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An ionic liquid as reaction media for radiation-induced grafting of thermosensitive poly (*N*-isopropylacrylamide) onto microcrystalline cellulose

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A B S T R A C T

This paper reports a homogeneous modification of microcrystalline cellulose (MCC) in ionic liquids via radiation-induced grafting. Thermosensitive poly (*N*-isopropylacrylamide) (PNIPAAm) was successfully grafted onto MCC in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) ionic liquid using γ-ray irradiation technique at room temperature. The grafting yield (GY) increased with dose up to 40 kGy, while decreased slightly with dose rate from 22 to 102 Gy/min. The results of TGA indicated that cellulose grafted PNIPAAm (cellulose-*g*-PNIPAAm) had higher thermal stability than that of ungrafted regenerated cellulose (reg-cellulose). The crystalline structure of original MCC was largely destroyed during the dissolution process according to the XRD profiles, and grafting PNIPAAm onto cellulose further decreased the intensity of crystallinity. SEM showed that reg-cellulose and cellulose-*g*-PNIPAAm films displayed dense and homogeneous morphology. Moreover, the resulting cellulose-*g*-PNIPAAm exhibited obvious thermal sensitivity with a lower critical solution temperature around 35 °C, which was observed from the swelling behavior in water at different temperatures.

1. Introduction

Cellulose is the most abundant natural polymer in the world. It is renewable, biodegradable and can be derivatized to produce various useful products (Schurz, 1999). Microcrystalline cellulose (MCC) can be obtained in industrial scale from wood and cotton cellulose and it is widely used in food, cosmetic and other industries (Uesu, Pineda, & Hechenleitner, 2000). As the oldest natural polymer, cellulose possesses low mechanical strength and poor weatherability (Carlmark & Malmstrom, 2003), but the properties of cellulose can be greatly improved by derivative reaction and grafting modification to possess new functional groups.

Many new chemical materials, such as high water-absorbing materials, ion exchange materials, thermoresponsive smart materials (Gupta & Khandekar, 2003), metal ion sorption materials (Chauhan, Guleria, & Sharma, 2005), reinforcing agents in composite materials (TrejoOReilly, Cavaille, & Gandini, 1997), photographic and motion picture films were produced by the grafting of different monomers onto cellulose. Moreover, thermosensitive cellulose material was produced by pre-irradiation grafting of *N*-isopropylacrylamide (NIPAAm) onto cotton cellulose fabric (Liu, Zhai, & Ha, 1999). However, most of the modifications of cellulose were carried out in heterogeneous and non-green solvent system, because it is extremely difficult to dissolve cellulose in water and most common organic solvents. A major problem with the heterogeneous system is the unequal accessibility between the OH groups in the amorphous regions and those in the crystalline regions, leading to inhomogeneous substitution (Wang, Li, Xiao, & Wu, 2009). The heterogeneous reaction and non-green solvents also remain limitations in terms of volatility, toxicity and instability in processing (Xu, Kennedy, & Liu, 2008). Therefore, the development of cellulose solvent has become the main factor that limited the modification and application of cellulose.

Swatloski, Spear, Holbrey, and Rogers (2002) found that ionic liquids could dissolve cellulose efficiently, which opened up a new way for the development of a class of cellulose solvent system. Room temperature ionic liquids (RTILs), which are often regarded as intrinsically “green” due to their negligible vapor pressure, have received immense attention. Besides, compared with volatile organic solvents, RTILs have a broader selection of anion and cation combinations (Dupont, de Souza, & Suarez, 2002), lower hydrophobicity (Huddleston et al., 2001), lower viscosity (Hagiwara & Ito, 2000), enhanced electrochemical stability (Matsumoto et al., 2000) and thermal stability (Kosmulski, Gustafsson, & Rosenholm, 2004). It was found that RTILs containing Cl^- have excellent capability to dissolve cellulose, such as 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) (Zhang, Wu, Zhang, & He, 2005). In recent years, RTILs have been used in cellulose materials processing, the homoge-

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neous derivative and functional modification of cellulose. For example, polymeric derivatives of the imidazolium-type ionic liquids, so-called polymeric ionic liquids, were compatible with cellulose and were applied to the synthesis of cellulose composites. Kadokawa et al. synthesized the composites composed of cellulose and a polystyrene-type polymeric ionic liquid. Swatloski, Holbrey, Weston, and Rogers (2006) and Wu et al. (2004) reported the synthesis of homogeneous magnetic cellulose materials and the homogeneous acetylation of cellulose in RTILs, respectively. Compared to heterogeneous reactions, the functional reactions of cellulose in RTILs showed many advantages, such as high uniformity in the reaction process, in no need of catalyst and relatively shorter reaction time (Feng & Chen, 2008). Comparing with conventional graft polymerization, the radiation-induced grafting is a convenient and powerful technique, which could be carried out at room temperature. Moreover, the natural polymer could be sterilized during irradiation simultaneously, which is very useful in medical materials. But until now the investigation about the radiation-induced grafting modification of cellulose in ionic liquids has not been reported.

