¹³C NMR Characteristics and Thermal Properties of Hydroxyethyl Cellulose Grafting Poly(caprolactone) Copolymer

MING GUO*, XIN XIN YIN and PENG WANG

Department of Chemistry, Zhejiang Agriculture and Forestry University, Lin'an 311300, P.R. China

*Corresponding author: Fax: +86 571 63730839; Tel: +86 571 63740852; E-mail: tdky@hotmail.com

Hydroxyethyl cellulose (HEC) grafting poly(caprolactone) (PCL) copolymer (HEC-g-PCL) was successfully synthesized by the protective technology of trimethylsilyl group. The poly(caprolactone) was grafted onto hydroxyethyl cellulose after the partial hydroxyl groups were firstly protected with trimethylsilyl group, then protective trimethylsilyl groups were taken off and the new graft copolymer was generated. The product was characterized by ¹³C NMR, the thermal properties analysis was also tracked with quadrate hyperthermic treatment. The results of the structure analysis indicated that poly(caprolactone) was connected to hydroxyethyl cellulose by chemical bond and the test showed that the thermal stability was changed along with the modified structure.

Key Words: Hydroxyethyl cellulose, Polycaprolactone, Trimethylsilyl groups, Copolymer.

INTRODUCTION

It is most significant in developing cellulosic modification materials which have advantages of low processing cost, non-toxicity and biodegradability *etc*.[1-3] As typical cellulose ester, hydroxyethyl cellulose can be used in the field of thickening agent, fluxion conditioner, medicine, *etc*.[4-6] However, hydroxyethyl cellulose hardly dissolves in non-water solvent, which limits its further application. Poly(caprolactone) (PCL) is one kind of polymers of hydrophobicity and biocompatility. It plays an important role in polymers and in the biomedical material area[7,8]. On account of poly(caprolactone)'s structure of molecule chain and high crystallinity, its constancy is better than others and the biodegradability of poly(caprolactone) is not perfect. If the modification material through the chemical graft reaction between the hydrophilic hydroxyethyl cellulose and the hydrophobic poly(caprolactone) could be successfully synthesized, then the new biodegradation material (HEC-g-PCL) will be gained. Meanwhile, the obtained new material with special structure should be endowed a lot of peculiar thermal properties. To our best of knowledge, the ¹³C NMR characteristics and thermal properties of hydroxyethyl cellulose grafting poly(caprolactone) (HEC-g-PCL) is still the new result for this kind of copolymer.

EXPERIMENTAL

Hydroxyethyl cellulose (HEC, Mw: 25000, Ms = 3.0) was supplied by Ruitai Cellulose Co. Ltd., (Shandong, China);

ε-caprolactone (CL, 99 %) was supplied by Acros Organics Co.; Hexamethyldisilazane (HMDS, AR, Shanghai Medical Chemical Reagent, China). Other chemical reagents were analytical grade and redistilled water was used throughout the experiment.

Preparation of HEC-g-PCL: The experimental installation was under a water-free and oxygen-free condition. 2 g hydroxyethyl cellulose was dissolved in 20 mL *N,N*-dimethyl formamide with the protection of nitrogen and 0.1 g NH_4Cl was added in the reaction flask. The temperature was raised to 105 ºC, then 12 mL hexamethyldisilazane was slowly titrated into this flask for 8 h reaction by stirring. The excessive redistilled water was added into a vessel into which the reaction mixture has been transferred. The crude product was obtained after the reaction mixture was stirred vigorously, precipitated and filtered. Then, the crude product was dissolved in acetone and filtered, excessive redistilled water was added into the filtered liquor and the process of stirring, sucking filtration was taken. The solid hydroxyethyl cellulose trimethyl-silicification intermediate (TMSHEC) was obtained. 0.4 g TMSHEC was transferred to a reaction flask which has 8 mL xylene. The temperature was raised to 80 ºC for 1.5 h reaction under the protection of nitrogen. Then 1 mL ε-caprolactone monomer and 0.25 mL $Sn(Oct)_2$ were added and the reaction was continued for 24 h at 120 ºC. The reaction product was dissolved with $CHCl_3$ and the reaction product was precipitated in petroleum ether and then washed several times with petroleum ether. The white polymer TMSHEC-g-PCL was obtained. 2 %

