

DSC Study on Regioselectively Substituted Cellulose Heteroesters

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ABSTRACT: Six kinds of regioselectively substituted cellulose heteroesters (cellulose propanoate diacetate, cellulose butanoate diacetate, cellulose acetate dipropanoate, cellulose butanoate dipropanoate, cellulose acetate dibutanoate, and cellulose propanoate dibutanoate) and three kinds of cellulose triesters (cellulose triacetate, cellulose tripropanoate, and cellulose tributanoate) were prepared from a microcrystalline cellulose, and their melting points were measured by differential scanning calorimetry. Based on the results of strong correlation between the melting point and the length of the acyl groups at the secondary hydroxyl groups at C2 and C3 positions, the latter was identified as playing a decisive role in the thermal properties of the cellulose fatty acid heteroesters. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1511–1515, 1997

Key words: regioselectively substituted cellulose heteroesters; cellulose triesters; melting point

INTRODUCTION

Cellulose is one of the most abundant organic renewable materials on earth, and is widely used in the purified, regenerated, and derivatized states. A number of researchers have extensively studied cellulose fatty acid esters' structures,^{1–4} reactivities,⁵ thermal behaviors,^{6–9} and so on. There are, however, only a few reports on the effects of the length of acyl substituents on their properties.^{6,7,9}

Malm and colleagues⁶ reported the properties of a series of cellulose triesters including melting points (T_m), density, tensile strength, and specific rotation. Especially, regarding the thermal prop-

erty of cellulose triesters, they found that T_m values pass through a minimum at cellulose trioctanoate.⁶ On the other hand, dielectric properties of cellulose triesters from acetate to octadecanoate were investigated by Morooka and associates,⁷ who concluded that all acylates had two types of relaxation processes and that the acylates having side-chain length longer than butanoate have an additional relaxation process. Recently, Glasser and coworkers⁹ reported that nonselectively substituted mixed esters of cellulose acetate with butanoate and hexanoate exhibited T_m reduction in relation to rising size and degree of substitution of the latter two larger acids. Based on these results, it could be concluded that the properties of cellulose triesters are variable by changing the length of substituted ester groups. However, previous studies were focused on the chain length-dependency of the properties of triesters and no invaluable data have been given regarding the effects of positions of esterification on their properties.

During the past few years, we have studied the

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molecular conformation and crystal structure of some regioselectively substituted cellulose heteroesters, with an emphasis not only on the length of the normal chain but also on the positions of the ester groups derived from hydroxyl groups.^{10,11} It was clarified that the types of acyl groups substituted at two secondary hydroxyl groups at C2 and C3 positions play a decisive role in molecular conformation and crystal structure of cellulose triesters, suggesting their effective contribution to the other physicochemical properties.

In the present paper, attempts were made to clarify the relationships between the positions of esterification at two kinds of hydroxyl groups, primary and secondary, and the thermal properties of regioselectively substituted cellulose heteroesters.

EXPERIMENTAL

Sample Preparation

Six kinds of regioselectively substituted cellulose heteroesters, cellulose propanoate diacetate (CPDA, 2,3-di-*O*-acetyl-6-*O*-propanoyl cellulose), cellulose butanoate diacetate (CBDA, 2,3-di-*O*-acetyl-6-*O*-butyryl cellulose), cellulose acetate dipropanoate (CADP, 6-*O*-acetyl-2,3-di-*O*-propanoyl cellulose), cellulose butanoate dipropanoate (CBDP, 6-*O*-butyryl-2,3-di-*O*-propanoyl cellulose), cellulose acetate dibutanoate (CADB, 6-*O*-acetyl-2,3-di-*O*-butyryl cellulose), and cellulose propanoate dibutanoate (CPDB, 2,3-di-*O*-butyryl-6-*O*-propanoyl cellulose), have been prepared from a microcrystalline cellulose (Avicel SF, Asahi Chemical Co., Ltd., Tokyo, $\overline{dp}_v = 133$) following the method described previously¹²: i.e., tritylation at C6 position, acylation at C2 and C3 positions, and detrylation and acylation at C6 position. The structures of these six kinds of cellulose heteroesters are shown in Figure 1.

Three kinds of cellulose triesters, cellulose triacetate (CTA), cellulose tripropanoate (CTP), and cellulose tributanoate (CTB), were prepared by acylating the same microcrystalline cellulose in a mixture of trifluoroacetic anhydride and corresponding normal aliphatic acid.^{7,13,14} The three kinds of cellulose triesters are also shown in Figure 1.

The accuracy of regioselectivity (>94%) and degree of acylations (>98%) were confirmed by ¹H-NMR analysis in deuterated chloroform.^{12,15}

Molecular Weight Measurement

Molecular weights of all cellulose esters were obtained by gel permeation chromatography (GPC) at 40°C, using a Shimadzu 10A GPC system and 6A refractive index detector with joint columns of Shodex K-80M and K-802 (each 4.6 × 300 mm). Chloroform was used as an eluent at the flow rate of 0.8 mL/min, and samples having concentration of 1.0 mg/mL were applied. The number-average and weight-average molecular weights (\overline{M}_n and \overline{M}_w) were calculated by using a Shimadzu Chromatopac C-R7A equipped with a GPC program. Polystyrene standards with a low polydispersity (Shodex Standard SM-105, 1.3 × 10³–3.0 × 10⁶) were used to generate a calibration curve.

DSC and TGA Measurements

Thermal analysis was performed with a Rigaku Thermal Analysis DSC 8230-B differential scanning calorimeter. DSC measurements were carried out under nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 350°C and a cooling rate of 3°C/min vice versa. Thermogravimetric analysis (TGA) was performed by a Shimadzu TGA-50 thermogravimetric analyzer. TGA measurements were performed under vacuum at heating rate of 10°C/min from room temperature to 450°C.

