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Synthesis and characterization of camphorsulfonyl acetate of cellulose

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Abstract—Novel cellulose derivatives were prepared from reacting (1*R*)-(+)-camphor-10-sulfonic chloride (CSC) with cellulose acetate (CA) in acetone and triethylamine. The reaction conditions, including reaction time and reactant molar ratios, were optimized. The structure of the products was confirmed by means of ^{1}H NMR, ^{13}C NMR, FT-IR and elementary analysis. The techniques were also used to determine the degree of the substitution of camphorsulfonyl groups (DS_{CS}). The data calculated from ^{1}H NMR, ^{13}C NMR, percent grafting (*G*%) and elementary analysis coincided with those from chemical analysis. Compared to cellulose acetate, the cellulose derivatives exhibited decreased thermal stability, improved solubility in organic solvents and enhanced enantioselectivity towards tyrosine isomers. The solubility and enantioselectivity increased with increasing degrees of camphorsulfonyl substitution.

Keywords: Cellulose acetate; Sulfonylation; Thermal stability; Enantioselectivity; Solubility

1. Introduction

Techniques for preparative-scale enantiomer resolution are urgently needed because of the growing interests of the pharmaceutical industry in single-enantiomer drugs.[1] It is known that an ideal enantioselective polymer membrane material must possess all of the following properties: enantioselectivity, permeability, mechanical strength, self-membrane forming ability and cost effectiveness.[2,3] As an important and traditional cellulose derivative, cellulose acetate (CA) has been widely used in producing fibres, selective membrane, bioactive and biocompatible materials, etc. Its derivatives with chiral recognition sites are now used as chiral stationary phases in HPLC and membranes for enantioseparation.[4,5] Considering that (1*R*)-(+)-camphor-10-sulfonic acid (HCSA) has acted as chiral resolution agent in crystallization and chromatography,[6] and the camphor structure proves to be a very useful chiral probe in HPLC, NMR and X-ray crystallographic determination of absolute configuration,[7] we expected that a material consisting of cellulose acetate and chiral camphor sulfonic acid might well fulfil the above requirements of enantioselective membranes owing to the chiral environment generated by the chiral active carbons on the ring backbone of cellulose and the optically active bulky pendants. To the best of our knowledge, the synthesis of camphorsulfonyl acetate of cellulose (CA–O–CS) has not yet been reported. We report in this paper the preparation of CA–O–CS and its use to prepare novel enantioselective membranes. Enantioselectivity of the material is demonstrated by the

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selective adsorption L-tyrosine over D-tyrosine by the CA–O–CS power and the selective permeation of D-tyrosine through the CA–O–CS membranes. The degree of substitution of camphorsulfonyl group (DS_{CS}) was determined by various approaches. The properties of the modified polymer, including solubility and thermal stability are also characterized for practical application purposes as a function of DS_{CS}.

2. Results and discussion

CA–O–CS was obtained by reacting CA with CSC. The reaction was performed under different conditions with results shown in Table 1. The data in Table 1 indicated that the percent grafting is greatly influenced by the nature of the solvent and the organic base used as the acidic scavenger. Pyridine has been reported to act as the solvent and the organic base in further esterification of cellulose acetate.[8,9] however, the best yields were achieved by us in the current work using acetone and triethylamine as solvent and acid scavenger, respectively. It might result from the fact that triethylamine salt formed after neutralization precipitated from the solvent phase. The dry and mild reaction conditions used avoided chain degradation that was quite sensitive to alkaline and acidic attacks in water.

Table 1 also shows that the percent grafting increases with increasing reaction time up to 24 h. After that percent grafting increases significantly with time. When the reaction was completed, about half of the available hydroxyl groups were sulfonylated, while only 8–9% free hydroxyl groups remained on the anhydroglucose unit (AGU). Although the degree of camphorsulfonyl substitution is not high, further sulfonylation of the residual hydroxyl groups are rather difficult probably due to the steric effect.[8] In this context, the camphorsulfonyl acetate of cellulose with DS_{CS} of 0.33 derived from CSC and CA using 5 wt‰ catalyst of 4-dimethylaminopyridine and a raw molar ratio of CSC:AGU-OH = 1.5:1 in acetone/triethylamine should be the optimistic product.