$NaHCO_3$ diluted solution, 36 % HCl diluted solution were prepared respectively. Isopropanol and diluted hydrochloric acid were measured and mixed to a prepared alcoholysis solution of isopropanol/water/hydrochloric acid (1:1, v/v). The synthetic TMSHEC-g-PCL was added to the isopropanol/ water/hydrochloric acid alcoholysis solution. The alcoholysis reaction began at 75 ºC for 15 min with stirring and then $NaHCO_3$ was used to adjust the solution system pH = 7.5. The precipitate was a filtered deposition and the graft copolymer (HEC-g-PCL) was finally obtained.

Characterization of reactant, intermediate product and graft copolymer: The Fourier transform infrared spectra of hydroxyethyl cellulose, intermediate product TMSHEC, TMSHEC-g-PCL and end product HEC-g-PCL were measured with a spectrophotometer (Prestige-21, Shimadzu, Japan). The ^1H NMR and ^{13}C NMR spectra of hydroxyethyl cellulose, TMSHEC, TMSHEC-g-PCL and HEC-g-PCL samples were measured by using a Bruker ADVANCE2B/400MHz nuclear magnetic resonance spectrometer (NMR, Bruker, Switzerland). The solvent of NMR used was D_2O, CD_3COCD_3, d^6-DMSO and d^5-pyridine and the internal standard was tetramethylsilane.

Thermal properties analysis: The DSC measurement of reactant, intermediates and end product using twice rise temperature treatment begin of low temperature were operated with DSC Q100 differential scanning calorimeter (TA, America). The test begin with -100 ºC, the speed-rate of heating is set as 10 ºC min^{-1} until the temperature reached 200 ºC after 30 min, this temperature is kept for 2 min, then the system temperature was cooled until it reached 0 ºC and the speed-rate of cooling was also stetted as 10 ºC min^{-1}. The temperature should be raised immediately again when 0 ºC was finished, the speed-rate of heating was kept at 10 ºC min^{-1} until the system touchs 100 ºC and then this quadrate hyperthermic experiment is finished. The flow unit of N_2 is 25 mL min^{-1} under whole test and the mass of samples are from 3.60 mg to 3.9 mg.

RESULTS AND DISCUSSION

Synthesis of HEC-g-PCL: The synthesis of HEC-g-PCL follows three steps (Fig. 1). Hexamethyl-disilazane as hydroxyl protection reagent reacts with the hydroxyl of hydroxyethyl cellulose to produce TMSHEC. Then caprolactone occurs opening loop reaction and polymer reaction, graft polymerization of poly(caprolactone) with TMSHEC is achieved, which generates the graft polymer TMSHEC-g-PCL. The TMS group of TMSHEC-g-PCL is taken off and HEC-g-PCL can thus be completely synthesized.

