

Effect of Molecular Structure on the Gas Permeability of Cellulose Aliphataate Esters^{*}

Jing Chen, Jin-ming Zhang, Ye Feng, Jia-song He and Jun Zhang^{**}

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract In this work, four kinds of cellulose aliphataate esters, cellulose acetate (CA), cellulose propionate (CP), cellulose butyrate (CB) and cellulose acetate butyrate (CAB) are synthesized by the homogeneous acylation reactions in cellulose/AmimCl solutions. These cellulose aliphataate esters are used to prepare gas separation membranes and the effects of molecular structure, such as substituent type, degree of substitution (DS) and distribution of substituents, on the gas permeability are studied. For CAs, as the DS increases, their gas permeabilities for all five gases (O₂, N₂, CH₄, CO and CO₂) increase, and the ideal permselectivity significantly increases first and then slightly decreases. At similar DS value, the homogenously synthesized CA (distribution order of acetate substituent: C6 > C3 > C2) is superior to the heterogeneously synthesized CA (distribution order of acetate substituent: C3 > C2 > C6) in gas separation. With the increase of chain length of aliphataate substituents from acetate to propionate, and to butyrate, the gas permeability of cellulose aliphataate esters gradually increases. The cellulose mixed ester CAB with short acetate groups and relatively long butyrate groups exhibits higher gas permeability or better permselectivity than individual CA or CB *via* the alteration of the DS of two substituents.

Keywords: Cellulose aliphataate ester; Structure; Gas permeability.

INTRODUCTION

Gas separation with membrane process is a promising technology and has been applied in industrial gas separations due to low cost, high energy efficiency, ease of processing and excellent reliability. For example, the separations of CO₂/CH₄ mixtures and CO₂/N₂ (treatment of flue gas) with polymer membranes have already been industrialized for more than 30 years^[1,2]. In the gas separation process, the membrane material is the most crucial factor^[3]. Gas separation properties of membrane materials could be tailored *via* the chemical modification to alter their microstructure^[4].

Cellulose-based material is one of the important polymers used in gas separation because of moderately rigid chains, good flexibility and mechanical strength^[5–9]. Various cellulose derivatives, such as cellulose acetate (CA), ethyl cellulose, silyl cellulose, cellulose butylcarbamate, and trifluoroacetylated cellulose have been reported to be used as the gas separation membrane materials^[10–12]. Among them, CA is the most widely developed material, and found to be the most suitable membrane for biogas separation and enrichment^[1]. However, so far, the relationship between the molecular structure and gas permeability of cellulose esters has not been thoroughly understood yet. It should be noted that, cellulose possesses a large amount of active hydroxyls

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^{**} Corresponding author: Jun Zhang (张军), E-mail: jzhang@iccas.ac.cn

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groups at the C2, C3 and C6 positions of each D-anhydroglucopyranose unit (AGU), which can be substituted with versatile functional groups^[13, 14]. However, because cellulose is insoluble in water and conventional organic solvents due to the well-developed hydrogen bonding networks in cellulose, all commercial cellulose derivatives are prepared by heterogeneous reactions with harsh conditions. Therefore, it is difficult to control the type, degree of substitution (DS) and distribution of functional substituent groups^[15]. Recently, certain ionic liquids (ILs) are found to have outstanding dissolving capability for cellulose, and suitable to be used as the reaction media for chemical modification of cellulose^[16–18]. Using ILs as the reaction media, various cellulose derivatives such as cellulose esters, ethers and graft copolymers, have been successfully prepared^[19–22]. As a novel kind of aprotic solvent, ILs are found to be an effective reaction media for homogeneous cellulose esterification, and the DS and distribution of substituent could be conveniently controlled as desired^[23–26].

In this work, a series of cellulose aliphataate esters with different substituents, DS and distribution of aliphataate groups, including cellulose acetate, propionate, butyrate and acetate butyrate, are synthesized in ILs. The relationship between molecular structure and gas permeation properties is investigated in detail.

EXPERIMENTAL

Materials

Cotton pulp (degree of polymerization *ca.* 730) was dried at 70 °C for 3 h under vacuum before use. AmimCl was synthesized according to our previous work^[27]. Acetic anhydride, propionyl chloride and butyl chloride were purchased from Alfa Aesar and used as received. CA_{2.40-b} (DS = 2.40) was obtained from Nantong Cellulose Fibers Co., Ltd., China, and purified by acetone. All other chemicals of analytical grade were purchased from Beijing Chemical Reagent Factory.