In this work, a thermosensitive cellulose graft copolymer was synthesized by the radiation-induced grafting of NIPAAm onto MCC in [Bmim]Cl. We investigated the radiation-induced grafting polymerization of cellulose using an ionic liquid as reaction media, which is expected to provide a new method for the homogeneous modification of cellulose.

2. Experimental

2.1. Materials

MCC was obtained from Sinopharm Chemical Reagent Co. Ltd with a degree of polymerization was 215–240. [Bmim]Cl (>99%) was purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China) and the water content in the [Bmim]Cl sample was less than 0.9%, measured by Karl-Fischer titration. Dimethyl sulfoxide (DMSO), analytical reagent, was procured from Beijing Chemical Plant and used without further purification. NIPAAm was the product of Wako Pure Chemical Industries, Ltd., Japan and PNIPAAm was purchased from Sigma–Aldrich.

2.2. Preparation of samples

The procedure for preparation of cellulose-*g*-PNIPAAm by radiation-induced grafting polymerization was shown in Scheme 1. Dry MCC was dispersed into [Bmim]Cl (ca. 2 g MCC/98 g [Bmim]Cl) with stirring for 24 h at 100 °C, yielding a clear solution of about 2 wt% cellulose. Subsequently, NIPAAm (10 g) and DMSO (20 g) were added into the solution of MCC and [Bmim]Cl. The mixture was ultrasonic treated at 40 °C to yield homogeneous transparent solution. After bubbling with N_2 for about 15 min, the solution was subjected to γ-ray irradiation from ^{60}Co source (Peking University, China) at room temperature with a dose rate of 20 Gy/min.

After irradiation, the solution was cast onto a glass plate and then immediately coagulated in ethanol to obtain the regenerated cellulose film with a thickness of about 0.50 mm (Zhang et al., 2005). The film was wholly transferred to a soxhlet extractor and extracted with acetone for 24 h to remove the ungrafted homopolymer and residual monomers. Then, cellulose-*g*-PNIPAAm was dried at about 40 °C in a vacuum oven to a constant weight. The grafting yield (GY) was calculated gravimetrically as following:

$$\mathrm{GY}(\%) = \frac{W_g - W_0}{W_0} \times 100 \tag{1}$$

where W_g was the weight of cellulose-*g*-PNIPAAm copolymer after extracting PNIPAAm homopolymer and unreacted monomer; W_0 was the weight of dry MCC before grafting. [Bmim]Cl was completely removed after the immersion in ethanol and extraction in acetone, which has been confirmed by the results of the elemental analysis using Elementar Analysensysteme GmbH (model: vario EL).

2.3. Characterization

Micro-FTIR analysis of original MCC, regenerated cellulose after irradiation (reg-cellulose) and cellulose-*g*-PNIPAAm with different grafting yields was performed on a Nicolet (Magna-IR 750) spectrometer. The spectra were measured in absorbance mode in the wave number range of 4000–600 cm^{-1}.

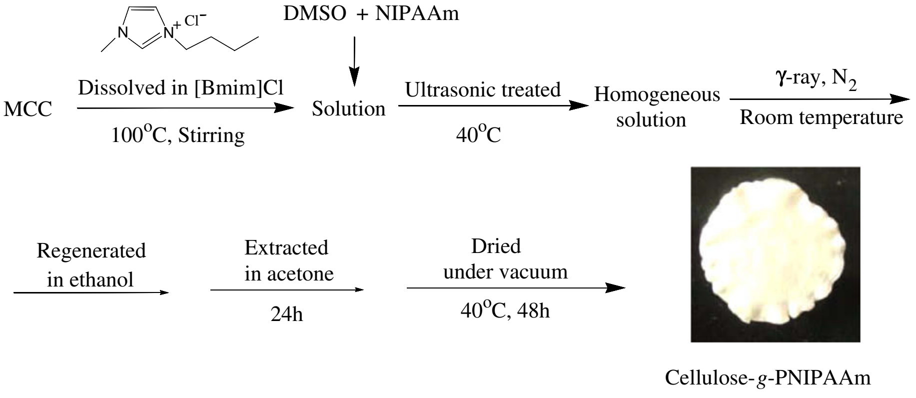
Wide angle X-ray diffraction (WAXD) was used to study the crystallinity of samples. WAXD was performed by XRD-Multiflex (Rigaku Corporation, Japan) using Ni-filtered CuK$_\alpha$ with 4 min^{-1} from 10° to 50°.

SDT Q600 (TA Instrument, USA) with alumina crucibles was used to perform thermogravimetric analysis (TGA) of original MCC, reg-cellulose, regenerated cellulose without irradiation, PNIPAAm and cellulose-*g*-PNIPAAm with different grafting yields under a nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 600 °C.

The morphological structure of the cellulose samples before and after grafting were observed using a scanning electron microscope (SEM, HITACHI S-4300) at a voltage of 15 kV. All the samples were sputter-coated with gold before the test.