The grafting ratio (G %) and graft efficiency (G_E) can be calculated and are 33.2 % and 12.42 % respectively. The experimental data indicates that poly(caprolactone) as a branch chain grafted on the hydroxyethyl cellulose backbone successfully. The mass ratio of poly(caprolactone) branch chain and hydroxyethyl cellulose backbone is about 1:2. In other words, the ratio denotes poly(caprolactone) branch chain occupies about 1/3 of the mass of the graft product. G_E = 12.42 % means the active hydroxyl belonging to hydroxyethyl cellulose molecule is only left in a limited amount after trimethyl-silicification substitution. By itself the limited activity, most of ε-caprolactone has a homo polymerization reaction and the resultant is finally washed.
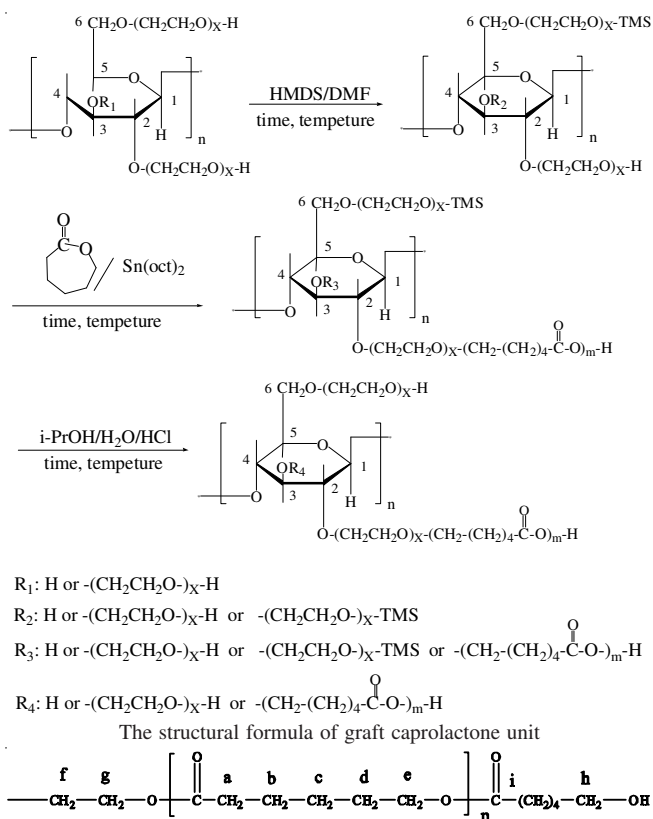

R_1: H or -(CH$_2$CH$_2$O-)$_X$-H

R_2: H or -(CH$_2$CH$_2$O-)$_X$-H or -(CH$_2$CH$_2$O-)$_X$-TMS

R_3: H or -(CH$_2$CH$_2$O-)$_X$-H or -(CH$_2$CH$_2$O-)$_X$-TMS or -(CH$_2$-(CH$_2$)$_4$-C-O-)$_m$-H

R_4: H or -(CH$_2$CH$_2$O-)$_X$-H or -(CH$_2$-(CH$_2$)$_4$-C-O-)$_m$-H

The structural formula of graft caprolactone unit

Fig. 1. Graft polymerization scheme of HEC-g-PCL

The IR and ^1H NMR of spectra of HEC, TMSHEC, TMSHEC-g-PCL and HEC-g-PCL have been investigated. IR spectra of HEC ($ν_{max}$, cm^{-1}): 3450 (-OH), 3000-2837 (-CH$_3$), (-CH$_2$-) and (C-H), 1200-1000 (C-O-C); IR spectra of TMSHEC ($ν_{max}$, cm^{-1}): 3480 (-OH), 3000-2837 (-CH$_3$), (-CH$_2$-) and (C-H), 251 (Si-Me), 891-875 (Si-Me), 841 (Si-Me), 752-749 (Si-Me), 1200-1000 (C-O-C); IR spectra of TMSHEC-g-PCL ($ν_{max}$, cm^{-1}): 3442 (-OH), 3000-2837 (-CH$_3$), (-CH$_2$-) and (C-H), 1251 (Si-Me), 900-875 (Si-Me), 840 (Si-Me), 753-748 (Si-Me), 1200-1000 (C-O-C), 1730 (C=O); IR spectra of HEC-g-PCL ($ν_{max}$, cm^{-1}): 3436 (-OH), 3000-2837 (-CH$_3$), (-CH$_2$-) and (C-H), 1200-1000 (C-O-C), 1730 (C=O). ^1H NMR of HEC (ppm): 4.98, 4.51, 3.51-3.85, 3.8, 1.8; ^1H NMR of TMSHEC: 4.98, 4.51, 3.51-3.85, 3.8, 1.8, 0.1; ^1H NMR of TMSHEC-g-PCL: 5.1, 4.0, 3.83, 2.3, 1.54, 1.30, 0.1; ^1H NMR of HEC-g-PCL: 5.1, 4.0, 3.82, 2.3, 1.54, 1.30. These spectra of IR and ^1H NMR show that the HEC-g-PCL has been successfully synthesized.