Synthesis of Cellulose Esters

According to the previous reports, four kinds of cellulose esters, cellulose acetate (CA), cellulose propionate (CP), cellulose butyrate (CB) and cellulose acetate butyrate (CAB) were synthesized by the homogeneous acylation reactions in cellulose/AmimCl solution. Detailed information about synthesized samples is shown in Table 1.

Table 1. The DS of CAs, CP, CB and CABs

Sample	DS(Total)	DS(Acetate)	DS(Propionate)	DS(Butyrate)
CA _{1.75-a}	1.75	1.75	0	0
CA _{2.43-a}	2.43	2.43	0	0
CA _{2.82-a}	2.82	2.82	0	0
CA _{2.40-b}	2.40	2.40	0	0
CP _{2.73}	2.73	0	2.73	0
CB _{2.83}	2.83	0	0	2.83
CA _{1.3} B _{1.5}	2.80	1.30	0	1.50
CA _{0.8} B _{2.0}	2.80	0.80	0	2.00
CA _{0.3} B _{2.6}	2.90	0.30	0	2.60
CA _{1.9} B _{0.6}	2.50	1.90	0	0.60

Membrane Fabrication

Nonporous planar membranes of cellulose esters were fabricated by casting their chloroform solutions (concentration 8 wt%) on clean glass plates and evaporating solvents at room temperature. Finally, the obtained homogeneous membranes (thickness: 30–50 µm) were dried under vacuum at 60 °C for 24 h.

Measurements

¹H-NMR spectroscopy

Samples (10 mg) were dissolved in CDCl₃ (0.5 mL). ¹H-NMR spectra were acquired on a Bruker AV400 spectrometer with 16 scans after adding a drop of deuterated trifluoroacetic acid, which shifted the peaks of active hydrogens to the low field. The DS of samples was calculated according to Goodlett *et al.*^[28]. The results are listed in Table 1.

¹³C-NMR spectroscopy

Samples (50 mg) were dissolved in DMSO-d₆ or CDCl₃ (0.5 mL). ¹³C-NMR spectra were acquired on a Bruker AV400 spectrometer with 8000–18000 scans to get the distribution of substituent groups in cellulose esters.

XRD analysis

X-ray diffraction patterns were collected on a Rigaku D/max-2500 X-ray diffractometer. The scanning 2θ ranged between 3° and 45° with a step scanning rate of 3°/min.

DSC

The differential scanning calorimetry (DSC) analyses were recorded on a TA Instruments Q2000 under nitrogen atmosphere. The temperature program runs as follow:

Samples were heated at a rate of 50 K/min from 25 to 250 °C to remove any thermal history. After a thermal stabilization period of 5 min at 250 °C, samples were cooled from 250 °C to −20 °C at a rate of 50 K/min. Then, samples were heated from −20 °C to 250 °C at a rate of 20 K/min again. All reported glass transition temperatures (*T_g*) were recorded from the second heating cycle.

Gas permeability test

Gas permeability was tested by a Labthink VAC-V2 Gas Permeability Tester. The gases used in our experiments were 99.995% O₂, 99.999% N₂, 99.99% CH₄, 99.99% CO and 99.999% CO₂. Permeability tests were conducted under 0.1 MPa pressure at 23 °C, following a sequence as O₂, N₂, CH₄, CO and CO₂ to avoid the plasticizing effect of CO₂ on these membranes. The effective area of the permeation cell was 4.95 cm². The permeability coefficient (*P*) was calculated according to the time-pressure curve. The diffusion coefficient (*D*), solubility coefficient (*S*) and ideal permselectivity (*α*) were determined by formulae (1), (2) and (3) respectively.

$$D = l^2/6\theta \quad (1)$$

$$S = P/D \quad (2)$$

$$\alpha = P_A/P_B \quad (3)$$

l, membrane thickness; *θ*, time lag, intercept of the asymptotic line of the time-pressure curve to the time axis; *P_A*, permeability coefficient of gas A; *P_B*, permeability coefficient of gas B.