2.4. Swelling behavior

The dried cellulose-*g*-PNIPAAm films were weighed and immersed in deionized water. The samples were swollen for 24 h to equilibration at different temperature from 15 °C to 65 °C. The



Scheme 1. Procedure for the preparation of cellulose-*g*-PNIPAAm in [Bmim]Cl by radiation-induced grafting polymerization.

equilibration degree of swelling (EDS) was calculated by gravimetric method as following:

$$\mathrm{EDS}(\%) = \frac{m_t}{m_o} \times 100 \tag{2}$$

where m_o was the weight of dry cellulose-*g*-PNIPAAm film and m_t was the weight of swollen film at equilibration after wiping surface water with tissue paper.

3. Results and discussion

3.1. Radiation-induced grafting of PNIPAAm onto MCC dissolved in ionic liquids

Study on the radiochemical stability of ionic liquids under gamma and beta irradiation indicates that ionic liquids are relatively radiation resistant and there is certainly no major decomposition of the organic component (Allen et al., 2002). During irradiation, high-energy ionizing radiation leads to the formation of solvated electrons and radical ions in ionic liquids (Wishart & Neta, 2003). Moreover, the polymerization in ionic liquids proceeded by the radical mechanism, similarly to the polymerization in organic solvents at room temperature (Liu & Wu, 2005). An ionic liquid as reaction media for radiation-induced grafting was reported here.

Fig. 1 showed the effects of dose (Fig. 1a) and dose rate (Fig. 1b) on the grafting yield of NIPAAm onto cellulose at room temperature with the mass ratio of NIPAAm to MCC as 5:1. The grafting yield increased with an increase of dose and tended to level off around 40 kGy, but decreased slightly with the increasing of dose rate in the range of 22–102 Gy/min. Under irradiation, grafting and homopolymerization of NIPAAm in [Bmim]Cl may be initiated by different free radicals. It was reported that every anhydroglucose unit of cellulose chains has three active hydroxyls. When cellulose are exposed to high energy radiation, the radicals form in such three reactive sites of cellulose (Lin, Kumar, Rozman, & Noor, 2005) and these reactive sites can initiate the graft polymerization of NIPAAm onto cellulose. With an increase in dose, more radicals and reactive sites could be generated on cellulose, which resulted in the increasing of grafting yield. However, when the dose continuously increased, the grafting yield did not increase subsequently. The major reason was due to the generation of PNIPAAm homopolymer in the system, which increased the viscosity and blocks the penetration of the monomer to reach the active sites of cellulose. Consequently, most of the monomer under this circumstance was consumed in the homopolymerization rather than in the grafting reaction onto cellulose. In further experiments, we will try to optimize the grafting system by selecting other ionic liquids as reaction media or adding inhibitor for decreasing the homopolymerization of NIPAAm. The graft polymerization above proceeded in homogenous system. Compared to the heterogeneous grafting, which is only the surface modification and limited in the amorphous regions of cellulose (Liu et al., 1999), the substituent groups of homogeneous grafting system can be introduced onto cellulose chains regularly and the uniformity of the products is better. In addition, several active species, such as solvated electrons (Wishart & Neta, 2003) and radicals can be formed in ionic liquids (Marcinek, Zielonka, Gebicki, Gordon, & Dunkin, 2001), and these species may have initiated the homopolymerization of NIPAAm, so as to cause the side reaction of graft polymerization. Furthermore, our previous experiments have indicated that [Bmim]Cl has good radiation stability under 500 kGy and the absorbed dose used in this work was lower than 100 kGy. It can be inferred that during the radiation-induced graft polymerization of cellulose, [Bmim]Cl had no change in chemical structure and mainly played a role as the solvent for cellulose.

Moreover, the effect of dose rate on the grafting yield might be attributed to that under irradiation, radicals were formed and their numbers increased with the increasing dose rate. The monomer diffusion rate to the vicinity of cellulose backbone was constant, irrespective of the dose rate. Thus, a greater availability of radical ions at a higher dose rate would increase the probability of homopolymerization, causing the decrease of grafting yield, as shown in Fig. 1b.

Effect of the mass ratio of NIPAAm to MCC on grafting yield was shown in Fig. 2. When the mass ratio of NIPAAm to MCC was 1:1, 3:1, 5:1, the grafting yield of NIPAAm onto cellulose was 15.1%, 35.5% and 52.9%, respectively. In other words, the grafting yield increased with the amount of monomer. Meanwhile, in order to study the effect of DMSO on the graft polymerization of cellulose, the radiation-induced graft polymerization of cellulose was carried out in pure [Bmim]Cl and [Bmim]Cl/DMSO solvent with the mass ratio of NIPAAm to MCC as 1:1, respectively. The grafting yield of the former was 15.4% (Fig. 2a), and the latter was 15.1% (Fig. 2b), which indicated that DMSO had little influence on the grafting yield of cellulose-*g*-PNIPAAm. Due to the high viscosity of

