassed syringes to determine monomer conversion and molecular weight.



Scheme 1. Chemical structure of DMA.



Scheme 2. Synthesis route for the macroinitiator (cell-B*i*B).



Scheme 3. Graft copolymerization of DMA on cellulose backbone in homogeneous solution via the ATRP route.

The samples were diluted with DMSO and filtering the solution through a silicon gel column to remove the Cu ions catalyst, and then plenty of hexane was

added to produce the precipitate of the products. The products were dried at 40 °C in vacuum overnight.

2.5. Isolation of the grafted PDMA chains by hydrolysis

The copolymers were hydrolyzed by 70% H_2SO_4 for 8h at boiling point. At the end, the residual polymer was participated into plenty of hexane and was dried by freeze drying, then the products were analyzed by GPC.

2.6. Characterization

The chemical structure was confirmed using an FT-IR (FT/IR-615, JASCO, Tokyo, Japan). ^{1}H- and ^{13}C-NMR spectra were obtained on a NMR spectrometer (α -300, JEOL, Tokyo, Japan) with D_2O as the solvent. The molecular weights of these polymers were determined by gel permeation chromatography (GPC). The mixture of methanol/water = 7/3 containing 10 mmol/L of lithium bromide was used as an eluent for the GPC measurement at a flow rate of 0.4 ml/min (Column: SB-804 HQ, Shodex, Tokyo, Japan). The number-averaged molecular weight (M_n) and weight-averaged molecular weight (M_w) were calculated using poly(ethylene glycol) standards.

X-ray photoelectron spectroscopy (XPS) was conducted on an AXIS-HSi (Shimadzu/KRATOS, Kyoto, Japan) employing Mg K_α excitation radiation (1253.6 eV). The take-off angle of the photoelectron for each atom was fixed at 90 deg.

For Atomic force microscopy (AFM) measurement, the sample was dissolved in DMF at a concentration of 8×10^{-6} g/m. Then a droplet (20 μl) of the solution was deposited onto freshly cleaved mica, and it was spin-coated at speed of 900 rpm for 8 s and then 4000 rpm for 30s. The height image of the copolymer on mica were measured by an AFM (Nanoscope IIIa, D.I.) in tapping mode with silicon TESP cantilevers. The scanning rate ranged from 0.5 Hz to 1.0 Hz, and 512×512 pixels images were record.

2.7. Coating of the cell-PDMA on cellulose membrane

The regenerated cellulose membrane, Cuprophan$^{(TM)}$, was obtained from Enka, A. G. (Wappertal-Barmen, Germany). The thickness of the membranes was 20 μm. First the cellulose membranes were cut into pieces with diameter of 1.5cm, and they were immersed into deionized water for 30 min, and then were dried at 35 °C in vacuum for 15h. Then the cellulose membranes were immersed into the 0.5 wt% aqueous solution of the cell-PDMA for 3 min, and the membranes were took out and dried under atmospheric conditions for 2h, and then was dried at 35 °C in vacuum for 15 h. The structure of the grafted DMA on the cellulose membranes were confirmed using XPS and FT-IR. The ratio of nitrogen atom (N) in the DMA unit versus carbon atom (C) was determined from the XPS elemental analysis.

2.8. Protein adsorption on the membrane surface

Amount of proteins adsorbed on the membrane was measured by almost the same method reported previously [20]. The round (diameter: 1.5 cm) cellulose membranes were placed into a 24-well plate. To equilibrate the membrane surface, phosphate buffer solution (PBS, pH 7.4, ionic strength : 0.15 mol/l) was added into each well and allowed to remain for 15 h at room temperature. Protein solutions were prepared in the concentration of 4.5 mg/ml of albumin, 1.6 mg/ml of γ -globulin, and 0.3 mg/ml of fibrinogen, which are 10% of the concentration of the human plasma level. After removing the PBS, 1.0 ml of each protein solution was poured onto each membrane and allowed to remain at 37 °C for 3 h. After rinsing the membrane three times with PBS, the membrane was taken out of the 24-well plate, and was rinsed again sufficiently with the 50 ml of PBS. The membrane was placed into a glass bottle with a 1 wt% aqueous solution of sodium dodecyl sulfate (SDS) and shaken (150 rpm) in a shaking bath for 3 h at room temperature to detach the adsorbed protein on the surface. A protein analysis kit (Micro BCA protein assay reagent kit, #23235, Pierce, Rockford, IL, USA) based on the bicinchoninic acid method was used to determine the protein concentration in the SDS solution.

