Synthesis and Phase Transition of Cellulose-*graft*-Poly(ethylene glycol) Copolymers

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ABSTRACT: Cellulose-*graft*-poly(ethylene glycol) copolymers were synthesized, and the thermal properties of the copolymers were investigated. The cellulose-*graft*-poly(ethylene glycol) copolymers showed solid–solid phase-transition behavior with a high thermal storage density and good thermal stability in the temperature region of 25–250°C. The phase-transition temperature and enthalpy of the cellulose-*graft*-poly(ethylene glycol) copolymers could be adjusted through changes in the poly(ethylene glycol) content. The prepared copolymers could be used as thermal energy storage materials. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1797–1803, 2008

Key words: differential scanning calorimetry (DSC); graft copolymers; phase behavior; synthesis; thermal properties

INTRODUCTION

Phase change materials (PCMs) are materials that can take in or release latent heat via a phase-transition process. PCMs have potential applications for energy storage and temperature control and can be used in solar energy utilization, intelligently air-conditioned buildings, insulation clothing, and so on.[1–3] Therefore, PCMs have attracted increasing interest because of the coming energy crisis around the world. PCMs can be classified into solid–liquid and solid–solid PCMs according to their working states. Polymeric solid–solid PCMs are more attractive because of the advantages of no leakage, ease of sealing, a relatively low phase-transition temperature, and high enthalpy.[4,5] Polymeric solid–solid PCMs can be prepared by physical blending and chemical modification.[6–9] However, the physical blending approach has the disadvantage of phase segregation, which leads to worse shape stability.[10,11] In contrast, the chemical approach is an essential method for preparing solid–solid PCMs. Poly(ethylene glycol) (PEG) is a well-defined macromolecule with the characteristics of nontoxicity, good biocompatibility, biodegradability, hydrophilicity, and ease of chemical modification, which have led to widespread applications of PEG in chemical, biomedical, and biotechnological fields.[12] Moreover, PEG is one of the promising working materials for PCMs because of its relatively large fusion heat, congruent melting behavior, resistance to corrosion, and wide melting-temperature range.[13]

Cellulose is one of the most abundant natural polymers and renewable raw materials, and it has been widely used in coatings, membranes, pharmaceuticals, and foodstuffs.[14] However, the strong intermolecular and intramolecular hydrogen bonds of cellulose lead to poor processability. Chemical modification via graft copolymerization is an attractive method for extending the applications of cellulose, by which novel hybrid materials with desired properties of both natural polysaccharides and synthetic polymers can be achieved. The modification of cellulose and its derivatives by graft copolymerization has been studied extensively.[15–20] In particular, 4-monomethoxytriphenylmethylcellulose (MMTritylcellulose) is an important intermediate material for the regioselective functionalization of cellulose because of its high reactivity, its solubility in common organic solvents, and the ease of removing the 4-monomethoxytriphenylmethyl (MMTrityl) moieties.[21–23]

The preparation of cellulose/PEG and cellulose diacetate/PEG solid-state PCMs has been reported.[24,25] However, toxic 2,4-tolylene diisocyanate has been used as the crosslinking reagent in dimethyl sulfoxide (DMSO)/polyformaldehyde media, and the resultant

materials have lower thermal storage density.[24,25] In this work, cellulose-g-PEG copolymers with different graft densities were synthesized from MMTritylcellulose. The thermal properties and morphology of the copolymers were investigated.

EXPERIMENTAL

Materials

Cellulose (Whatman CF-11, England), 4-monomethoxytrityl chloride (97%), and poly(ethylene glycol) monomethyl ethers (mPEGs) with number-average molecular weights of 2000 and 1100 g/mol (PEG$_{2k}$ and PEG$_{1.1k}$, respectively; Fluka, Switzerland) were used as received. DMSO and pyridine (Beijing Chemical Engineering Plant, Beijing, China) were freshly distilled over CaH$_2$ under reduced pressure before use. All other reagents (analytical-grade) were used as received.

Synthesis of cellulose-g-PEG

The synthesis procedure for cellulose-g-PEG is shown in Scheme 1, and the details are as follows.

#### Poly(ethylene glycol) monomethyl ether iodide (mPEGI)

mPEGI was synthesized with a modified form of the Rydon reaction.[26] mPEG, triphenyl phosphate, and methyl iodide (molar ratio = 1 : 2 : 2) were added to a flask fitted with a reflux condenser and a CaCl$_2$ drying tube. The mixture was stirred at 120°C in darkness for 6 h and then cooled to room temperature. The mixture was then dissolved in toluene, precipitated in diethyl ether, filtered, and washed. The product was dried *in vacuo* at room temperature, and the result was pale yellow mPEGI.