RESULTS AND DISCUSSION***The Influence of Degree of Substitution and Distribution of Substituents on Gas Permeability***

Cellulose acetate (CA), one of the most common gas separation membrane materials^[29], is chosen as the research object to study the influence of DS and distribution of substituent on gas permeability. Three CAs (CA_{1.75-a}, CA_{2.43-a} and CA_{2.82-a}) are homogeneously synthesized in AmimCl according to our previous work^[30]. The DS values of them are 1.75, 2.43 and 2.82 respectively. Figure 1 shows the ¹³C-NMR spectrum of CA_{2.43-a} and the distribution of substituents in CA_{2.43-a} and CA_{2.40-b}. Calculating from the integration of carbonyl peaks, the reactivity of acetate group is preferred at C6-OH, and the distribution order of the acetate group is C6 > C3 > C2 in CA_{2.43-a}. Another CA, CA_{2.40-b}, is an industrial product and synthesized by a heterogeneous method, thus the distribution order of the acetate group is C3 > C2 > C6 proven by the ¹³C-NMR spectrum^[30].

XRD spectra of pure cellulose and four CAs are shown in Fig. 2. In XRD spectra of homogeneously synthesized CAs, diffraction peaks of cellulose at 14.9° (101), 16.5°(10 $\bar{1}$) and 22.6° (002) disappear, and there are only wide diffraction peaks. The results suggest that all of the homogeneously synthesized CAs are amorphous. In comparison to them, heterogeneously synthesized CA_{2.40-b} has relatively strong diffraction peaks at 10° and 17.5°, which confirm that CA_{2.40-b} is partially crystalline.

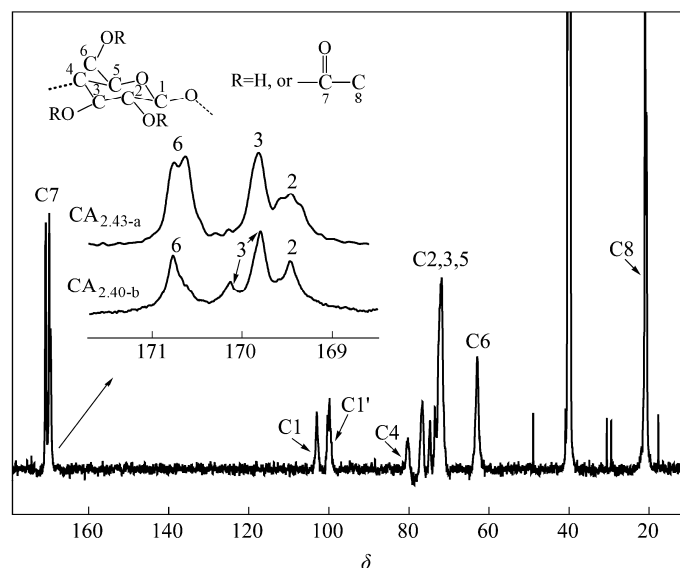


Fig. 1 ^{13}C -NMR spectrum of $\text{CA}_{2.43-\text{a}}$ and the distribution of substituents in $\text{CA}_{2.43-\text{a}}$ and $\text{CA}_{2.40-\text{b}}$.