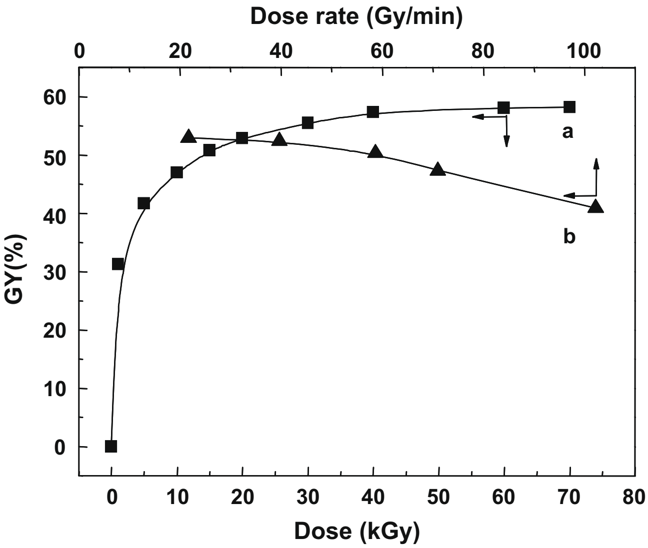


Fig. 1. The grafting yield of PNIPAAm onto cellulose as a function of dose (a) and dose rate (b) at room temperature.

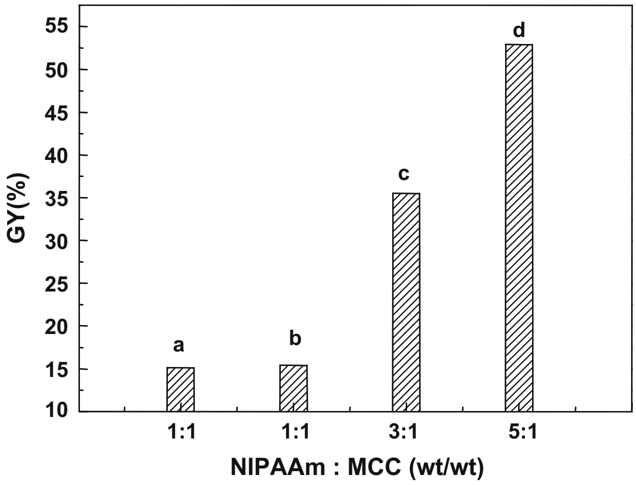


Fig. 2. Effect of mass ratio of NIPAAm to MCC and the presence of DMSO on grafting yield. Grafting condition: 20 kGy; 20 Gy/min; room temperature, NIPAAm/MCC/DMSO = 1/1/0 (a); NIPAAm/MCC/DMSO = 1/1/10 (b), 3/1/10 (c), 5/1/10 (d).

[Bmim]Cl, the DMSO was used as diluent to increase the contact between monomer with cellulose.

3.2. Characterization of the cellulose-g-PNIPAAm

Original MCC, reg-cellulose, PNIPAAm and cellulose-*g*-PNIPAAm with different grafting yields were characterized by FT-IR, WAXD and TGA.

As shown in Fig. 3 the micro-FTIR spectra of reg-cellulose was similar to that of original MCC. The following characteristic bands in the IR spectrum of original MCC (Fig. 3a) were observed: a large absorption band at 3300–3500 cm^{-1} corresponding to the vibration of valence for OH groups; a band at 2700–2900 cm^{-1} attributed to CH_2 groups; characteristic bands at 1161 and 1109 cm^{-1} for C—O—C from the glucosidic units (Suflet, Chitanu, & Popa, 2006). The sharp bands at 1387 and 1367 cm^{-1} in cellulose-*g*-PNIPAAm (Fig. 3c), which were initially absent in ungrafted MCC (Fig. 3a and b), were assigned to the isopropyl group of NIPAAm (Gupta & Khandekar, 2003). The appearance of an absorption band at 1654 cm^{-1} (Fig. 3c–e) and 1546 cm^{-1} corresponds to C═O stretching and N—H stretching of NIPAAm, respectively (Ying, Kang, Neoh, Kato, & Iwata, 2004). Moreover, the intensity of the two peaks increased with the grafting yield of cellulose-*g*-PNIPAAm. The results of micro-FTIR spectra proved that PNIPAAm was successfully grafted onto cellulose.

The crystalline state of original MCC, reg-cellulose, PNIPAAm and cellulose-*g*-PNIPAAm were shown in Fig. 4 on the basis of WAXD patterns. MCC diffraction patterns (Fig. 4a) showed typical cellulose I structure, with a sharp peak at 22.5°, and a wide peak between 14° and 17.5°. After dissolution and subsequent coagulation with ethanol, reg-cellulose (Fig. 4b) exhibited a typical diffraction peak between 20.3° and 21.2°. The results showed that after the dissolution and regeneration in [Bmim]Cl, the crystal structure of MCC was transformed from cellulose I to cellulose II (Raymond, Kvick, & Chanzy, 1995). Compared to original cellulose, the crystallinity of reg-cellulose decreased significantly. This indicated that the ionic liquid broke intermolecular and intramolecular hydrogen bonds of original MCC during the dissolution process (Zhang et al., 2005). The XRD spectrums of cellulose-*g*-PNIPAAm with different grafting yields (Fig. 4c–e) were similar to that of reg-cellulose (Fig. 4b) and the intensity of peak decreased slightly with the increasing of grafting yield, due to the amorphous structure of grafted PNIPAAm chains (Hezazy, Abd El-Rehim, Khalifa, & Ali, 1999).