Mercerized cellulose

Microcrystalline cellulose (7.5 g) was stirred in an aqueous sodium hydroxide (NaOH) solution (25 wt %, 135 mL) at room temperature for 2 days, and then 180 mL of methanol was added. The suspension was filtered and washed with methanol, and the resultant mercerized cellulose was dried at 50°C *in vacuo*.

MMTritylcellulose

Mercerized cellulose (1.5 g) was suspended in dry pyridine (32 mL) and stirred at 60°C for 5 h. The mixture was cooled to room temperature, and 4-monomethoxytrityl chloride (7.14 g) in a dry pyridine solution was added dropwise. The mixture was then fluxed at 95°C for 69 h, cooled to room temper-
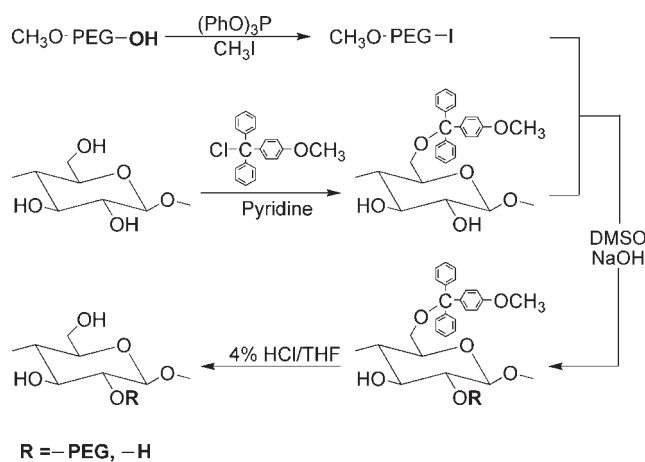
Scheme 1 Synthesis of the cellulose-g-PEG copolymer.

ature, precipitated in excess methanol, and filtered. The product was then dissolved in DMSO, precipitated in methanol, filtered, washed, and dried at 50°C *in vacuo*.

MMTritylcellulose-g-PEG

MMTritylcellulose (0.2 g) was dissolved in anhydrous DMSO (10 mL) at room temperature, and then powdered NaOH (0.16 g) was added. The mixture was stirred for 2 h under nitrogen, and a certain amount of mPEGI (depending on the desired graft density of the resultant copolymer) was added. The mixture was stirred for 48 h at 70°C under nitrogen, and then the solution was precipitated in diethyl ether. The obtained sticky product was then dissolved in chloroform, washed with excess deionized water, concentrated, and mixed with deionized water. The mixture was dialyzed against water for 120 h and freeze-dried to obtain MMTritylcellulose-g-PEG.

Cellulose-g-PEG

MMTritylcellulose-g-PEG (0.2 g) was suspended in 1 mL of tetrahydrofuran (THF), and concentrated aqueous hydrochloric acid (HCl; 37%) in THF (4%, v/v) was added dropwise to MMTritylcellulose-g-PEG at room temperature under nitrogen. After 5 h of stirring at room temperature, THF was removed by rotary evaporation, and the residue was precipitated in cold acetone, filtered, washed, and dried.

Characterization

The chemical structures of the samples were characterized with NMR (DMX 300, Bruker, Germany) and FTIR (Equinox 55, Bruker, Germany). Elemental analyses were performed on a Flash 1112 elemental analyzer (Italy).
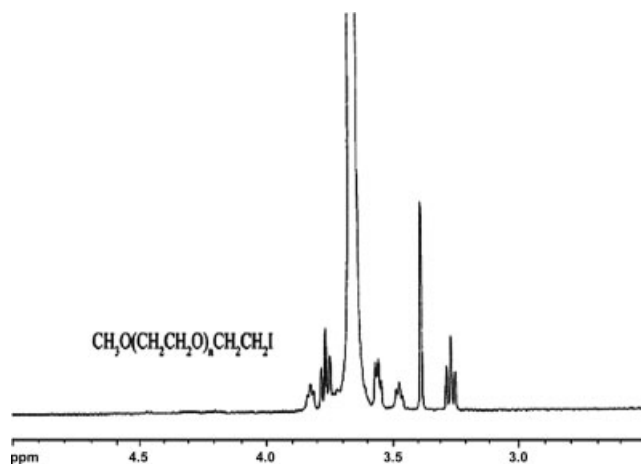
Figure 1 ^{1}H-NMR spectrum of mPEG$_{2k}$I in CDCl$_3$.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler–Toledo DSC 822^e differential scanning calorimeter (USA). The samples were heated from 0 to 100°C at 10°C/min in a nitrogen atmosphere, held at 100°C for 5 min, cooled to 0°C at 10°C/min, held at 0°C for 5 min, and then heated from 0 to 100°C at the same rate. The first cooling and second heating DSC traces were taken for estimating the thermal behaviors of the copolymers. Thermogravimetric analysis (TGA) was performed on a Pyris 1 thermogravimetric analyzer (Perkin Elmer, USA) from 25 to 700°C under a nitrogen atmosphere at a heating rate of 10°C/min.