Figure 1 gives the typical ^{13}C NMR spectrum of CA–O–CS (in Me_2SO-d_6). The assignments are made according to the differences in intensity, line shape and position of the signals. The signals at δ 25.0 (C-7), 26.2 (C-5), 40.1 (C-4), 42.3 (C-6), 47.8 (C-10) and 57.6 (C-1) are attributed to the carbon of camphorsulfonyl (CS) groups, while the peak δ 19.3 is assigned to the dimethyl carbon of CS groups. The signals of carbonyl carbon of CS and acetyl groups appear at δ 213.8 and 169.4–170.4, respectively. The well-resolved lines for C-1 (δ 99.2), C-4 (74.8), C-6 (62.2) carbon atoms of the anhydroglucose unit, as well as the poorly-resolved lines for C-2, -3, -5 (δ 71.40–68.1) carbon atoms appearing at δ 62.2–99.6 are attributed to the signals of cellulose backbone. In addition, the peak of C-3 of camphorsulfonyl groups and that of the anhydroglucose unit partly overlap.

The structures of the resultant derivatives were confirmed by the ^1H NMR spectrum in $CDCl_3$ (Fig. 2). The peak assignments were performed by comparing the peak areas, and by comparing the spectrum with that of cellulose.[10] The proton signals of camphorsulfonyl

Table 1. Effects of reaction conditions on DS_{CS}

DS_{CS}	Cat. (‰)	Concentration (mol/L)	Reaction time (h)	CSC/AGU-OH (mol/mol)	Medium	Percent grafting (%)
0.04	5	0.38	20	2:1	Pyridine	3.16
0.05	5	0.24	24	1.5:1	Pyridine	4.01
0.08	1	0.38	15	1.5:1	Acetone/$(Et)_3N$	6.29
0.19	5	0.24	20	2:1	Acetone/$(Et)_3N$	15.35
0.23	5	0.24	20	1.5:1	Acetone/$(Et)_3N$	17.23
0.25	5	0.24	24	1.5:1	Acetone/$(Et)_3N$	20.12
0.32	5	0.21	24	1.5:1	Acetone/$(Et)_3N$	25.67
0.33	5	0.21	48	1.5:1	Acetone/$(Et)_3N$	26.13

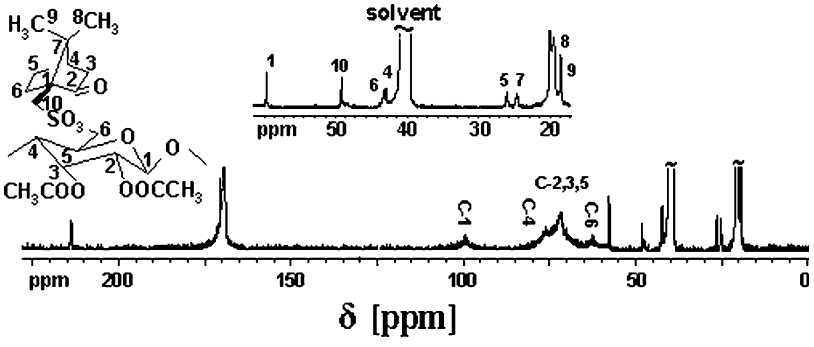


Figure 1. Typical ^{13}C NMR spectra of CA–O–CS.