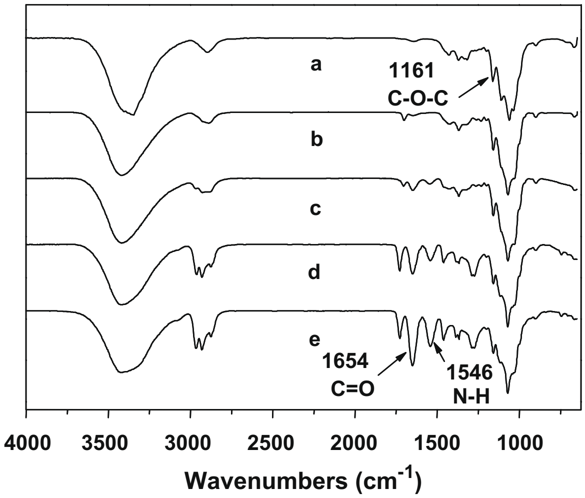


Fig. 3. FT-IR spectra of the original MCC (a), reg-cellulose (b), cellulose-*g*-PNIPAAm with different grafting yields, GY = 15.1% (c); GY = 35.5% (d); GY = 52.9% (e).

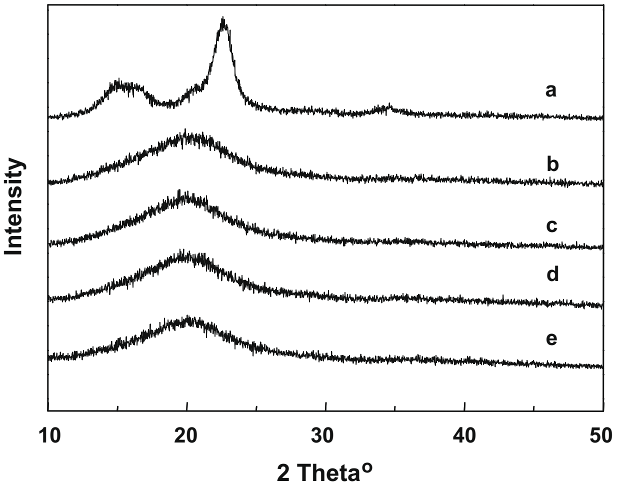


Fig. 4. WAXD spectra of the original MCC (a), reg-cellulose (b), cellulose-*g*-PNIPAAm with different grafting yields, GY = 15.1% (c); GY = 35.5% (d); GY = 52.9% (e).

The TGA curves of original MCC, reg-cellulose, PNIPAAm and cellulose-*g*-PNIPAAm with different grafting yields were shown in Fig. 5. All samples have a small weight loss at low temperature (<120 °C) range, corresponding to the loss of absorbed water from the samples. The temperature corresponding to the peak height in the DTG curve is taken as T_{max} and has been found to be shifted to 272.2 °C in regenerated cellulose after irradiation, in comparison to T_{max} of 342.2 °C in original MCC and 332.1 °C in regenerated cellulose without irradiation, which was not shown in Fig. 5. The decrease in T_{max} of cellulose without irradiation was related to the decrease of crystallinity in the process of dissolution and regeneration (Kadokawa, Murakami, Takegawa, & Kaneko, 2009), and the degradation during the irradiation process. Comparing with the ungrafted cellulose, the thermal degradation of cellulose-*g*-PNIPAAm (GY = 52.9%, Fig. 5f) showed two separated pyrolysis within a wider temperature range rather than one pyrolysis except for weight loss at low temperature (<120 °C). The first process was the degradation of cellulose, and the second process was due to the grafted PNIPAAm. As shown in Fig. 5, the cellulose-*g*-PNIPAAm with the GY of 15.1%, 35.5%, 52.9%, showed T_{max} at 273.5, 284.1, 338.2 °C, respectively. These observations have clearly indicated that cellulose-*g*-PNIPAAm has higher thermal stability compared

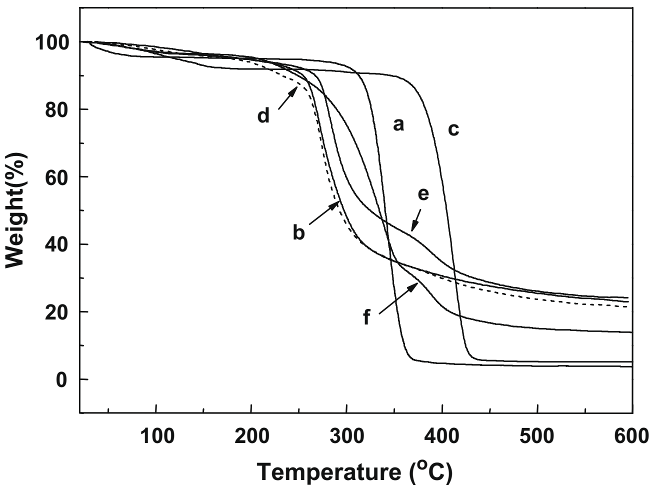


Fig. 5. TGA curves of the original MCC (a), reg-cellulose (b), PNIPAAm (c), cellulose-*g*-PNIPAAm with different grafting yields, GY = 15.1% (d); GY = 35.5% (e); GY = 52.9% (f).