3. RESULTS AND DISCUSSION

The cell-B*i*B was prepared by partial esterification of the hydroxyl groups of the glucose units of cellulose with B*i*BBr in the presence of pyridine. The reaction was carried out homogeneously in DMAc/LiCl solution at room temperature for 23 h. The formation of the ester bond resulted in the appearance of the characteristic peaks at 1743 cm^{-1} for the C=O stretching band in the FTIR spectrum, as shown in **Figure 1**.

The substitution of the hydroxyl groups on the cellulose backbone with B*i*BBr was also confirmed by

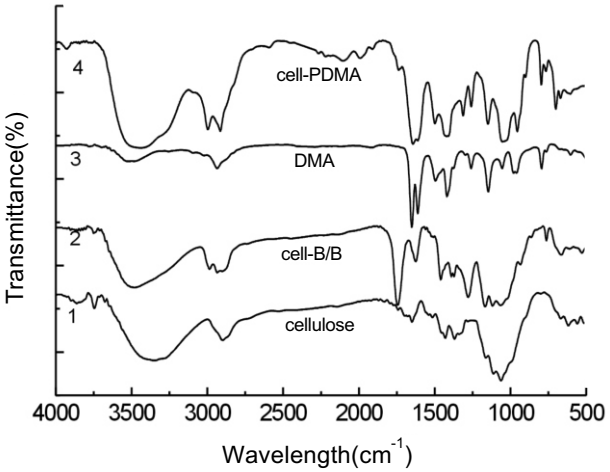


Figure 1. FT-IR spectra of cotton (1), cell-B*i*B (2), DMA (3) and cell-PDMA (4).