Wide-angle X-ray diffraction (WAXD) patterns of the samples were recorded with a Rigaku D/max 2500 X-ray powder diffractometer (Japan) with Cu Kα (λ = 1.541 Å) radiation generated at 40 kV and 200 mA. The samples were examined in the 2θ range of 10–40°. Polarized optical microscopy (POM) observations were performed with an Olympus BH-2 (Japan) equipped with a Mettler FP 52 hot stage.
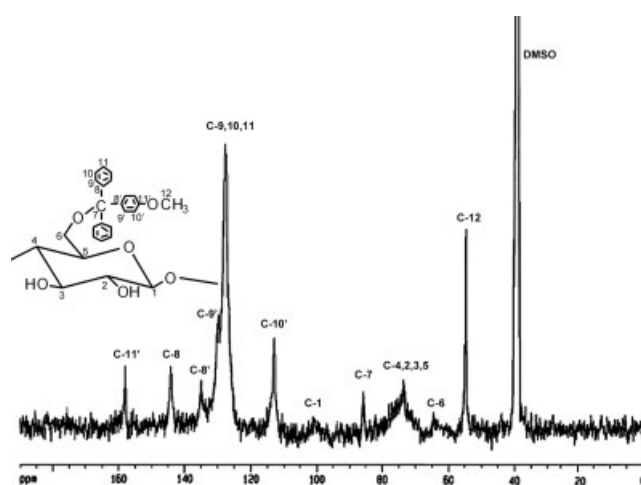

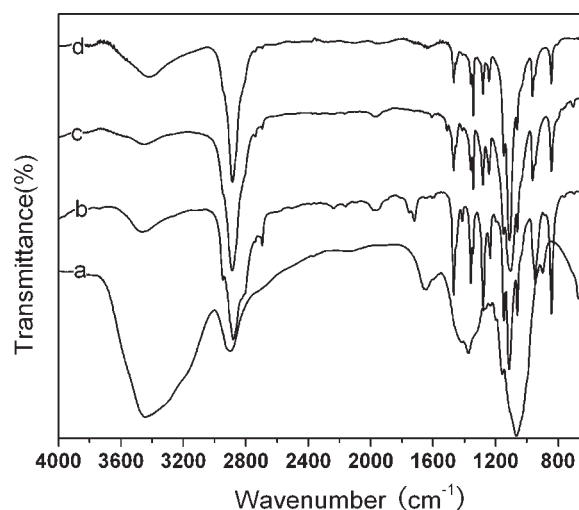**Figure 3** FTIR spectra of (a) mercerized cellulose, (b) mPEG$_{2k}$, (c) MMTritylcellulose-*g*-PEG$_{2k}$, and (d) cellulose-*g*-PEG$_{2k}$ with a PEG concentration of 85 wt %.

RESULTS AND DISCUSSION

Figure 1 shows the ^{1}H-NMR spectrum of mPEGI. There are signals around δ = 3.26 ppm in addition to the characteristic chemical shift of the mPEG protons. These signals come from the protons of —CH$_2$I and indicate the successful synthesis of mPEGI.