to the ungrafted regenerated cellulose. Besides, T_{max} of cellulose-*g*-PNIPAAm increased with the grafting yield, due to the high thermal stability of PNIPAAm (Fig. 5c, $T_{max} = 413.1\ ^\circ C$). In addition, the residual mass percent of original MCC was about 5%, while that of reg-cellulose and cellulose-*g*-PNIPAAm with different grafting yields were about 20%, which was due to the formation of nonvolatile carbonaceous material in the regenerated sample (Swatloski et al., 2002). In addition, the residual mass percent decreased with the increasing of grafting yield, because PNIPAAm grafted on cellulose can degrade completely above its degradation temperature.

SEM micrograms of reg-cellulose films and cellulose-*g*-PNIPAAm films with different grafting yields were shown in Fig. 6. It can be seen that the surface of reg-cellulose films and cellulose-*g*-PNIPAAm films display dense and homogeneous morphology. SEM images also revealed the differences before and after grafting of cellulose. Compared to cellulose-*g*-PNIPAAm films, the surface of reg-cellulose film (Fig. 6A) was relatively flat. After PNIPAAm was grafted onto cellulose, the microphase separation was observed on the surface of cellulose-*g*-PNIPAAm films and it increased with the grafting yield (Fig. 6B–D).

3.3. Temperature sensitivity

The relation between the degree of swelling and grafting yield of cellulose-*g*-PNIPAAm at 25 °C was represented in Fig. 7a. It was found that the equilibrium degree of swelling (EDS) steeply increased with the grafting yield, due to the increase of grafted PNIPAAm in cellulose-*g*-PNIPAAm (Liu et al., 1999).

The variation in degree of swelling of cellulose-*g*-PNIPAAm as a function of temperature in range of 15–55 °C (Fig. 7b) has clearly indicated the thermoresponsive behavior of cellulose-*g*-PNIPAAm. The EDS of cellulose-*g*-PNIPAAm has shown a marked decreasing around 35 °C. Generally, the temperature at which the swelling degree of the sample decreases dramatically is regarded as the lower critical solution temperature (LCST). Thus, the LCST of cellulose-*g*-PNIPAAm is around 35 °C, which is slightly higher than that of pure PNIPAAm and is closer to the body temperature. This can be attributed to the unique and rapid alternation of the hydrophilic and hydrophobic states of cellulose-*g*-PNIPAAm. At temperatures below the LCST the polymer chains have a coil structure and the

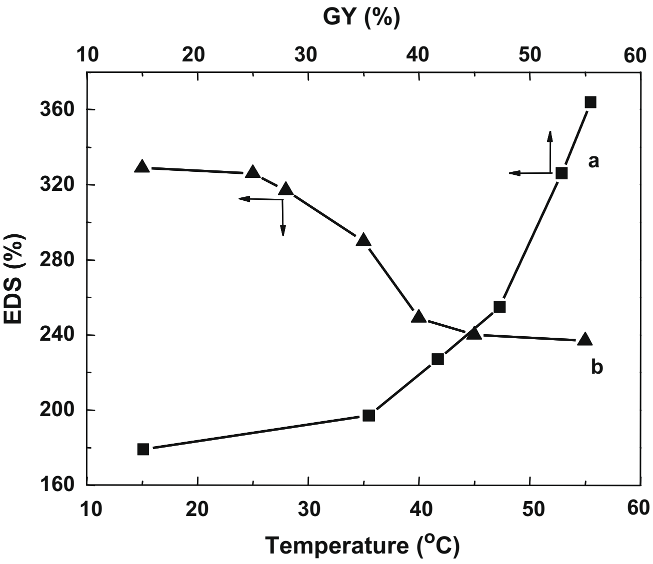


Fig. 7. The degree of swelling of cellulose-*g*-PNIPAAm with different grafting yields at 25 °C (a) and the relationship between degree of swelling and temperature in cellulose-*g*-PNIPAAm [GY = 52.9% (b)].