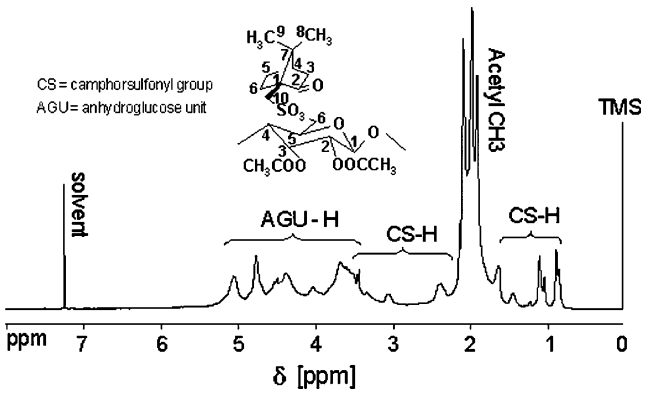


Figure 2. Typical ^{1}H NMR spectra of CA–O–CS (in $CDCl_3$).

substitution mainly appearing at the high magnetic field were assigned as follows: H-8 and -9 (δ 0.833–1.232, 6H), H-5 (1.119–1.459, 2H), H-4 (1.662, 1H) and H-6, H-10 (2.384, 2H, 3.048, 2H), respectively. The proton resonance of the AGU is shown in the δ 3.355–5.050. When the OH groups were substituted, the peaks (AGU-H-3 and H-6) shifted to lower magnetic field than that of cellulose. The wide and strong signals in the δ 3.044–3.685 can be attributed to the resonance of free hydroxyl groups remaining on AGU other than that of H-5 and H-3 at AGU and camphorsulfonyl, respectively. In contrast to the case of CSC, the signal of camphorsulfonyl groups adjacent to CA skeletons shifted towards lower magnetic field regime due to the deshielding effect of cellulose backbone.

The spectra in Figure 3 reveal that the resultant derivatives exhibit not only the characteristic bands of skeletal vibration of cellulose but also the scattering of the newly introduced sulfonyl ester. That is, the stretching modes of O–H of AGU (3494 cm^{-1}) and C–H of methyl and methylene (2990–2850 cm^{-1}), the asymmetry and symmetry stretching of C=O of acetyl (1751 and 1232 cm^{-1}, respectively), the asymmetry stretching

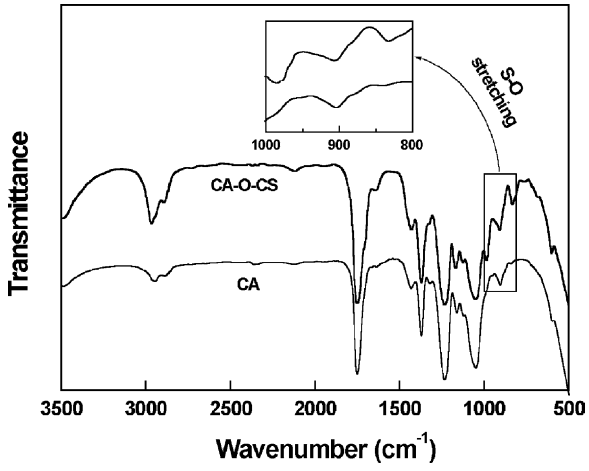


Figure 3. Annotations on the bands in FT-IR spectra of CA and CA–O–CS.

of S=O and the deformations of C–H (1369 cm^{-1}), the symmetry stretching of S=O and stretching of C–O–C (1166 cm^{-1}), the skeletal stretching of C–O of pyranose ring (1049 cm^{-1}) and the stretching of S–O (906 and 831 cm^{-1}). It is seen that the differences between the two spectra in Figure 3 are relatively unobvious, mainly due to the fact that the asymmetrical and symmetrical stretching modes of S=O (ν_{aso_2} 1420–1330 cm^{-1}, and ν_{so_2} 1200–1140 cm^{-1}) of camphorsulfonyl groups partly conceal the peaks of C–H deformation and C–O antisymmetrical stretching of acetyl, respectively. In addition, the asymmetry stretching band of C=O of CS is also hard to be distinguished because of the wide scattering of C=O band of cellulose acetate (1700–1800 cm^{-1}). Nevertheless, the structural changes can still be confirmed by the enhanced intensity of the peaks at 2900, 1750, 1370 and 1170 cm^{-1}, and the appearance of the stretching modes of S–O at 982 and 831 cm^{-1}.