MMTritylcellulose was synthesized under heterogeneous conditions. The degree of substitution (DS) of MMTrityl was estimated by elemental analysis as follows:
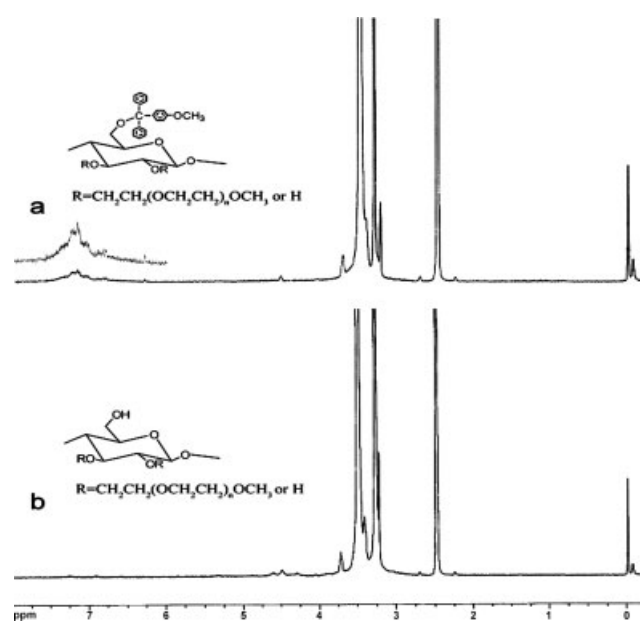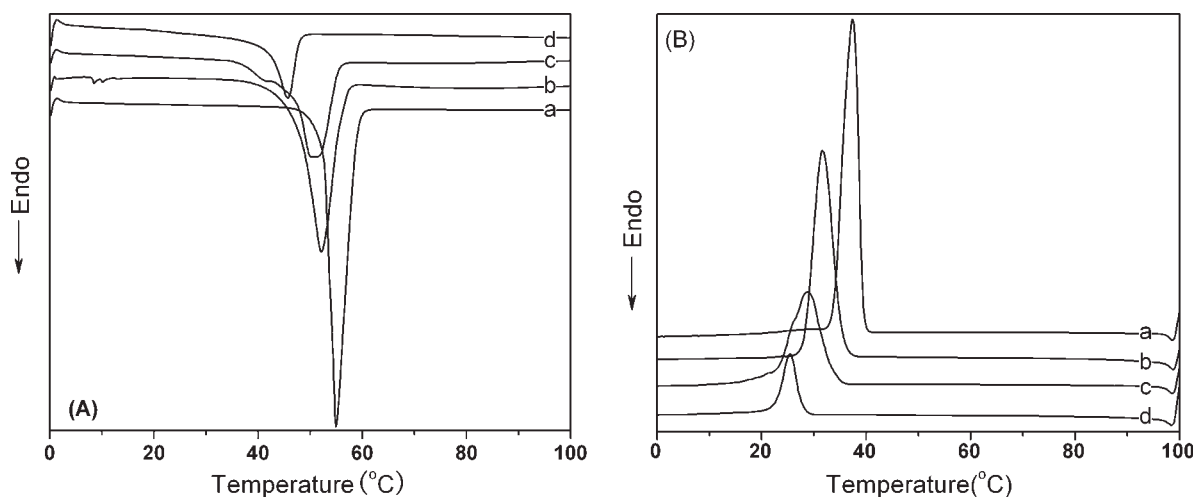

Figure 2 ^{13}C-NMR spectrum of MMTritylcellulose in DMSO-d_6.

Figure 4 ^{1}H-NMR spectra of (a) MMTritylcellulose-*g*-PEG$_{2k}$ and (b) cellulose-*g*-PEG$_{2k}$ in DMSO-d_6. The concentration of PEG was 85 wt %.

Figure 5 DSC (A) heating and (B) cooling curves of mPEG$_{2k}$ and cellulose-g-PEG$_{2k}$ copolymers with PEG concentrations of (a) 100, (b) 94, (c) 85, and (d) 50 wt %.

$M_{\text{MMTritylcellulose}}$

$$= M(C_6H_{10}O_5) + M(C_{20}H_{17}O \times DS) - M(H \times DS)$$
$$= C_{6+20DS}H_{10+16DS}O_{5+DS} = 162 + 272DS \quad (1)$$

where M is the molar mass of the related groups. In this work, the elemental analysis results were 71.08% carbon and 6.03% hydrogen, which corresponded to DS = 0.93. The chemical structure of MMTritylcellulose was further confirmed by ^{13}C-NMR (Fig. 2), and the peak assignment was carried out on the basis of the literature.[27,28] The strong signals at 110–160 ppm come from the aromatic carbon atoms of the MMTrityl groups, and the signal around 55 ppm comes from the —OCH$_3$ group (C-12). Meanwhile, there is a separate peak for C-7 around 85 ppm. The singlets at δ = 60–100 ppm

are attributable to the carbon atoms of the anhydroglucose.

MMTritylcellulose-g-PEG was synthesized by the treatment of MMTritylcellulose with mPEGI with a procedure similar to that used for the alkylation of tritylcellulose.[28–30] As expected, the content of the grafted PEG chains increased with increasing mPEGI content in the feed. The graft content was calculated as follows: graft content = $[(W_g - W_0)/W_0] \times 100$, where W_g and W_0 are the weights of MMTritylcellulose-g-PEG and MMTritylcellulose, respectively. Figure 3 shows the FTIR spectra of the cellulose, mPEG, and MMTritylcellulose-g-PEG copolymers. The characteristic absorbance bands of mPEG at 842, 948, 1112, and 2883 cm^{-1} appear in the spectrum of the MMTritylcellulose-g-PEG copolymer [Fig. 3(c)], and this indicates that the PEG chains were successfully

TABLE I
DSC Results for PEG and Its Copolymers

	PEG (wt %)[a]	Heating				Cooling			Phase transition
		ΔH_m (J/g)	ΔH_m^* (J/g)	T_m (°C)	Crystallinity (%)	ΔH_c (J/g)	ΔH_c^* (J/g)	T_c (°C)	
Cellulose-g-PEG$_{2k}$	100	199.7	199.7	54.9	97.4	177.8	177.8	37.3	Solid–liquid
	94	177.4	188.8	52.1	92.1	157.7	167.8	31.6	Solid–liquid
	85	149.1	175.4	50.4	85.6	132.5	155.9	28.9	Solid–solid
	50	66.5	133.0	45.7	64.9	48.9	97.8	25.6	Solid–solid
Cellulose-g-PEG$_{1.1k}$	100	191.2	191.2	42.7	93.3	180.7	180.7	29.4	Solid–liquid
	95	171.1	179.0	42.2	87.3	165.2	173.9	22.9	Solid–liquid
	85	140.9	167.1	41.6	81.5	129.1	157.7	19.4	Solid–solid
	75	125.3	165.8	40.9	80.9	118.2	151.9	18.3	Solid–solid
	60	80.3	133.8	40.2	65.3	70.3	117.1	12.2	Solid–solid