Analysis of ^{13}C NMR spectroscopy: ^{13}C NMR is a high performance approach for characterizing the cellulose derivatives[9]. Fig. 2 shows the ^{13}C NMR of hydroxyethyl cellulose. The C_6 carbon signal of cellulose ring can be observed at δ = 69.5 ppm, δ = 71.6 ppm for C_2 of cellulose ring, δ = 73.7 ppm for C_3 of cellulose ring, δ = 81.2 ppm for C_5 of cellulose ring, δ = 84.6 ppm for C_4 of cellulose ring, δ = 102.5 ppm for C_1 of cellulose ring, respectively. The peak at δ = 60.2 ppm is due to -CH$_2$- (f, g) carbon of the hydroxyethyl group.

The ^{13}C NMR of TMSHEC was recorded in Fig. 3. The peaks at δ = 63.7-84.4 ppm are due to C_2-C_6 carbon of cellulose ring and carbon signal at 103.0 ppm for C_1 of cellulose ring. The peak at δ = 63.5 ppm is due to -CH$_2$- (f, g) carbon of
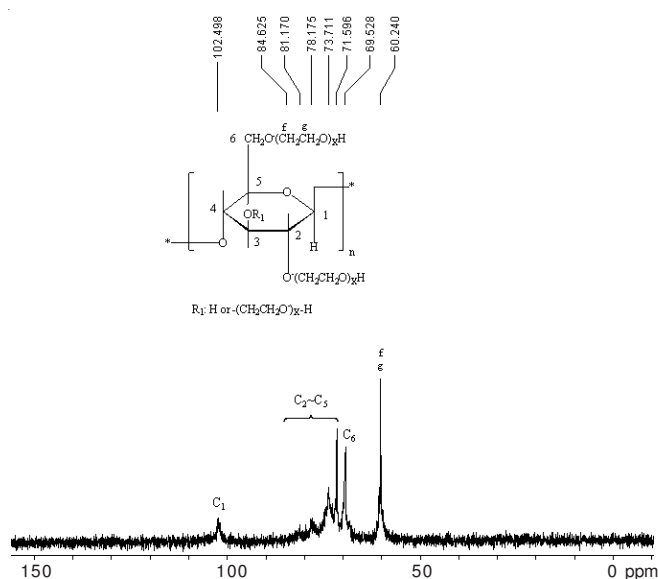
Fig. 2. ^{13}C NMR spectra of hydroxyethyl cellulose
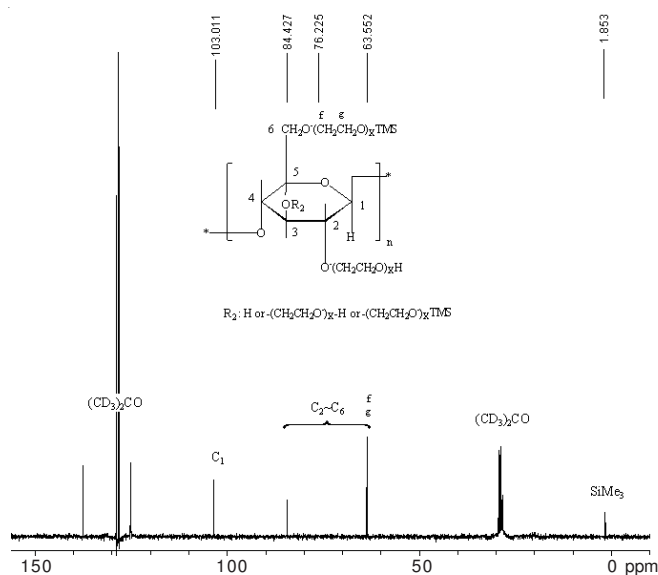
Fig. 3. ^{13}C NMR spectra of TMSHEC

hydroxyethyl group. The new peak at $\delta = 1.85$ ppm is originated from the signal of -(CH$_3$)$_3$Si-, it confirms that the trimethyl-silicification reaction of hydroxyethyl cellulose has actually occurred.