The degree of camphorsulfonyl substitution (DS_{CS}) was estimated by chemical analysis, ^{1}H NMR, ^{13}C NMR, elementary analysis and percent grafting determination. Chemical analysis, which has been traditionally used to estimate the degree of acetyl substitution in cellulose acetate, works also for quantifying the content of camphorsulfonyl groups in CA–O–CS. Since the acetyl groups of the cellulose derivatives can be completely hydrolyzed without affecting the camphorsulfonyl groups under the conditions of chemical analysis, the camphorsulfonyl groups bonded to the AGU result in a rise of the molecular weight of the cellulose units, and hence the reduced apparent content of acetate acid. Accordingly, the degree of camphorsulfonyl substitution is obtained from the variations in the apparent percentage of acetic acid. In ^{1}H NMR spectra, estimation of DS_{CS} was carried out by measuring the peak area ratio of acetyl methyl (δ 1.921–2.094) to sulfonyl methyl of C-10 (δ 0.833–1.232). For ^{13}C NMR spectra, DS_{CS} was yielded from the intensity ratio of the acetyl carbonyl carbon peak (~170 ppm) to that of CS (~213 ppm). The values of DS_{CS} determined by various approaches are plotted against those from chemical analysis in Figure 4. Evidently, the DS_{CS} data are in good agreement with each other. It is therefore believed that the procedure based on chemical analysis described in the present paper offers a reliable, economic and simple way for quantification of the substituting degree of partially sulfonylated acetate cellulose and other analogous cellulose derivatives.

The curves of thermogravimetry (TG) and derivative thermogravimetry (DTG) in Figure 5 and the corresponding data summarized in Table 2 reveal that the thermal stability and thermal degradation behaviour of cellulose acetate have changed considerably after camphorsulfonyl attachment. Three distinct weight loss processes are observed for CA and CA–O–CS: dehydration, 28–46% weight loss resulting from a one-step

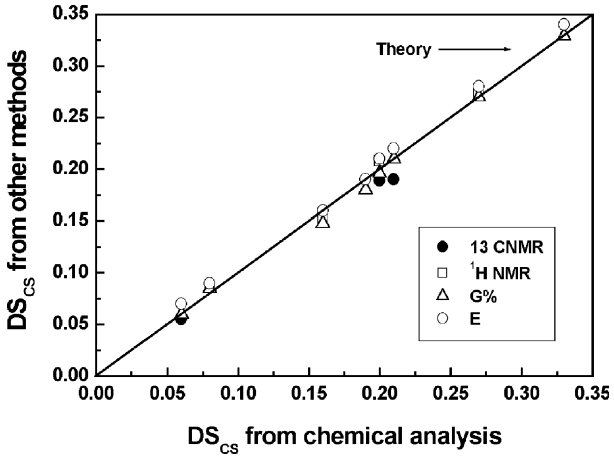


Figure 4. DS_{CS} values determined by elementary analysis (E), ^{1}H NMR, ^{13}C NMR and percent grafting (G%) in relation to those by chemical analysis.

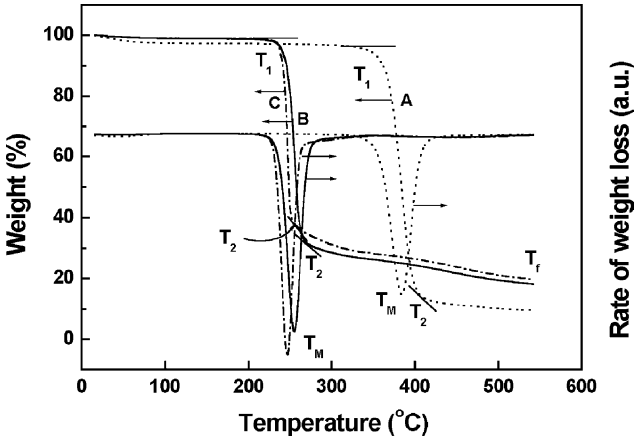


Figure 5. TG and DTG curves of CA (curve A) and CA–O–CS (curve B with DS_{CS} of 0.08, and curve C with DS_{CS} of 0.20).