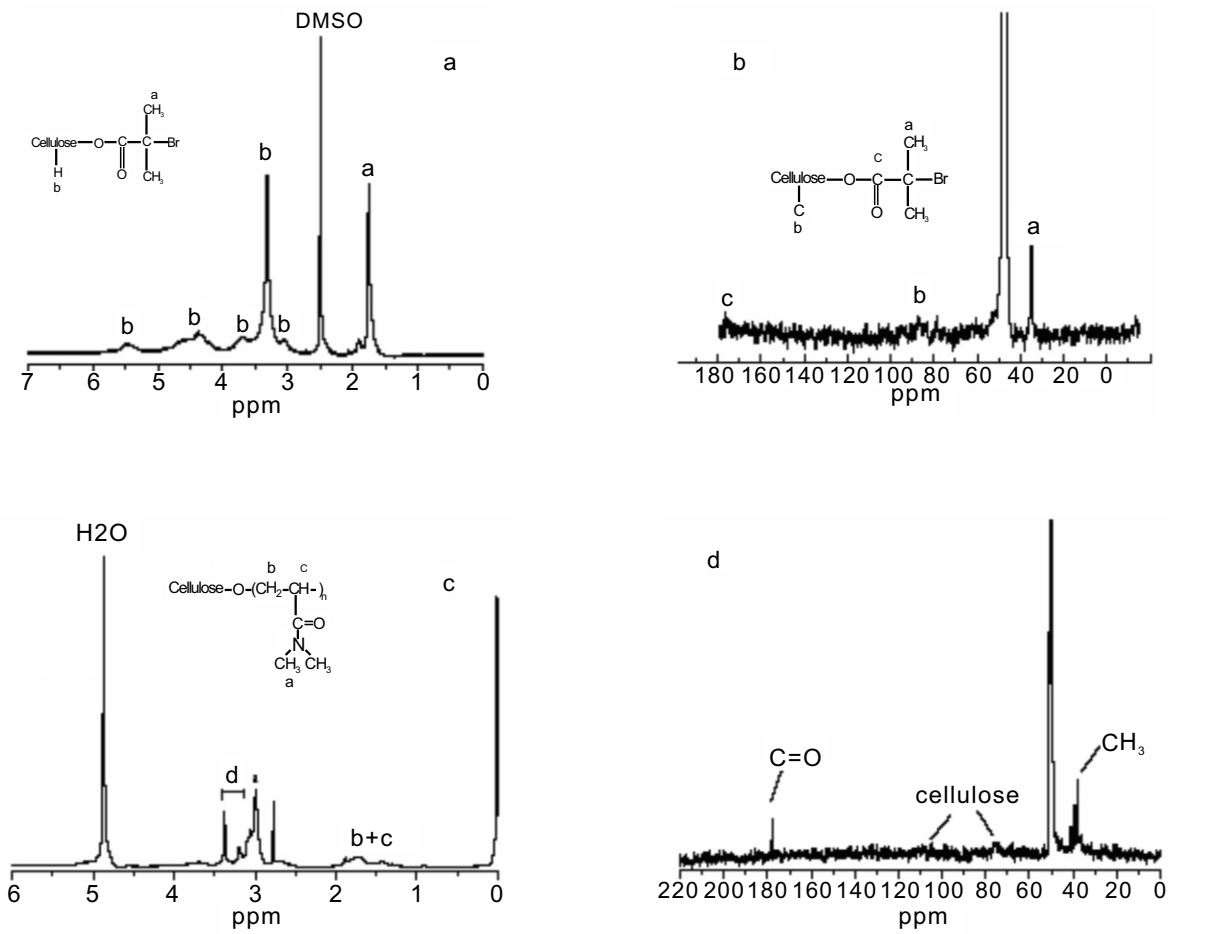


Figure 2. ^{1}H-NMR and ^{13}C-NMR spectra of cell-B*i*B (a, b) and cell-PDMA (c, d).

both the ^{1}H-NMR and ^{13}C-NMR. As shown in **Figure 2a**, there appears a new single peak at 1.8 ppm (peak a) for methyl protons in the ester group of B*i*B, and the peaks at δ = 2.8-5.6 ppm (peak b) for the methylene protons and hydroxyl protons in the glucose units of cellulose [21]. The total substitution degree (DS) of B*i*B is obtained by the ratio of the integral of the methyl groups to the integral of protons of glucose, and the DS is 0.2. **Figure 2b** shows the ^{13}C-NMR of the cell-B*i*B, and clearly both the methyl carbon from B*i*B (peak a) and the carbon in glucose (peak b) appear, and the peak c at 176 ppm attributed to the C=O carbon of B*i*B [22].

The as-prepared cell-B*i*B can be dissolved well in DMSO. The graft copolymerization of DMA to cellulose was carried out in DMSO at 100 °C, [DMA]:[cell-B*i*B]:[CuBr]:[bpy] = 88:1:2.9:1.3, and $[DMA]_0$ = 2.7 M. **Figure 3** shows the kinetic plot of the reaction, and the variation of $\ln([M]_0/[M])$ is linear with time, indicating a constant concentration of propagating radicals which is the characteristic of the controlled/"living" radical polymerization.

The chemical structure of the cell-PDMA was identified by FT-IR spectroscopy, NMR and GPC. As shown in **Figure 1**, when the FT-IR spectrum of cell-PDMA was compared with that of the cell-B*i*B and DMA monomer, the absorptions at 1642 cm^{-1} appeared after grafting, which was assigned to the free C=O of PDMA, and the peaks at about 3100-3500 cm^{-1} was assigned to the OH group of cellulose [23].

Figure 2c shows a ^{1}H-NMR spectrum for the cell-PDMA in methanol-d_4 at 25 °C, the spectra is about the same as that of PDMA. The resonance bands observed at 2.9-3.1 ppm are attributed to the dimethyl group, and those observed at 1.3~1.8 ppm is attributed to the methyl amd methylene protons of PDMA [24]. Part of the resonance bands of cellulose protons are overlapped with that of PDMA while there appear peaks at 2.9-4.0 ppm for the characteristics of cellulose. **Figure 2d** shows a ^{13}C-NMR spectrum for cell-PDMA in D_2O at 25 °C. The characteristic of the resonance peak for PDMA was observed at 35 ppm, which is attributed to the dimethyl moiety [25]. The weak peaks appear at 75-85 ppm are attributed to the carbon for cellulose back bone, and the peak appear at 182 ppm is attributed to the carbon for the carbonyl groups.