^{13}C NMR of TMSHEC-g-PCL shows the peak at near $\delta = 103$ ppm is due to C$_1$ carbon signal on the hydroxy-ethyl cellulose backbone, $\delta = 63.7$-76.1 ppm are attributed to C$_2$ -C$_6$ carbon signal of cellulose ring, $\delta = 1.57$ ppm is originated from the carbon signal of -(CH$_3$)$_3$Si-, $\delta = 173.1$ ppm is due to carbonyl group(i) carbon signal in the polycaprolactone unit. The multiple peaks at $\delta = 63.5$ ppm are well assigned to -CH$_2$- (e, f, g) carbon signal. The peaks at $\delta = 33.8$ ppm and $\delta = 28.2$ ppm are attributed to -CH$_2$- (a, d) carbon signal respectively. The two sites of -CH$_2$-(b) and -CH$_2$- (d) in the polycaprolactone unit have been distinguished in the ^{13}C NMR spectrum, the carbon signal of -CH$_2$- (b) and -CH$_2$-(d) separately locate at $\delta = 24.49$ ppm and $\delta = 28.2$ ppm. The peak at $\delta = 25.28$ ppm is due to -CH$_2$-(c) carbon signal.

Fig. 4 shows the ^{13}C NMR of HEC-g-PCL. The peak at $\delta = 100$ ppm is due to C$_1$ carbon signal on the hydroxyethyl cellulose backbone, $\delta = 63.9$-74.5 ppm are attributed to C$_2$-C$_6$ carbon signal of cellulose ring; $\delta = 173.1$ ppm is due to carbonyl group (i) carbon signal in the polycaprolactone unit. The multiple peaks at $\delta = 63.5$ ppm are due to -CH$_2$- (e, f, g) carbon signal. $\delta = 33.9$ ppm and $\delta = 28.4$ ppm can be assigned to -CH$_2$- (a) and -CH$_2$- (d) carbon signal, $\delta = 25.5$ ppm and $\delta = 24.6$ ppm for the -CH$_2$- (c) and -CH$_2$- (b) carbon signal. The experimental data indicated that the caprolactone molecule has a ring-opening polymerization reaction and is linked to hydroxyethyl cellulose by ester bond and the HEC-g-PCL was successfully synthesized. In addition, the peaks corresponding to glucoside and poly(caprolactone) segment also exist and the carbon chemical shift of every group in Fig. 4, but the peak at $\delta = 1.57$ ppm, which is due to the chemical shift of -(CH$_3$)$_3$Si carbon disappeared in Fig. 4. This ^{13}C NMR spectrum indicates that the TMS group has been successfully removed.

Analysis of thermal properties: The thermal stability has an important meaning in processing, fusion characteristics, mechanical properties *etc.* of the cellulose-base derivatives[10,11]. In this paper, the hyperthermic experiment of hydroxyethyl cellulose, TMSHEC, TMSHEC-g-PCL and the graft product HEC-g-PCL has been done and the thermal stability analyzed. Fig. 5 shows the quadrate hyperthermic curves of hydroxyethyl cellulose and TMSHEC.

From the Fig. 5, the initial fusion peak (85.9 ℃) of hydroxyethyl cellulose has been observed under the DSC experimental temperature, but the apparent thermal effect is not occurred in the procedure of the second heating-up process. After the hydroxyethyl cellulose is protected, the apparent thermal effect and fusion peak are also not occurred throughout the experimental temperature, it indicates that the thermal stability of TMSHEC is proved. Fig. 6 shows the quadrate hyperthermic curve of the TMSHEC-g-PCL.

The fusion temperature (T$_m$) and crystallization temperature (T$_c$) of TMSHEC-g-PCL can be obtained from Fig. 6. The T$_m$ and T$_c$ are 63.70 ℃ and 28.91 ℃ for pure poly(caprolactone)[12]. After poly(caprolactone) is linked to the skeleton of TMSHEC successfully, the T$_{m1}$ and T$_c$ of TMSHEC-g-PCL are 60.6 ℃ and 24.2 ℃ respectively. It is also known from Fig. 6, the quadrate fusion temperature T$_{m2}$ is 50.8 ℃, T$_{m2}$ is lower than the initial fusion temperature T$_{m1}$.