pyrolysis, and complete oxidation of the residue. The main decomposition process (from temperature T_1 to T_2) of modified CA is shifted from 370–388 °C (for CA) to 230–260 °C (for CA–O–CS). Besides, the CA–O–CS with higher DS_{CS} has more char residue at the final stage of pyrolysis ($T_f \sim 550$ °C) but lower peak decomposition temperature (T_M). It means that the thermal stability of the resultant derivatives decreases with a increase in DS_{CS}, which is contrary to the case when cellulose hydroxyls are substituted by some long chain organic acids.[11] The following issues might be responsible for the decay. (1) The camphorsulfonyl groups act as autocatalysts deteriorating the thermal stability of CA–O–CS and promoting char formation because the decomposition product (i.e., SO_2) would accelerate dehydration of hydroxyl groups.[12] (2) The degradation processes of CA and its derivatives are similar to that of cellulose, including dehydration and depolymerization.[13,14] The introduction of large camphorsulfonyl groups results in partial destruction of inter- and inner-molecular hydrogen bonds, and hence increases the distance between the macromolecular chains, which would intensify decomposition of CA–O–CS. (3) The crystallinity of CA decreases after the substitution of AGU free hydroxyls with bulk camphorsulfonyl groups.

The introduction of camphorsulfonyl groups significantly enhances the solubility of cellulose acetate in many organic solvents, such as benzene and dichloromethane (see Table 3). The higher DS_{CS} is, the better the solubility is. However, the derivatives of cellulose acetate still cannot dissolve in water and methanol. The solubility behaviours of the modified polymer can be partly attributed to the variation in its molecular structure. That is, the hydrophobic alkyl and bulky ring moieties, and the hydrophilic AGU and sulfonic ester fragments should take the responsibility. Furthermore, the increased inter-molecular gaps, created by the introduction of the bulky substituents, decrease interchain forces and facilitate dissolution. The improvement of the solubility has broadened the fabrication window for membrane forming. The polymer can be easily turned into membrane-like material by the solution casting method.

In the present study, enantioselectivity of the newly synthesized products was characterized by their optical rotation, selective adsorption and permeability of D-tyrosine and L-tyrosine, respectively (Table 4). Optical activity is proportional to the total contributions from all the stereocentres in the polymer. The optical rotation, $[\alpha]_D$, which is a function of DS_{CS}, may thus be regarded as a characteristic signature of the products. The larger $[\alpha]_D$ is, the higher DS_{CS} is. This demonstrates the success of chiral modification and likelihood enantioselectivity of the camphorsulfonyl acetate of cellulose. Additionally, the higher stereospecific adsorption and the lower enantioselective permeation for L-tyrosine than D-tyrosine summarized in Table 4

Table 2. Weight loss and the characteristic temperatures of CA and its derivatives

DS_{CS}	First process of weight loss		Second process of weight loss		Third process of weight loss		T_M (°C)	Residual weight at 550 °C (%)
	T_1 (°C)	Weight loss (%)	T_2 (°C)	Weight loss (%)	T_3 (°C)	Weight loss (%)		
0	50–315	1.56	315–408	84.16	408–550	6.61	383.6	7.67
0.08	50–229	1.25	229–269	67.27	269–550	16.41	254.0	15.07
0.20	50–227	1.03	227–254	60.82	254–550	22.30	247.2	15.85

The definitions of the parameters are given in Figure 5.