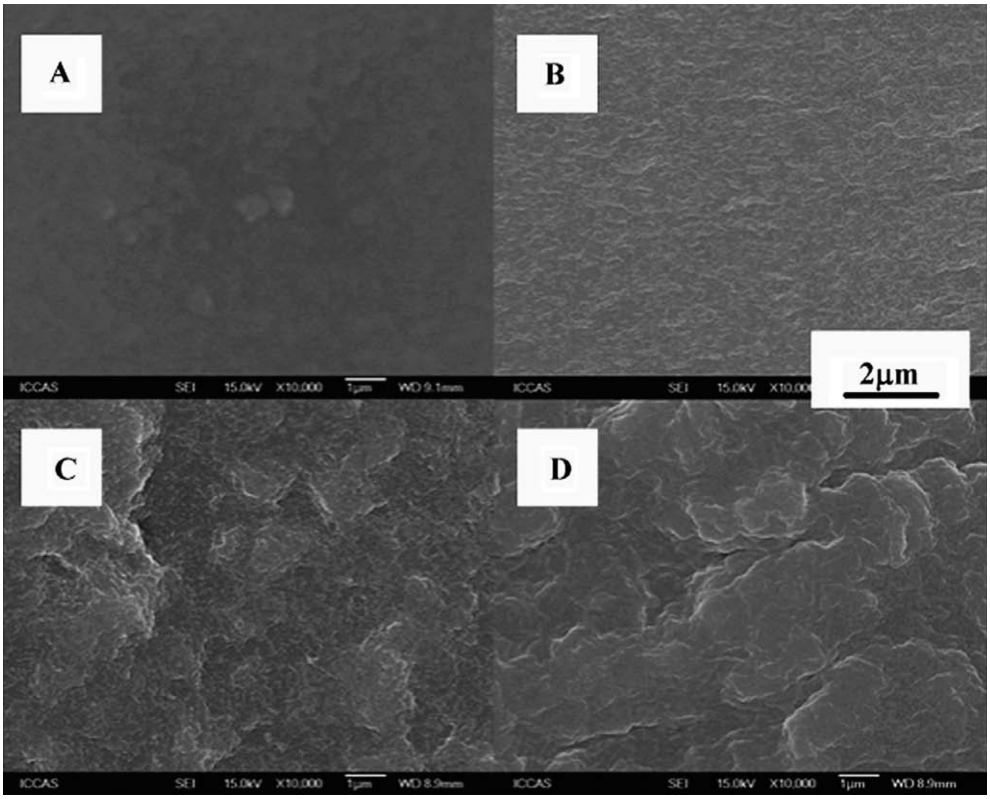


Fig. 6. Surface morphologies of reg-cellulose (A) and cellulose-*g*-PNIPAAm with different grafting yields, GY = 15.1% (B); GY = 35.5% (C); GY = 52.9% (D).

hydrophilic groups of the grafting copolymer form hydrogen bonds with water molecule. When the temperature was raised above the LCST, the polymer chains underwent a sharp coil-to-globule transition to form inter- and intrachain association, resulting in hydrophobic aggregation, a release of water molecule and a decrease of EDS (Wu & Zhou, 1995). Cellulose-*g*-PNIPAAm films combined with the advantages of cellulose and PNIPAAm, such as temperature sensitive, nontoxic and biodegradable. Therefore cellulose-*g*-PNIPAAm copolymer could be expected to have a potential application in drug release system, adsorption materials and functional membrane materials, which will be investigated in our further research work.

4. Conclusion

In this work PNIPAAm was successfully grafted onto MCC by simultaneous γ-irradiation from the homogeneous mixture in [Bmim]Cl. The grafting yields reached 52.9% at adsorbed dose of 20 kGy with the mass ratio of NIPAAm to MCC as 5:1. It should be noted that this is the first example of the radiation-induced grafting modification of cellulose using an ionic liquid as reaction media. Moreover, the grafting of PNIPAAm has improved the thermal stability of regenerated cellulose after radiation. The cellulose-*g*-PNIPAAm film is dense and has rough surface indicating the microphase separation. The EDS of cellulose-*g*-PNIPAAm films in water at 25 °C increased obviously with the increasing of grafting yield. The resulting cellulose-*g*-PNIPAAm has a obvious thermosensitivity in water and exhibits a lower critical solution temperature (LCST) at about 35 °C, which is closer to the body temperature. Therefore, the cellulose-*g*-PNIPAAm copolymers prepared via radiation-induced graft polymerization in ionic liquid with good thermal sensitivity at about 35 °C and high thermal stability could be expected to have a potential application in drug release system, adsorption materials and functional membrane materials.

Acknowledgements

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References

Allen, D., Baston, G., Bradley, A. E., Gorman, T., Haile, A., Hamblett, I., et al. (2002). An investigation of the radiochemical stability of ionic liquids. *Green Chemistry, 4*(2), 152–158.

Carlmark, A., & Malmstrom, E. E. (2003). ATRP grafting from cellulose fibers to create block-copolymer grafts. *Biomacromolecules, 4*(6), 1740–1745.

Chauhan, G. S., Guleria, L., & Sharma, R. (2005). Synthesis, characterization and metal ion sorption studies of graft copolymers of cellulose with glycidyl methacrylate and some comonomers. *Cellulose, 12*(1), 97–110.

Dupont, J., de Souza, R. F., & Suarez, P. A. Z. (2002). Ionic liquid (molten salt) phase organometallic catalysis. *Chemical Reviews, 102*(10), 3667–3691.

Feng, L., & Chen, Z. I. (2008). Research progress on dissolution and functional modification of cellulose in ionic liquids. *Journal of Molecular Liquids, 142*(1–3), 1–5.

Gupta, K. C., & Khandekar, K. (2003). Temperature-responsive cellulose by ceric(IV) ion-initiated graft copolymerization of *N*-isopropylacrylamide. *Biomacromolecules, 4*(3), 758–765.

Hagiwara, R., & Ito, Y. (2000). Room temperature ionic liquids of alkylimidazolium cations and fluoroanions. *Journal of Fluorine Chemistry, 105*(2), 221–227.