ΔH_c = enthalpy of crystallization per gram of the copolymer; ΔH_c^* ($\Delta H_c/w$) = enthalpy of crystallization per gram of PEG in the copolymer; ΔH_m = enthalpy of melting per gram of the copolymer; ΔH_m^* ($\Delta H_m/w$) = enthalpy of melting per gram of PEG in the copolymer; T_c = solidification temperature; T_m = melting temperature; w = PEG content in the copolymer (wt %).
[a] Estimated gravimetrically and with elemental analysis.
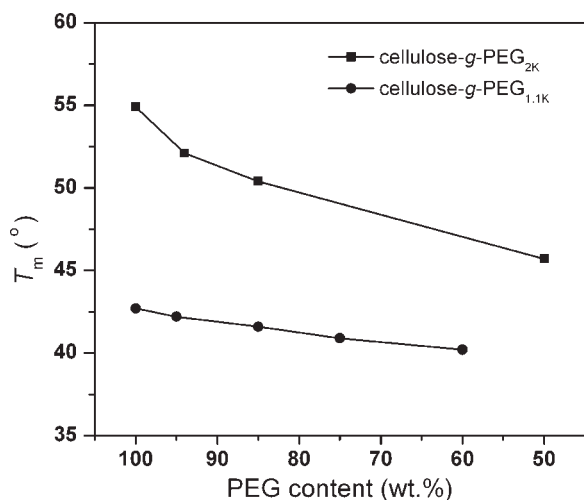
Figure 6 Phase-transition temperature (T_m) as a function of the PEG concentrations in the copolymers: (a) cellulose-*g*-PEG$_{2k}$ and (b) cellulose-*g*-PEG$_{1.1k}$.

grafted onto the cellulose backbone. Moreover, the absorbance bands at 1509 and 1607 cm^{-1}, corresponding to MMTrityl moieties, disappeared in the spectrum of the cellulose-*g*-PEG copolymers, and the absorbance band at 3497 cm^{-1} was strengthened simultaneously after MMTritylcellulose-*g*-PEG copolymers were treated by HCl/THF [Fig. 3(d)]; this suggested the absolute removal of the MMTrityl moieties from the cellulose backbone.

Figure 4 shows ^{1}H-NMR spectra of the MMTritylcellulose-*g*-PEG and cellulose-*g*-PEG copolymers. The strong signals at δ = 3.66 and 3.38 ppm are attributable to the protons of —$(CH_2CH_2O)_n$— and —OCH_3 of PEG side chains, respectively. The signals at δ = 6.0–8.0 ppm [Fig. 4(a)], which are attributable to the aromatic protons of MMTrityl moieties, disappeared after MMTritylcellulose-*g*-PEG was treated with HCl/THF [Fig. 4(b)], and this also con-

firms the absolute removal of the MMTrityl moieties from the cellulose backbone.

Figure 5 shows DSC curves of the cellulose-*g*-PEG copolymers with different PEG contents. Because PEG was the working material in the phase transition of the copolymers, it was important to obtain the crystallinity percentage of pure PEG in the copolymers. Moreover, cellulose made no contribution to the phase transition of the copolymers. Therefore, the crystallinity percentage could be estimated as follows:

$$\text{Crystallinity } (\%) = (\Delta H_m^* / \Delta H_m^0) \times 100\% \qquad (2)$$