Table 3. Influence of DS_{CS} on solubility

DS_{CS}	Solubility[a]						
	H_2O	C_6H_6	Me_2SO	CH_2Cl_2	$CHCl_3$	$CH_3COOC_2H_5$	Acetone
0	—	—	+	—	—	—	+
0.09	—	±	+	±	±	±	+
0.15	—	±	+	+	+	+	+
0.23	—	+	+	+	+	+	+
0.32	—	+	+	+	+	+	+

—: Insoluble; +: soluble; ±: highly swollen.
[a] Visually judged.

Table 4. Influence of DS_{CS} on enantioselective recognition ability

DS_{CS}	$[\alpha]_D^{20}$[a]	Adsorption (%)			Permeation rate		
		$A_{D\text{-tyrosine}}$	$A_{L\text{-tyrosine}}$	$\%ee_A$[b]	$P_{D\text{-tyrosine}}$	$P_{L\text{-tyrosine}}$	$\%ee_P$[c]
0	7.32	6.2	8.3	14.5	3.67×10^{-5}	3.56×10^{-5}	1.52
0.09	17.86	10.5	16.8	23.1	7.43×10^{-6}	5.85×10^{-6}	11.89
0.15	21.45	11.6	20.8	28.4	2.89×10^{-6}	1.85×10^{-6}	21.94
0.23	26.38	12.1	25.4	35.5	1.54×10^{-6}	8.24×10^{-7}	30.28
0.32	28.54	12.8	30.7	41.1	1.21×10^{-6}	6.38×10^{-7}	30.95

[a] Measured in a 1–2 g/dL (w/v) Me_2SO solution.
[b] $\%ee_A = (A_{L\text{-tyrosine}} - A_{D\text{-tyrosine}})/(A_{L\text{-tyrosine}} + A_{D\text{-tyrosine}}) \times 100\%$.
[c] $\%ee_P = (P_{D\text{-tyrosine}} - P_{L\text{-tyrosine}})/(P_{D\text{-tyrosine}} + P_{L\text{-tyrosine}}) \times 100\%$.

reveal clearly the enantioselectability of resultant derivatives. The introduction of chiral camphorsulfonyl groups has improved the enantioselective adsorption of cellulose acetate, which is evidenced by the higher stereospecific tendency for L-tyrosine than D-tyrosine in all the cases. The higher DS_{CS}, the higher enantiomer excess percent (%ee) of the adsorption. The best enantioselective adsorption is achieved at %ee of 41.1. Furthermore, the presences of chiral camphorsulfonyl groups result in reduce of the permeation rate, but the permeation rate of D-tyrosine ($P_{D\text{-tyrosine}}$) is higher than that of L-tyrosine ($P_{L\text{-tyrosine}}$) in all case. The reduced diffusion rate of L-tyrosine relative to that of D-tyrosine should have resulted from the increased affinity of the L-isomer owards camphorsulfonyl acetate of cellulose, which is in agreement with the result of static adsorption. The strong interaction leads to increased adsorption capacity but decreased permeability of the membrane. The appropriate amphiphilic performance of the membrane material might play a significant role in the enantioselective recognition.[15]