Fig. 7 shows the quadrate hyperthermic curve of HEC-g-PCL. Compared to Fig. 6, the DSC curves of two products are similar except that the exothermal peak and endothermic peak of TMSHEC-g-PCL become more sharper, it could be deduced that the micro-structure and thermal properties of HEC-g-PCL is similar to TMSHEC-g-PCL.

Fig. 7 showed the T$_{m1}$ and T$_c$ of HEC-g-PCL are 58.2 ℃ and 18.6 ℃, which decreased significantly compared with TMSHEC-g-PCL. Fig. 7 also shows that the quadrate melting temperature T$_{m2}$ is lower than initial melting temperature T$_{m1}$ and the T$_{m2}$ is 48.2 ℃.

Fig. 8 showed the quadrate hyperthermic curve of the hydroxyethyl cellulose, TMSHEC, TMSHEC-g-PCL and HEC-g-PCL, the DSC curves with the time as their abscissa. As shown in Fig. 8, hydroxyethyl cellulose holds a wide
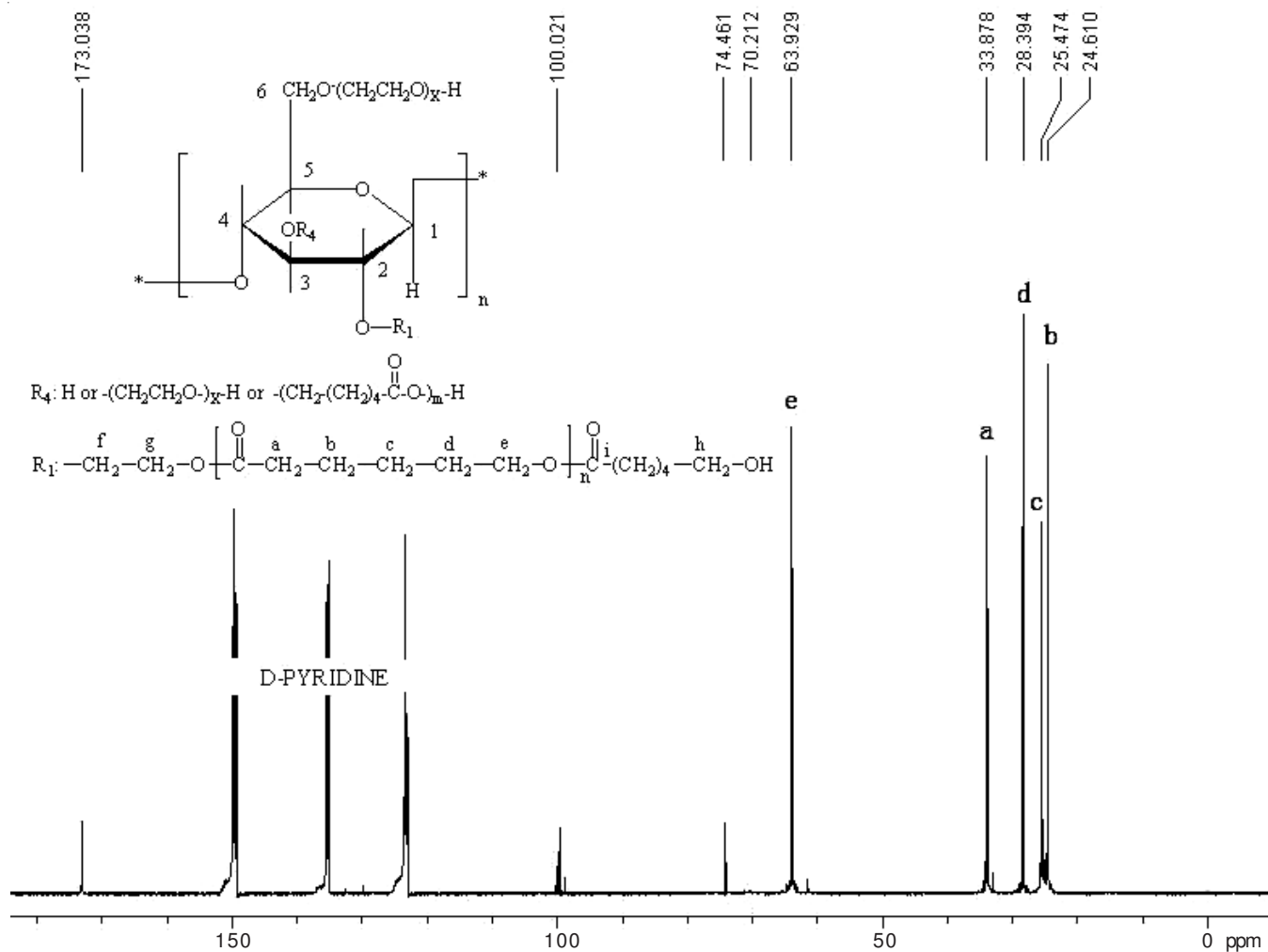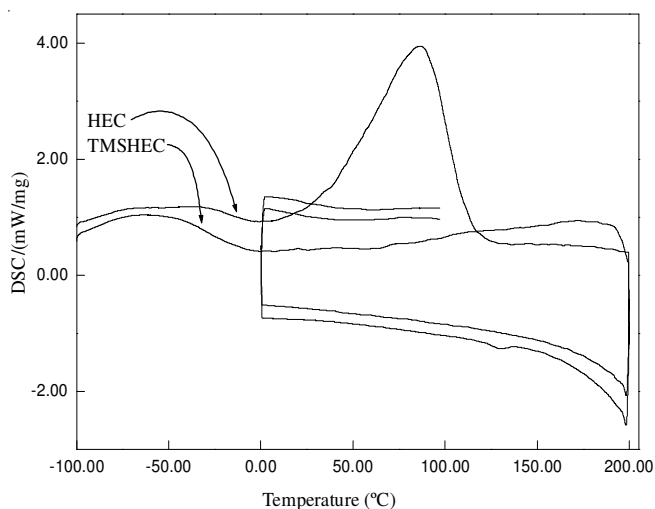
Fig. 4. ^{13}C NMR spectra of HEC-g-PCL
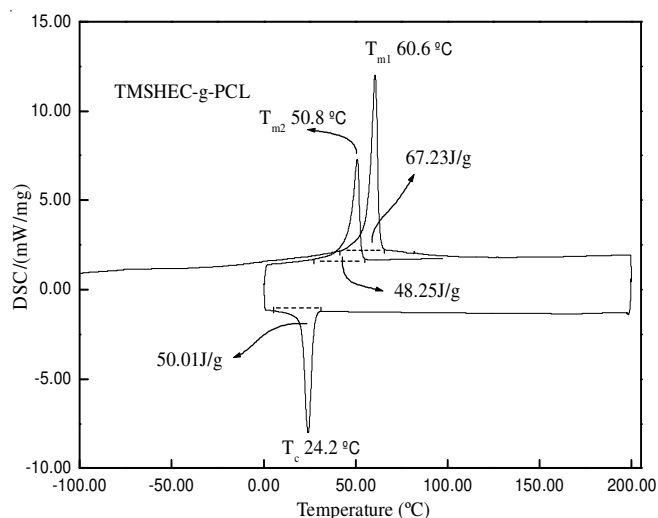