where ΔH_m^0 is the enthalpy of 100% crystalline PEG ($\Delta H_m^0 = 205$ J/g)[31] and ΔH_m^* is the enthalpy of PEG in the copolymers. The latter was estimated as follows: $\Delta H_m^* = \Delta H_m / w$, where ΔH_m is the enthalpy of the copolymer and w is the PEG content (wt %) in the copolymer. As listed in Table I, the degree of crystallinity of PEG decreased with a reduction of the PEG content, for cellulose did not contribute to the crystallization. The DSC results indicate that the pure mPEG$_{2k}$ showed a phase transition from a crystalline state to an amorphous state with a rather large enthalpy at 54.9°C during heating and from an amorphous phase to a crystalline phase at 37.3°C during cooling. For the cellulose-*g*-PEG$_{2k}$ copolymers, the phase-transition temperatures were in the regions of 52.1–45.7 and 31.6–25.6°C during heating and cooling, respectively. The melting temperature of polymer crystals is directly related to the thickness of the crystalline lamellae. A lower melting temperature is related to a thinner lamella and vice versa.[32] The decrease in the phase-transition temperature indicated thinner lamellae with decreasing PEG content in the copolymer (Table I). The decrease in the enthalpy was due to the decrease in
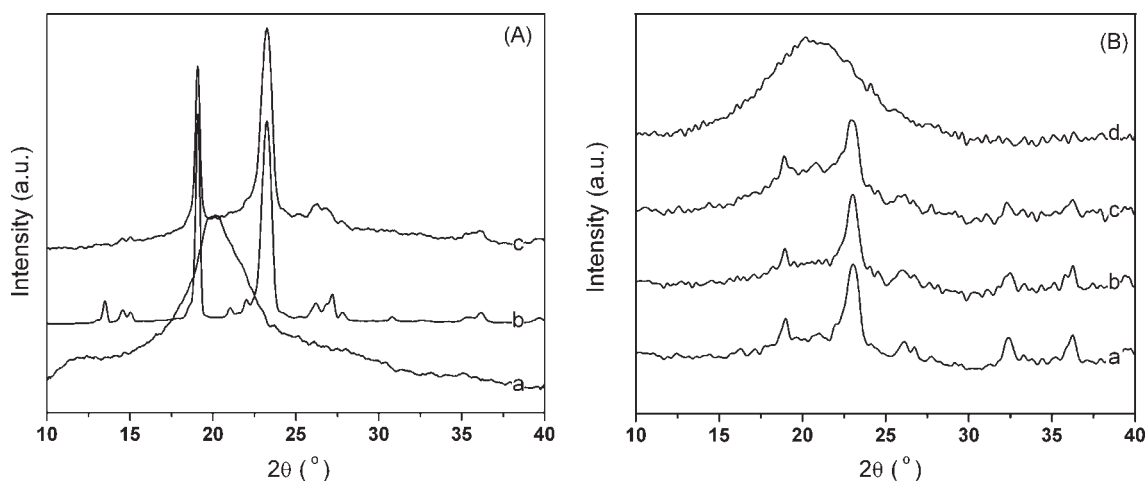

Figure 7 (A) WAXD patterns of (a) mercerized cellulose, (b) mPEG$_{2k}$, and (c) cellulose-*g*-PEG$_{2k}$ at room temperature and (B) WAXD patterns of cellulose-*g*-PEG$_{2k}$ at (a) 30, (b) 40, (c) 50, and (d) 60°C.

the working material content and the crystallinity of PEG in the copolymers (Table I). The phase-transition temperature and enthalpy of the copolymers decreased with the decrease in the PEG content (Fig. 6). Moreover, the phase-transition temperature of cellulose-g-PEG$_{2k}$ was higher than that of cellulose-g-PEG$_{1.1k}$ with the same PEG content (Fig. 6). This was due to the fact that PEG is a linear polymer with repeated CH$_2$CH$_2$O units. With the same PEG content, PEG$_{1.1k}$ had more end groups, and the crystallinity and crystalline perfection were less than those of PEG$_{2k}$; the PEG$_{1.1k}$ copolymers also had a lower phase-transition temperature than PEG$_{2k}$. This result agreed with the literature.[25]

Figure 7(A) shows the WAXD diffraction patterns of mPEG, cellulose, and cellulose-g-PEG at room temperature. The results show that the copolymers have a diffraction pattern similar to that of pure mPEG, and this indicates that the crystal structure of the grafting copolymers is similar to that of mPEG. However, the diffraction peaks of the grafting copolymers are wider than those of mPEG. The results indicate that the crystallites of the PEG side chains in the copolymers are smaller and less perfect than those of pure mPEG samples, and this agrees with the crystallinity results in Table I. The phase-transition behavior of the grafting copolymers was also investigated with WAXD at different temperatures [Fig. 7(B)], and no change in the crystalline structure of PEG in the copolymers was observed at temperatures lower than the melting temperature of PEG. At temperatures above the melting temperature of PEG (e.g., 60°C), only an amorphous diffraction peak is shown on the WAXD curve. The temperature-dependence WAXD experiments were consistent with those of DSC.