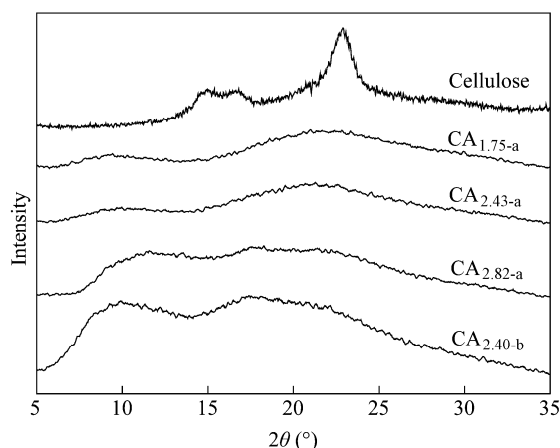


Fig. 2 XRD spectra of cellulose and CAs

The crystal phase transformation of CAs has been investigated also by DSC (Fig. 3). In DSC curves of homogeneously synthesized CAs, there is only a glass transition. In the second heating run, the glass transition temperatures (T_g) are recorded. From Fig. 3(b), we can see that the T_g slightly decreases as the DS increases. The heterogeneously synthesized $\text{CA}_{2.40-\text{b}}$ exhibits a crystal melting peak at 232.9 °C in the first heating run of DSC. In the second heating run, the crystal melting peak becomes very small and the T_g is similar to that of $\text{CA}_{2.43-\text{a}}$. These phenomena confirm homogeneously synthesized CAs are amorphous, while $\text{CA}_{2.40-\text{b}}$ exhibits a partial crystal structure, which is in accordance with the XRD results. Because high T_g and crystallinity are unfavorable to gas molecule permeation, the gas permeabilities of homogeneously synthesized CAs should increase as the DS increases and be better than that of $\text{CA}_{2.40-\text{b}}$.

The results of gas permeability test support the above conjecture. As the DS of homogeneously synthesized CAs increases, gas permeability coefficients (P) for all the five gases increase (Table 2). P of $\text{CA}_{2.82-\text{a}}$ is almost 2 times of $\text{CA}_{1.75-\text{a}}$. And, for almost all the gases, the P of $\text{CA}_{2.43-\text{a}}$ and $\text{CA}_{2.82-\text{a}}$ is higher than that of heterogeneously synthesized CA.

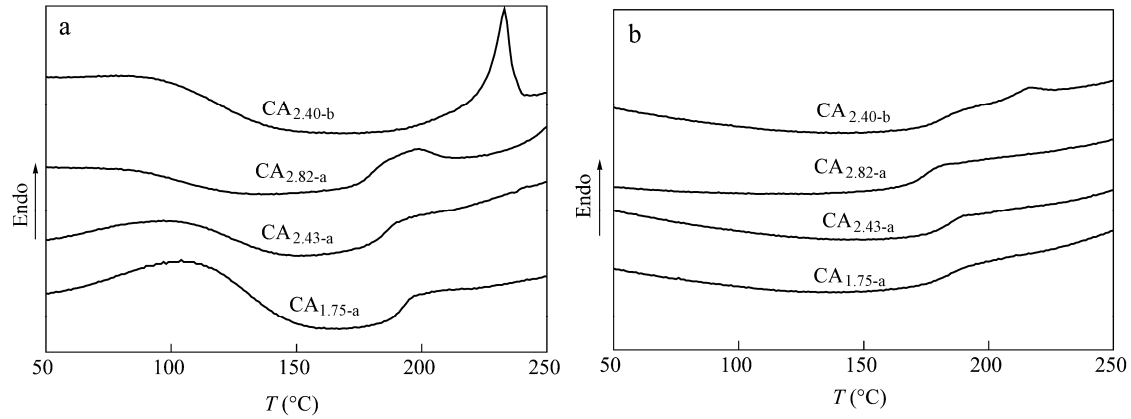


Fig. 3 DSC curves of CAs: (a) the first heating run and (b) the second heating run

Table 2. Gas permeabilities of CAs, CP_{2,73}, CB_{2,83} and CAs

Samples	T_g (°C)	O ₂			N ₂			CH ₄			CO			CO ₂		
		<i>P</i>	<i>S</i>	<i>D</i>	<i>P</i>	<i>S</i>	<i>D</i>	<i>P</i>	<i>S</i>	<i>D</i>	<i>P</i>	<i>S</i>	<i>D</i>	<i>P</i>	<i>S</i>	<i>D</i>
CA _{1,75-a}	205.5	0.68	0.44	1.53	0.2	0.28	0.72	0.16	0.32	0.50	0.21	0.37	0.56	2.21	8.50	0.26
CA _{2,43-a}	187.6	1.04	0.41	2.51	0.37	0.48	0.77	0.16	0.39	0.41	0.26	0.36	0.72	4.21	8.77	0.48
CA _{2,82-a}	185.7	1.34	0.44	3.02	0.42	0.27	1.58	0.28	0.14	1.98	0.44	0.25	1.79	4.93	8.22	0.60
CA _{2,40-b}	187.2	0.76	0.28	2.73	0.23	0.20	1.17	0.16	0.34	0.47	0.24	0.22	1.09	2.48	8.86	0.28
CP _{2,73}	149.8	4.22	0.41	10.3	1.23	0.19	6.6	1.11	—	—	1.51	0.18	8.59	23.1	5.26	4.39
CB _{2,83}	101.5	8.70	0.20	44.6	3.7	0.18	20.3	6.3	0.23	27.4	—	—	—	60.0	2.54	23.6
CA _{0,3} B _{2,6}	114.3	13.7	0.37	37.0	7.28	0.40	18.2	8.61	0.43	19.8	6.00	0.18	33.4	74.3	3.31	22.4
CA _{0,8} B _{2,0}	122.4	11.3	0.35	32.5	5.41	0.43	12.6	5.88	0.45	13.0	4.35	0.19	23.1	58.3	3.74	15.6
CA _{1,3} B _{1,5}	142.5	5.30	0.81	6.55	2.30	0.89	2.58	2.36	0.44	5.34	2.02	0.38	5.31	31.6	—	—
CA _{1,9} B _{0,6}	171.9	1.57	0.20	8.0	0.34	0.17	1.97	0.40	0.48	0.83	0.46	0.16	2.95	8.39	7.11	1.18