Fig. 5. DSC curves of HEC and TMSHEC

Fig. 6. DSC curve of TMSHEC-g-PCL

endothermic peak, but the exothermic peak does not appear and the endothermic and exothermic peaks can not be obviously observed for TMSHEC. The DSC curves of TMSHEC-g-PCL and HEC-g-PCL are very similar except that the former's endothermic and exothermic peaks are much sharper. The explanation of DSC curves is as following: hydroxyethyl cellulose belongs to amorphous polymer. When it is heated,

the hydrogen bonds among the molecules are destroyed and they form a wide endothermic peak. When hydroxyethyl cellulose is being cooled down, the hydrogen bonds can't reconstruct, so hydroxyethyl cellulose doesn't exhibit an exothermic peak. The hydrogen bonds among the TMSHEC molecules are broken after hydroxyethyl cellulose trimethyl-silicification, so TMSHEC doesn't exhibit obvious endothermic
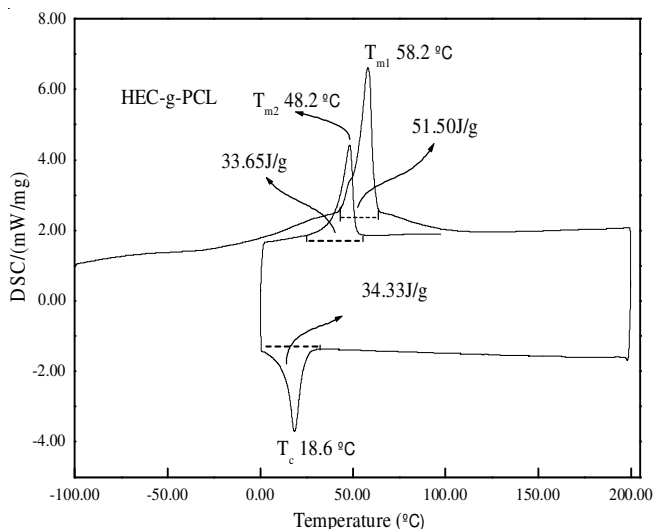
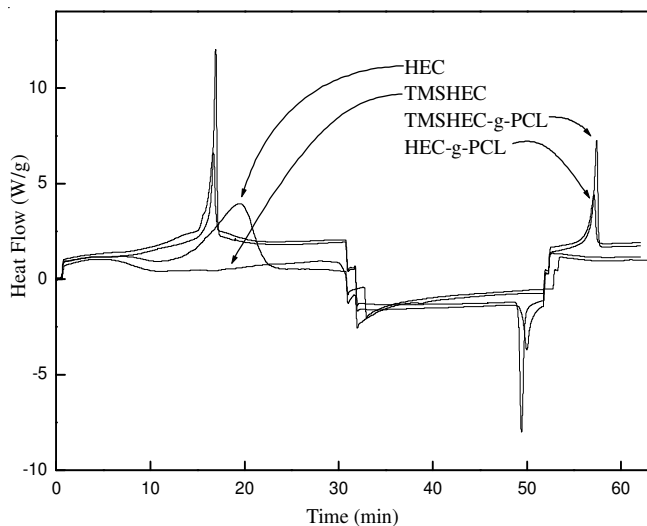Fig. 7. The DSC curve of HEC-g-PCL

Fig. 8. DSC curve of hydroxyethyl cellulose, TMSHEC, TMSHEC-g-PCL and HEC-g-PCL (with time as abscissa)

and exothermic peaks. The crystallinity of TMSHEC-g-PCL increases after poly(caprolactone) grafting onto TMSHEC molecule, thus, the crystalline area will be destroyed and re-crystallized in the quadrate hyperthermic test and the sharper

endothermic and exothermic peaks are formed. The molecule structure of HEC-g-PCL is looser after the trimethylsilyl (TMS) groups are eluted. The crystallinity of HEC-g-PCL is lower than TMSHEC-g-PCL, so the DSC curve of HEC-g-PCL show less sharp peaks.

Conclusion

By using the protective technology of trimethylsilyl (TMS) groups, the cellulosic chemical modification material HEC-g-PCL was successfully synthesized by taking hydroxyethyl cellulose as the grafting skeleton and poly(caprolactone) as the grafting branch. ^{13}C NMR was used to characterize the structure of the intermediates and target product and the results of synthesis verify the designed reaction. The DSC experiment shows that the thermal behaviour characteristics of synthetic products change when a poly(caprolactone) branch is introduced into the skeleton of amorphous hydroxyethyl cellulose.

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