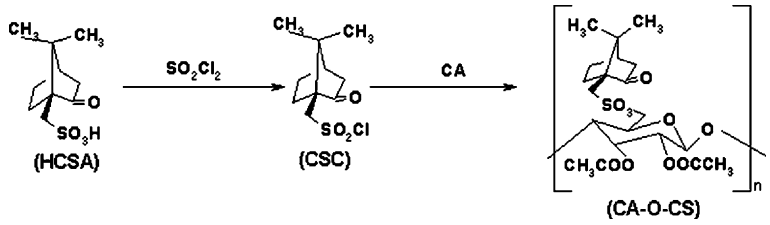
3. Experimental

3.1. Synthesis of (1*R*)-(+)-camphor-10-sulfonyl chloride (CSC)

(1*R*)-(+)-camphor-10-sulfonyl chloride (CSC) acting as the chiral auxiliary was prepared from (1*R*)-(+)-camphor-10-sulfonic acid (HCSA).[16] $SOCl_2$ (70 mL, 962 mmol) was dripped into HCSA (50 g, 217 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C and then heated to 40–50 °C for 2 h. $SOCl_2$ was removed via reduced pressure distillation. The crude material, followed by repeated recrystallization in ligroin, then dried under vacuum, gave the desired product (56 g, 98%), colourless, mp 65–66 °C (Ref. 18: 63–66 °C); $[\alpha]_D$ +32 (*c* 1.0, $CHCl_3$); IR (mulled in mineral oil): *v* 1739 cm^{-1} (C=O), 1376 and 1184 cm^{-1} (O=S=O), 586 cm^{-1} (S–Cl); ^1H NMR (400 MHz, $CDCl_3$): δ 0.902 (s, 3H, H-9), 1.117 (s, 3H, H-8), 1.471 (m, 1H, H-4), 1.751 (m, 1H, H-4), 1.946 (d, 1H, $J_{3,2}$ 18.4 Hz, H-3), 2.139 (t, 2H, $J_{4,5}$ 4.4, H-5), 3.684 (d, 1H, $J_{2,3}$ 18.4, H-2), 4.265 (d, 1H, $J_{2,3}$ 18.4, H-2); ^{13}C NMR (400 MHz, $CDCl_3$): δ 19.5 (2C, $2CH_3$), 25.1 (C-7), 26.7 (C-4), 42.2 (C-3), 42.6 (C-5), 48.1 (C-10), 59.5 (C-6), 64.2 (C-3); Anal. Calcd for $C_{10}H_{15}O_3S_1Cl_1$: C, 47.90; H, 5.99; S, 12.77. Found: C, 47.32; H, 5.84; S, 12.40.

3.2. Chemical modification of CA with CSC

Commercially available cellulose acetate was used in the present study. Its total degree of acetyl substitution (DS_{AC}) is 2.42 and the individual degree of substitution (IDS_{AC}) at −2, −3 and −6 positioned hydroxyls in the anhydroglucose are 0.85, 0.84, 0.73, respectively. DS_{AC} and IDS_{AC} were determined by chemical analysis and propanoation method, respectively. Shown in Scheme 1, the cellulose acetate typically modified with CSC is processed as follows: CSC solution (3 g, 11 mmol of CSC dissolved in 20 mL acetone) was dripped to CA solution (5 g, 19 mmol of CA dissolved in 50 mL dry acetone) in ice-bath accompanied by stirring and



Scheme 1. Schematic drawing of the synthesis of CA–O–CS.

nitrogen protection. The CA solution containing 4-dimethylaminopyridine (0.025 g) as the catalyst and Et_3N (1.5 mL, 11 mmol, with the same equivalent as that of AGU-OH) was stirred at 0–5 °C for 3 h, and then at room temperature for 2 days. Eventually, it was poured into MeOH. The white fine precipitate was collected and purified by repeatedly washing. Further purification of the product was performed by Soxhlet extraction with MeOH for the first 2 h, after which the solvent was changed for fresh one and the extraction was conducted for the additional 24 h. Then the end product was dried under vacuum at 85 °C and stored in desiccators. Yield: 7.29 g, 99.2%.

3.3. General methods

^{13}C NMR and ^{1}H NMR spectra were recorded with Bruker DRX-400 spectrometers (for 400 MHz for ^{1}H, 100 MHz for ^{13}C) at 25 °C for Me_2SO-d_6 or $CDCl_3$ or deuterated acetone solution as indicated. FT-IR spectra were collected on Analect RFX-65A spectrometer (wave number range: 400–4000 cm^{-1}). CA and CA–O–CS were tested via pressing with KBr to pellets or polymeric films. Elementary analyses were processed on Heraeus CHN-O-RAPID. Optical rotations were determined at 25 °C with a Model W22-1S automatic polarimeter. Melting points were inspected with a X-4 digital display binocular microscope. TG data were recorded by a NETZSCH TG 209. Temperature range: 23–550 °C; Heating rate: 20 °C/min; N_2 flow: 60 mL/min. The fractional fixation of CS on the cellulose acetate, G, is defined as follows:

$$G = \frac{W_1 - W_0}{W_0}$$

where W_0 and W_1 refer to weights of CA and CA–O–CS, respectively.