Note: The unit of *P*: barrer; 1 barrer = 1×10^{-10} cm³ (STP)·cm/(cm²·s·cmHg). The unit of *S*: 10⁻² cm³ (STP)/(cm³·cmHg). The unit of *D*: 10⁻⁸ cm²/s.

Based on the dissolution-diffusion mechanism of gas permeation, gas molecules first dissolve in the membrane and then diffuse through the membrane. The solubility coefficient (*S*) and diffusion coefficient (*D*) are two important factors influencing gas permeability. According to the results listed in Table 2, the *S* of homogeneously synthesized CAs shows relatively small change as the DS increases, and is slightly higher than that of heterogeneously synthesized CA_{2,40-b}, because the *S* is mainly dependent on the crystallinity of membrane materials. The *D* for all five gases increases significantly as the DS increases, because the *D* is relevant to the chain segmental mobility, which is reflected by the T_g value. Thus, the *D* plays a major role in improving gas permeability of homogeneously synthesized CAs.

Comparing the *D* of CA_{2,43-a} with that of CA_{2,40-b}, we find that the *D* of CA_{2,43-a} is larger for gases with small dynamics diameter (e.g. CO₂) than that of CA_{2,40-b}, while smaller for gases with large dynamics diameter (O₂, N₂, CH₄, CO). Therefore, we can deduce that homogeneously synthesized CA maybe has different microstructure from heterogeneously synthesized CA, which is more favorable to permselectivity.

The ideal permselectivities (α) of CAs are calculated and shown in Table 3. For homogeneously synthesized CAs, the ideal permselectivity increases first and then slightly decreases as DS increases. CA_{2,43-a} performs the best permselectivity. In comparison to CA_{2,40-b}, CA_{2,43-a} has better ideal permselectivity, probably due to its different packed microstructure of polymer chains. For example, the $\alpha_{\text{CO}_2/\text{CH}_4}$ of CA_{2,43-a} reaches 26.3, while that of CA_{2,40-b} only 15.5.