Figure 8 presents typical POM images of mPEG and cellulose-g-PEG. A spherulite crystalline morphology with an obvious cross-extinction pattern under polar light was observed at room temperature for mPEG [Fig. 8(a)]. In the case of cellulose-g-PEG, the spherulite crystalline morphology was also observed, but the spherulites were much smaller than those of pure mPEG [Fig. 8(a,b)]; this indicated that the crystallization of PEG in the copolymers was disturbed by cellulose. While the samples were heated, no change in the morphology of the samples was observed below the phase-transition temperature. When the samples were heated to a temperature above the phase-transition temperature (e.g., 50.4°C), the spherulites disappeared rapidly [Fig. 8(c)]. It was further confirmed that a phase transition took place for the copolymer at this temperature. Furthermore, no flow phase was observed under a normal light microscope in the temperature range of 50–100°C, and this indicated that the molten PEG was fixed by the cellulose skeleton and lost its
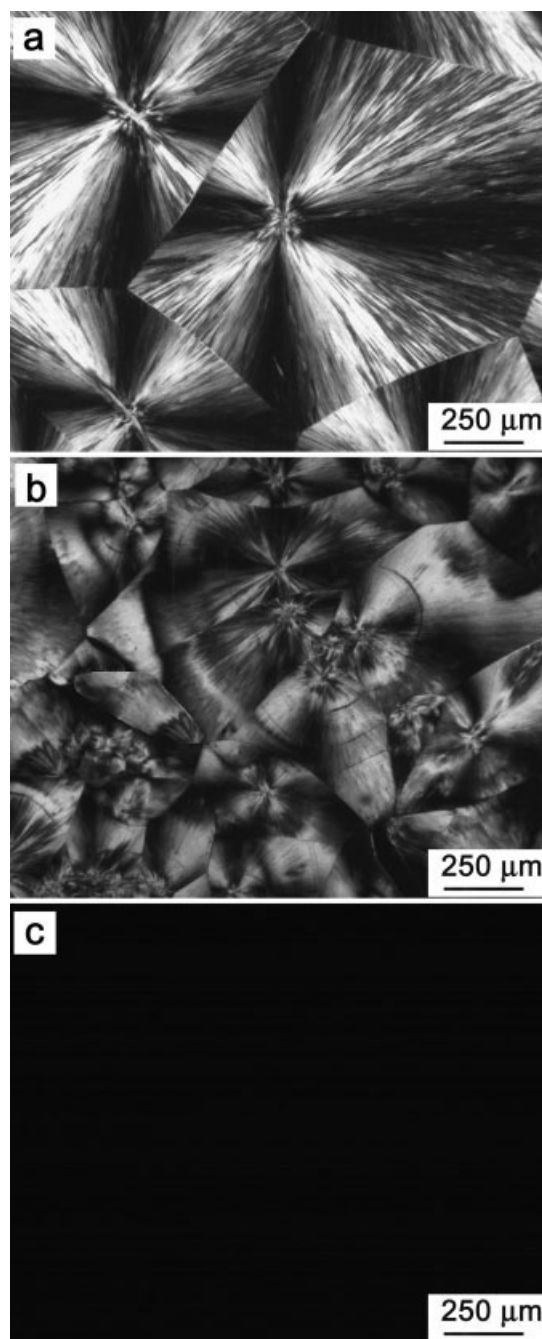
Figure 8 POM microphotographs of (a) mPEG$_{2k}$, (b) cellulose-g-PEG$_{2k}$ at 25°C, and (c) cellulose-g-PEG$_{2k}$ at 51°C.

intrinsic macroflowing property, so the phase transition around 50°C was a solid–solid phase transition. The phase-transition behaviors of the copolymers are summarized in Table I. The copolymers showed a solid–liquid phase transition when the cellulose content in the copolymers was lower than 15 wt %, whereas there was a solid–solid phase transition for those copolymers with cellulose contents higher than 15 wt %. The former was due to the fact that the limited cellulose backbone was insufficient to prevent the diffusion of liquid PEG.[33]
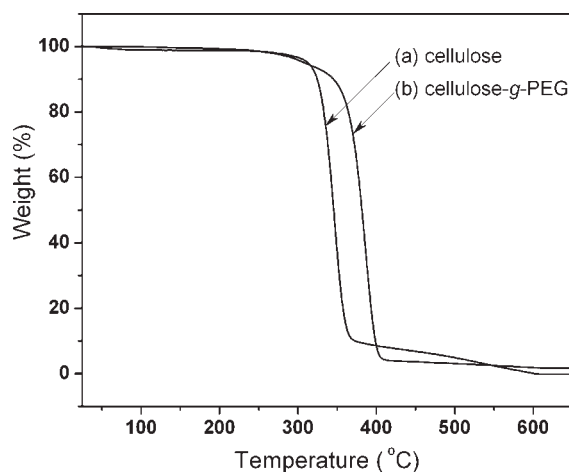
Figure 9 TGA of (a) cellulose and (b) the copolymer cellulose-*g*-PEG$_{2k}$ with a PEG concentration of 85 wt %.

The thermal stability of PCMs is very important,[34] and the applications of normal solid-state PCMs, such as those containing polyols, paraffin, or fatty acids, are limited because of thermal decomposition, degradation, evaporation, and sublimation.[35] The copolymers in this work had good thermal stability, as indicated by the TGA experiments (Fig. 9). The results showed that the samples were stable below 250°C. Moreover, after the cellulose-*g*-PEG copolymers were heated from room temperature to 100°C and then cooled to room temperature for 100 cycles, no obvious change in the phase-transition behaviors was observed. The results confirmed that the cellulose-*g*-PEG copolymers were stable in the temperature region of 20–100°C.