The grafted PDMA chains were converted to individual molecules through hydrolysis of the backbone

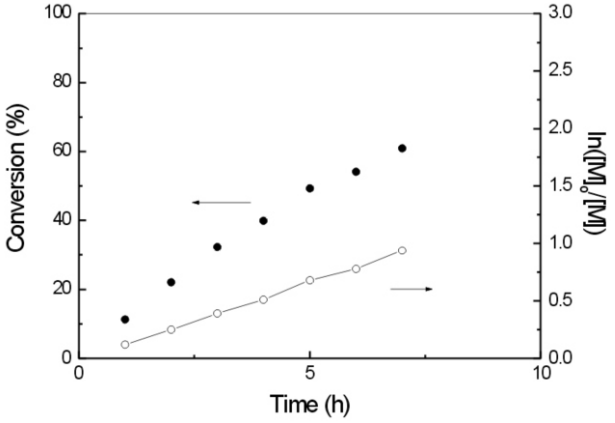


Figure 3. Time-conversion and the first-order kinetic plot for the polymerization of DMA initiated by the cell-B*i*B in the homogeneous solution of DMSO at 100 °C. [M_0] and [M] are concentrations of monomer at polymerization time = 0 and at corresponding time, respectively.

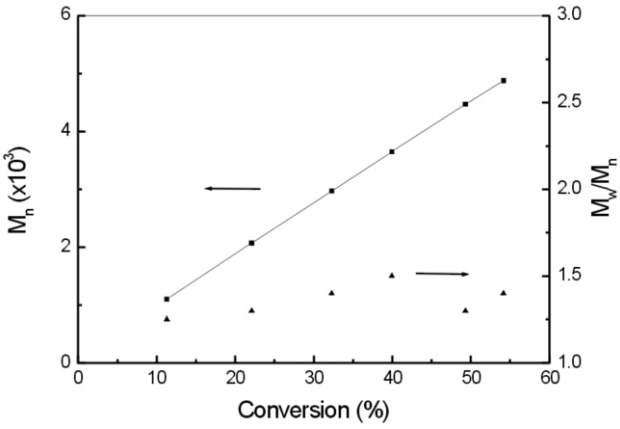


Figure 4. Dependence of M_n and M_w/M_n on monomer conversion in the graft polymerization of DMA in DMSO, the PDMA was hydrolyzed from the side chain of the copolymer before the GPC measurements.

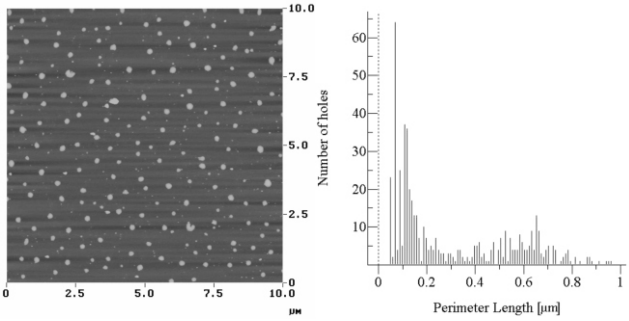
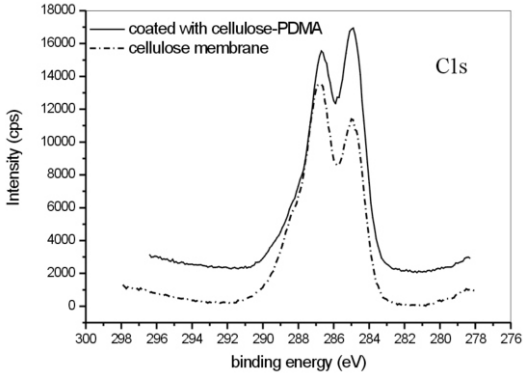


Figure 5. Typical AFM image of the cell-PDMA (a) and the perimeter distribution of the particles (b).



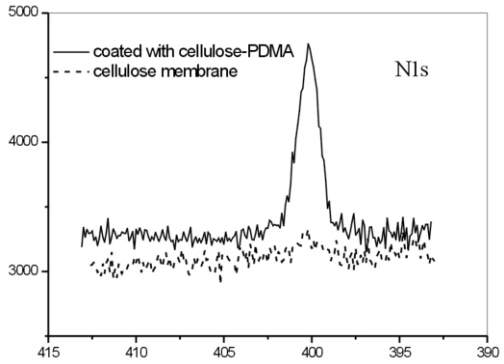


Figure 6. XPS spectra of P_{2p}, N_{1s}, C_{1s}, and O_{1s} observed on the original cellulose membrane (down row) and that coated with the cell-PDMA (upper row).