3.4. Chemical analysis and propanoation method

DS_{CS} was determined by chemical analysis method as described in the following.[17] The sample (0.3 g) was added to a flask containing 75% aqueous alcohol solution (40 mL) and then heated to 60 °C for 30 min. Afterwards, 40 mL of 0.5 M NaOH aqueous solution was added to the system, which was further heated for additional 15 min. Finally, the sample was cooled to room temperature and titrated with 0.5 M NaOH after 72 h. After 10 h the solution was back-titrated with 0.5 M HCl. Phenolphthalein was used as the indicator. The DS_{CS} values of the samples were deduced from the following formula:

$$\text{Acetic acid } (\%) = \frac{6000DS_{AC}}{162 + DS_{AC} + 214DS_{CS}} = \frac{(D - C)N_{NaOH} - (A - B)N_{HCl}}{W} \times 6.005$$

where D and B represent millilitres of HCl and NaOH solutions consumed for titration of blank, respectively. C and A denote millilitres of HCl and NaOH solutions consumed for titration of the sample. W means grams of the sample. $DS_{AC} = 2.42$ representing the total degree of substitution of acetyl group in the sample.

To estimate IDS_{AC} values, propanoation processes[18] in which the free hydroxyl groups in CA would be fully substituted by propanoyl groups were carried out. CA (1.0 g) was dissolved in 10 mL pyridine, and 15 mL of propionic anhydride and 0.5 g of 4-dimethylaminopyridine as catalyst were added in the solution. The solution was then stirred for 1 h at 100 °C under N_2 and then poured into MeOH after cooling. The white fine precipitate was washed repeatedly with MeOH, filtrated and dried for 24 h under vacuum. As previously reported, IDS_{AC} was estimated in the quantitative ^{13}C NMR by the integrated intensity ratio of two triplet signals assigned to C=O at C-6, -3 and -2 positions of the propanoyl and acetyl C=O from down- to up-field, respectively.

3.5. Enantioselective adsorption

CA–O–CS powder was added to a 0.100 wt% solution of D-tyrosine and L-tyrosine, respectively. The mixtures were stirred for 24 h, and then filtered, washed with water for 24 h to desorb the tyrosine from the polymer. The aqueous solution containing the desorbed tyrosine was concentrated and its concentration was determined using a 7504 DC UV–visible spectrophotometer. Enantioselectivity of adsorption was estimated by the enantiomer excess percent (%ee) from the following formula:

$$\%ee_A = \frac{A_{\text{L-tyrosine}} - A_{\text{D-tyrosine}}}{A_{\text{L-tyrosine}} + A_{\text{D-tyrosine}}} \times 100\%$$

where A denotes the amount of the adsorbed tyrosine.

3.6. Enantioselective permeation

The nonporous membrane prepared by casting acetone solution of CA–O–CS was placed between two 500 mL cells. Then, 0.5 wt % aqueous solution of D-tyrosine or L-tyrosine and water were filled in the cells called donor cell and acceptor cell, respectively. After a while, the amount of the tyrosine that permeated through the membrane from the donor cell to the acceptor cell was determined at the wavelength of 272 nm by a UV–visible spectrometer. The permeation rate (P) was estimated from $P = QL/At$, where Q is the quantity of the permeated tyrosine, t the permeation time, L and A the thickness and area of the membrane, respectively. Accordingly, the enantiomer excess of permeation ($\%ee_p$) is obtained from the expression:

$$\%ee_P = \frac{P_{\text{D-tyrosine}} - P_{\text{L-tyrosine}}}{P_{\text{D-tyrosine}} + P_{\text{L-tyrosine}}} \times 100\%$$

Acknowledgements

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