CONCLUSIONS

Cellulose-*g*-PEG copolymers were synthesized and characterized. The obtained graft copolymers showed solid–solid phase-transition behavior with a higher thermal storage density and good thermal stability. The phase transition was the transition between the crystalline and amorphous states of the PEG side chains of cellulose-*g*-PEG copolymers. The phase-transition temperature could be adjusted from room temperature to 50°C though changes in the content and molecular weight of PEG side chains. The resultant grafting copolymers could be potentially used as solid-state PCMs for thermal energy storage and temperature-control applications.

References

1. Farid, M. M. J Solar Energy Res 1986, 4, 11.
2. Amar, M. K.; Mohanned, M. F. Energy Conv Manag 2004, 45, 263.
3. Harlan, S. L. ACS Symp Ser 1991, 457, 248.
4. Haws, D. W.; Banu, D.; Feldma, D. Sol Energy Mater 1990, 21, 61.
5. Liang, X. H.; Guo, Y. Q.; Ding, E. Y. Macromolecules 1995, 28, 6551.
6. Ding, E. Y.; Jiang, Y.; Guo, Y. Q. J Macromol Sci Phys 2001, 40, 1053.
7. Guo, Y. Q.; Tong, Z.; Chen, M. C.; Liang, X. H. J Appl Polym Sci 2003, 88, 652.
8. Su, J. C.; Liu, P. S. Energy Conv Manag 2006, 47, 3185.
9. Zhang, X. X.; Tao, X. M.; Yick, K. L.; Fan, Y. F. J Appl Polym Sci 2005, 97, 390.
10. Lim, J. S.; Fowler, A. J.; Bejan, A. J Heat Transfer 1993, 115, 1044.
11. Inada, H.; Tu, D. Nippon Kikai Gakkai Ronbunshu B 1996, 62, 2790.
12. Han, S.; Kim, C.; Kwon, D. Polymer 1997, 38, 317.
13. Harris, J. M.; Zalipsky, S. Poly(ethylene glycol): Chemistry and Biological Applications; American Chemistry Society: Washington, DC, 1997.
14. Klemm, D.; Fink, H. P. Angew Chem Int Ed 2005, 44, 3358.
15. Shukla, S. R.; Athalye, A. R. J Appl Polym Sci 1992, 44, 435.
16. Wang, C.; Dong, Y.; Tan, H. J Polym Sci Part A: Polym Chem 2003, 41, 273.
17. Anna, C.; Eva, M. J Am Chem Soc 2002, 124, 900.
18. Teramoto, Y.; Yoshioka, M.; Shiashi, N.; Nishio, Y. J Appl Polym Sci 2002, 84, 2621.
19. Eromosele, C. O.; Nwokata, S. P. J Appl Polym Sci 2004, 91, 278.
20. Shen, D. W.; Huang, Y. Polymer 2004, 45, 7091.
21. Ute, H.; Thomas, H.; Dieter, K. Macromol Chem Phys 1999, 200, 896.
22. Heinze, T.; Rottig, K. Macromol Rapid Commun 1994, 15, 311.
23. Kern, H.; Choi, S. W.; Wenz, G. Carbohydr Res 2000, 326, 67.
24. Lv, S. H.; Guo, Y. Q.; Chen, M. Z.; He, T. Polym Mater Sci Eng 2004, 20, 62.
25. Jiang, Y.; Ding, E. Y.; Li, G. K. Polymer 2002, 43, 117.
26. Rydon, H. N. Org Synth 1971, 51, 44.
27. Takahashi, S.; Fujimoto, T.; Barua, B. M.; Miyanoto, T.; Inagaki, H. J Polym Sci Part A: Polym Chem 1986, 24, 2981.
28. Camacho, G. J. A.; Erler, U. W.; Klemm, D. O. Macromol Chem Phys 1996, 197, 953.
29. Hearon, W. M.; Hiatt, G. D.; Fordyce, C. R. J Am Chem Soc 1943, 65, 2449.
30. Brian, R.; Harkness; Gray, D. G. Macromolecules 1990, 23, 1452.
31. Martuscelli, E.; Silvestre, C.; Addonizio, M. L.; Amelino, L. Makromol Chem 1986, 187, 1557.
32. Hoffman, J. D.; Miller, R. L. Polymer 1997, 38, 3151.
33. Guo, Y. Q.; Liang, X. H. J Macromol Sci Phys 1999, 38, 449.
34. He, T. B.; Hu, H. J. Functional Polymer and New Technology; Chemical Industrial: Beijing, 2001.
35. Feldman, D.; Shapiro, M. M.; Banu, D. Sol Energy Mater 1986, 13, 1.