Hezazy, E. S. A., Abd El-Rehim, H. A., Khalifa, N. A., & Ali, A. E. (1999). Preparation and characterization of supported hydrogels obtained by radiation grafting of binary monomers. *Radiation Physics and Chemistry, 55*(2), 219–229.

Huddleston, J. G., Visser, A. E., Reichert, W. M., Willauer, H. D., Broker, G. A., & Rogers, R. D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chemistry, 3*(4), 156–164.

Kadokawa, J. I., Murakami, M. A., Takegawa, A., & Kaneko, Y. (2009). Preparation of cellulose–starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid. *Carbohydrate Polymers, 75*(1), 180–183.

Kosmulski, M., Gustafsson, J., & Rosenholm, J. B. (2004). Thermal stability of low temperature ionic liquids revisited. *Thermochimica Acta, 412*(1–2), 47–53.

Lin, O. H., Kumar, R. N., Rozman, H. D., & Noor, M. A. M. (2005). Grafting of sodium carboxymethylcellulose (CMC) with glycidyl methacrylate and development of UV curable coatings from CMC-g-GMA induced by cationic photoinitiators. *Carbohydrate Polymers, 59*(1), 57–69.

Liu, Y. D., & Wu, G. Z. (2005). On the mechanism of radiation-induced polymerization of vinyl monomers in ionic liquid. *Radiation Physics and Chemistry, 73*(3), 159–162.

Liu, J. Q., Zhai, M. L., & Ha, H. F. (1999). Pre-irradiation grafting of temperature sensitive hydrogel on cotton cellulose fabric. *Radiation Physics and Chemistry, 55*(1), 55–59.

Marcinek, A., Zielonka, J., Gebicki, J., Gordon, C. M., & Dunkin, I. R. (2001). Ionic liquids: Novel media for characterization of radical ions. *Journal of Physical Chemistry A, 105*(40), 9305–9309.

Matsumoto, H., Yanagida, M., Tanimoto, K., Nomura, M., Kitagawa, Y., & Miyazaki, Y. (2000). Highly conductive room temperature molten salts based on small trimethylalkylammonium cations and bis(trifluoromethylsulfonyl)imide. *Chemistry Letters*(8), 922–923.

Raymond, S., Kvick, A., & Chanzy, H. (1995). The structure of cellulose-Ii – a revisit. *Macromolecules, 28*(24), 8422–8425.

Schurz, J. (1999). 'Trends in Polymer Science' A bright future for cellulose. *Progress in Polymer Science, 24*, 481–483.

Suflet, D. M., Chitanu, G. C., & Popa, V. I. (2006). Phosphorylation of polysaccharides: New results on synthesis and characterisation of phosphorylated cellulose. *Reactive and Functional Polymers, 66*(11), 1240–1249.

Swatloski, R. P., Holbrey, J. D., Weston, J. L., & Rogers, R. D. (2006). Preparation of magnetic cellulose composites using ionic liquids. *Chimica Oggi – Chemistry Today, 24*(2), 31.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellose with ionic liquids. *Journal of the American Chemical Society, 124*(18), 4974–4975.

TrejoOReilly, J. A., Cavaille, J. Y., & Gandini, A. (1997). Cationic copolymerization of styrenes with an isocyanate-bearing homologue. *Reactive and Functional Polymers, 32*(1), 9–19.

Uesu, N. Y., Pineda, E. A. G., & Hechenleitner, A. A. W. (2000). Microcrystalline cellulose from soybean husk: Effects of solvent treatments on its properties as acetylsalicylic acid carrier. *International Journal of Pharmaceutics, 206*(1–2), 85–96.

Wang, Z. M., Li, L., Xiao, K. J., & Wu, J. Y. (2009). Homogeneous sulfation of bagasse cellulose in an ionic liquid and anticoagulation activity. *Bioresource Technology, 100*, 1687–1690.

Wishart, J. F., & Neta, P. (2003). Spectrum and reactivity of the solvated electron in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide. *Journal of Physical Chemistry B, 107*(30), 7261–7267.

Wu, J., Zhang, J., Zhang, H., He, J. S., Ren, Q., & Guo, M. (2004). Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromolecules, 5*(2), 266–268.

Wu, C., & Zhou, S. Q. (1995). Laser-light scattering study of the phase-transition of poly(*N*-Isopropylacrylamide) in water. 1. Single-chain. *Macromolecules, 28*(24), 8381–8387.

Xu, Q., Kennedy, J. F., & Liu, L. J. (2008). An ionic liquid as reaction media in the ring opening graft polymerization of epsilon-caprolactone onto starch granules. *Carbohydrate Polymers, 72*(1), 113–121.

Ying, L., Kang, E. T., Neoh, K. G., Kato, K., & Iwata, H. (2004). Drug permeation through temperature-sensitive membranes prepared from poly(vinylidene fluoride) with grafted poly(*N*-isopropylacrylamide) chains. *Journal of Membrane Science, 243*(1–2), 253–262.

Zhang, H., Wu, J., Zhang, J., & He, J. S. (2005). 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose. *Macromolecules, 38*(20), 8272–8277.