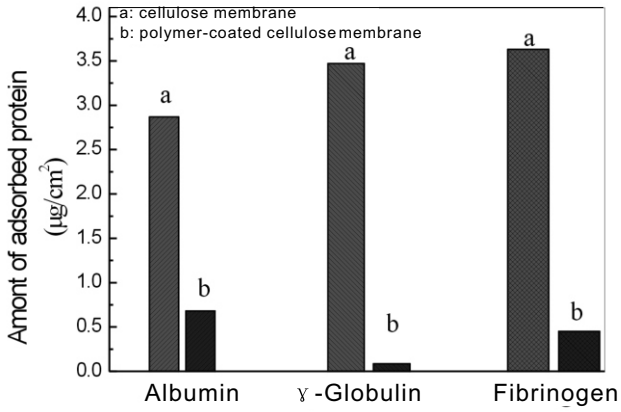


Figure 7. Amount of proteins adsorbed on original cellulose membrane (a) and cellulose membrane coated with cell-PDMA (b).

to determine their molecular weight. **Figure 4** shows the plot of M_n and the M_w/M_n versus the monomer conversion during the polymerization. The molecular weight of the graft copolymer is increased linearly with the monomer conversion, and the polydispersity is decreased with the monomer conversion. The results also confirmed that the graft copolymerization is a controlled/"living" radical polymerization.

Figure 5 shows the AFM image of the cell-PDMA copolymer deposited on surface of the new cleaved mica. Many nanoparticles appear with a homogeneous size, and **Figure 5b** gives the perimeter distribution of the particles. Clearly, there are two kinds of particles exist, one with the diameter about 200 nm, and the other about 38 nm in diameter. Huang also reported similar result when they measrued the size of celluose-PS graft copolymer by AFM, and they concluded that the smaller particles are the graft copolymer and the bigger one are the micelles of the graft copolymer when comparing the AFM data to dynamic laser light scattering results. Here, we believe that the smaller particles result from the cell-PDMA copolymer while the bigger one is the aggregates or micelle of the graft copolymer.

The as-prepared cell-PDMA was a water-soluble polymer having both affinities to the cellulose base membrane, and its potential blood compatibility could improve the surface blood compatibility of the cellulose membrane by a convenient technique, such as coating by its aqueous solution. Coating of cellulose membrane with the cell-PDMA was carried out by immersing the membrane into its aqueous solution following a dry process under vacuum. The amount of the copolymer immobilized on the membrane was measured by XPS. **Figure 6** shows the XPS chart of both the original cellulose membrane and the copolymer coated cellulose membrane (upper row). The peaks attributed to nitrogen (400 eV) atoms was observed on the surface of membrane coated with the cell-PDMA. For the membrane coated with the copolymer, the atomic concentrations of nitrogen and carbon are 1.82% and 66.16%, respectively. The mole fraction of DMA on the membrane surface is 0.028 by calculation, which defined as [number of DMA unit (mol)]/[number of DMA unit (mol) + number of cellulose unit (mol)] was calculated from the value of N/C.

The adsorption of proteins during contact with blood on artificial surface is the initials step in a sequence of events which cause activation of several cascades of proteolysis systems in the plasma, e.g., complement, coagulation pathway, etc. therefore, the amount of proteins adsorbed on the surface is one of the important factors for evaluating the hemocompatibility of materials. Here, the adsorption of three typical plasma proteins such as albumin, γ -globulin, and fibrinogen on the cell-PDMA coating cellulose membranes and original cellulose membranes were measured. As shown in **Figure 7**, the amounts of each absorbed protein on the membrane coated with cell-PDMA was 70-80% reduced by comparison with those on the original cellulose membrane for all of the proteins examined in this study. That is, grafting of PDMA chains on the cellulose plays an important role to reduce protein adsorption.

4. CONCLUSION

In this study, we have successfully synthesized the cell-PDMA in homogeneous media using an ATRP controlled/"living" radical polymerization. The characterizations indicate that the graft copolymerization is efficient and the obtained copolymer owns well-defined structures.After coated the cell-PDMA onto the surface of commercial cellulose membrane, there obtained membrane with good hemocompatibility, which was confirmed by the protein adsorption experiments. This provides a new chance to modify the surface of polysaccharide materials to improve their hemocompatibility. The cell-PDMA has a strong potential application on surface treatment to enhance separation ability and selectivity on every cellulose membrane including CA and nitrocellulose, which are applied in biotechnology research and bioengineering field.

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