Table 3. Ideal permselectivities of CAs, CP_{2.73}, CB_{2.83} and CABs

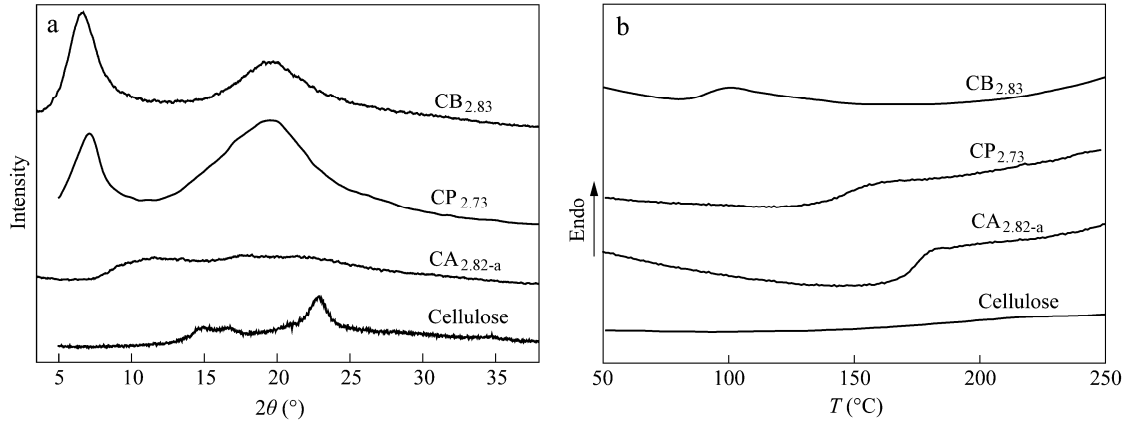
Ideal permselectivity	$\alpha_{\text{O}_2/\text{H}_2}$	$\alpha_{\text{CO}_2/\text{H}_2}$	$\alpha_{\text{CO}_2/\text{CH}_4}$	$\alpha_{\text{N}_2/\text{CH}_4}$	$\alpha_{\text{CO}_2/\text{CO}}$
CA _{1.75-a}	3.4	6.2	7.8	1.3	5.9
CA _{2.43-a}	2.8	11.4	26.3	2.3	16.2
CA _{2.82-a}	3.2	11.7	17.6	1.5	11.2
CA _{2.40-b}	3.3	10.8	15.5	1.4	10.3
CP _{2.73}	3.4	18.8	20.8	1.11	15.3
CB _{2.83}	2.3	16.2	9.5	0.58	-
CA _{0.3} B _{2.6}	1.9	10.2	8.6	0.8	12.4
CA _{0.8} B _{2.0}	2.1	10.8	9.9	0.9	13.4
CA _{1.3} B _{1.5}	2.3	13.7	13.4	1	15.6
CA _{1.9} B _{0.6}	4.6	24.7	21.0	0.85	18.2

The Influence of Chain Length of Aliphatic Substituents on Gas Permeability

Cellulose propionate (CP_{2.73}) and cellulose butyrate (CB_{2.83}) with DS of 2.73 and 2.83 respectively are homogeneously synthesized in AmimCl. The influence of aliphatic chain length of aliphatic substituent on gas permeability of cellulose esters is studied by comparing CA_{2.82-a}, CP_{2.73} and CB_{2.83}.

From XRD spectra (Fig. 4a), we can see that cellulose aliphates with long aliphatic chains in aliphatic substituents have strong crystallization diffraction peaks. CA_{2.82-a} has no obvious diffraction peak, while CP_{2.73} shows strong diffraction peaks at 7.2° and 20.0°, and CB_{2.83} at 6.7° and 20.0°. These results indicate that CP_{2.73} and CB_{2.83} are crystalline, while CA_{2.82-a} is amorphous.

The T_g of cellulose aliphates decreases obviously as the aliphatic chain length of substituent increases (Fig. 4b). The T_g of CA_{2.82-a}, CP_{2.73} and CB_{2.83} appears at 185 °C, 148.5 °C and 90.6 °C respectively. Because the T_g could reflect the chain segment mobility which is related to the diffusion of gas molecules, the gas diffusion coefficients (D) of CA_{2.82-a}, CP_{2.73} and CB_{2.83} should increase in turn.

**Fig. 4** (a) XRD spectra and (b) DSC curves of CA_{2.82-a}, CP_{2.73} and CB_{2.83}.

The gas permeabilities (P), diffusion coefficient (D) and solubility coefficient (S) of CA_{2.82-a}, CP_{2.73} and CB_{2.83} are shown in Table 2. It can be seen that the P exhibits an obvious improvement with the increase of aliphatic chain length in aliphatic substituents. The P of CP_{2.73} is more than 3 times that of CA_{2.82-a}, and P of CB_{2.83} is more than 6 times that of CA_{2.82-a}. Notably, P_{CH_4} and P_{CH_2} of CB_{2.83} are 22 and 12 times those of CA_{2.82-a} respectively, which is in accordance with the typical theory of group contribution. The D increases also as the aliphatic chain length increases, which has been forecasted according to the above T_g results. Because CP_{2.73} and CB_{2.83} have high crystallinity, the S decreases as the aliphatic chain length increases, which is unfavorable to the improvement of P .

Compared with CA_{2.82-a}, the ideal permselectivity (α) of CP_{2.73} significantly increases (Table 3), especially in the separation of CO₂/N₂ and CO₂/CO. But, if the aliphataate chain length further increases, the α decreases. Interestingly, the α_{N_2/CH_4} of CB_{2.83} (0.58) is much smaller than that of CA_{2.82-a} and CP_{2.73} (above 1), that is to say, CB_{2.83} exhibits higher gas permeability for CH₄ than for N₂ while CA_{2.82-a} and CP_{2.73} are just the opposite. The higher permeability of CB for CH₄ may be explained by the improvement of the miscibility between CH₄ and CB induced by increased aliphataate chain length.

Cellulose Mixed Esters with Tunable Gas Permeability

Based on the above results, the long butyrate group has the most advantage in the improvement of D , but disadvantage in the S , due to low T_g and high crystallinity. In order to further improve P , a series of cellulose acetate butyrate mixed esters (CAB) are synthesized to reduce the crystallinity. The DS of acetate group (DS_A) is varied from 0.3 to 1.9, and the DS of butyrate group (DS_B) from 0.6 to 2.6.

From XRD spectra (Fig. 5), it is clear that, as the DS_A increases, two diffraction peaks of CABs at 8° and 20° become weak obviously. Therefore, the S of CABs should increase in comparison to CB_{2.83}. However, the T_g of CABs increases with the increase of DS_A, which means the D of CABs maybe decrease in comparison to CB_{2.83}.

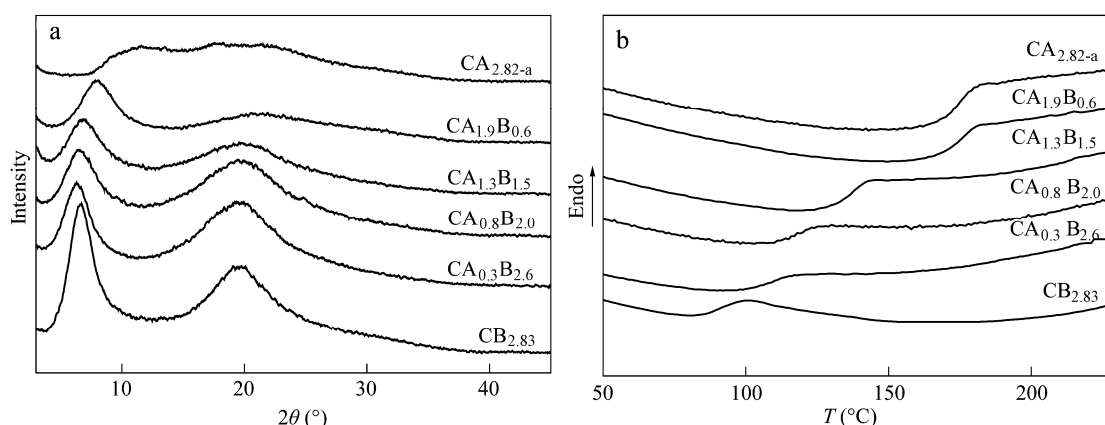


Fig. 5 (a) XRD spectra and (b) DSC curves of CABs and CB_{2.83}.

As a result, in comparison to CB_{2.83}, the P of CABs increases dramatically first and decreases then, while the α decreases slightly first and increases then, as the DS_A increases (Table 3). The CA_{0.3}B_{2.6} gives the highest gas permeability, and the CA_{1.9}B_{0.6} has the best gas permselectivity.

CONCLUSIONS

The relationships between chemical structures and gas permeabilities of cellulose aliphataate esters are investigated by changing the type, degree of substitution (DS) and distribution of substituents in cellulose esters. It has demonstrated that gas permeability of cellulose acetate increases as the DS increasing. At the similar DS value, homogeneously synthesized CA has higher gas permeability and better ideal permselectivity than those of heterogeneously synthesized CA. Compared with the distribution of acetate groups of C3 > C2 > C6 in heterogeneously synthesized CA, acetate distribution C6 > C3 > C2 in homogeneously synthesized CA may be lead to the formation of different packed microstructure of polymer chains, which is more favorable to the improvement of gas permeability. Gas permeability coefficient (P) of cellulose aliphataate esters is significantly enhanced with the increase of aliphataate substituent's chain length. The improvement of diffusion coefficient (D) plays a major role in the enhancement of P . Cellulose mixed esters CAB synthesized by introducing acetate and butyrate simultaneously show tunable gas permeability and permselectivity. By adjusting the DS of the acetate substituent and butyrate substituent, the CAB exhibits higher gas permeability or better permselectivity than individual CA or CB.

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