RESULTS AND DISCUSSION

Table I summarizes the given molecular weight data, \overline{M}_n and \overline{M}_w , polydispersity ($\overline{M}_w/\overline{M}_n$) and number-average degree of polymerization (\overline{DP}_n) of six kinds of regioselectively substituted cellulose heteroesters and three kinds of cellulose triesters. TGA showed that all cellulose heteroesters and triesters were carbonized near 360°C. Every sample gave a single melting transition; the observed melting points (T_m) are also listed in Table I.

Regarding T_m of cellulose triesters, our values are closely related to those reported previously by Morooka and colleagues⁷ and Nishino and associates¹⁶; each difference being within 5–10°C. De Oliveira and Glasser⁸ reported that T_m of cellulose propanoate changed from 180 to 250°C depending on molecular weight (segment size), and that highest degree of crystallinity was observed in segments having DP values between 40 and 50.

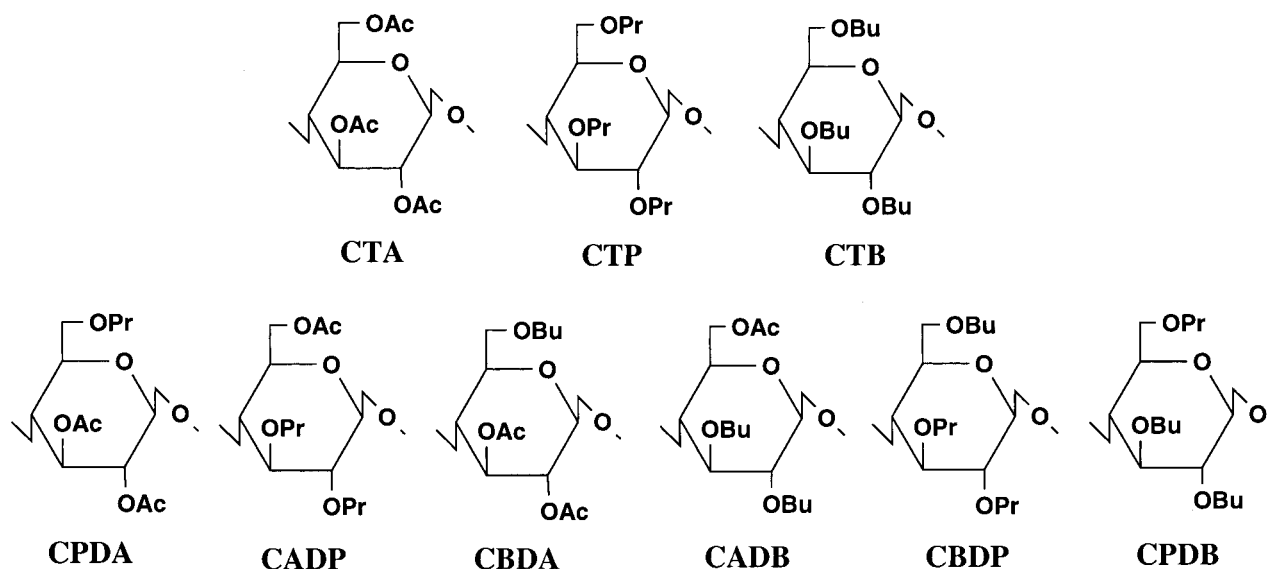


Figure 1 Six kinds of regiosubstituted cellulose heteroesters and three kinds of cellulose triesters.

In our study, low molecular weight dispersity and high crystallinity of the cellulose heteroesters are evidenced by small values of $\overline{M}_w/\overline{M}_n$ (<2.0) and small deviation in \overline{DP}_n (45–70). Therefore, the effect of molecular weight on thermal behaviors of cellulose heteroesters seems negligibly small and the influences of chain length of acyl substituent and position of acylation on thermal properties could be selectively characterized.

Figure 2 shows a map of the T_m values of the six cellulose heteroesters and the three triesters plotted against ester groups substituted at the two secondary hydroxyl groups at C2 and C3 posi-

tions, with different symbols being used to specify the difference in length of ester group at C6 position. The T_m values clearly declined with increasing the size of the acyl groups substituted at the two secondary hydroxyl groups. On the other hand, if T_m values were plotted against ester groups at C6 positions in cellulose heteroesters, the same tendency could not be attained (data not shown).

In addition, all the T_m values had good connectivities with the unhydromonomer molecular weights as shown in Figure 3(A–C). Within the three sets of four different acylates having a series

Table I Characteristics of Cellulose Triesters and Heteroesters

Sample ^a	\overline{M}_n ^b	\overline{M}_w ^c	$\overline{M}_w/\overline{M}_n$	\overline{DP}_n ^d	T_m (°C)
CTA	2.1×10^4	3.7×10^4	1.75	74	272
CTP	2.4×10^4	6.2×10^4	2.52	75	216
CTB	3.1×10^4	8.8×10^4	2.80	84	172
CPDA	1.7×10^4	3.3×10^4	1.96	56	240
CBDA	2.1×10^4	3.5×10^4	1.70	66	250
CADP	1.6×10^4	2.7×10^4	1.72	51	224
CBDP	2.2×10^4	3.2×10^4	1.40	66	213
CADB	1.5×10^4	2.6×10^4	1.64	46	214
CPDB	1.6×10^4	3.1×10^4	1.88	46	193

^a See also Figure 1.

^b Number-average molecular weight.

^c Weight-average molecular weight.

^d Number-average degree of polymerization.

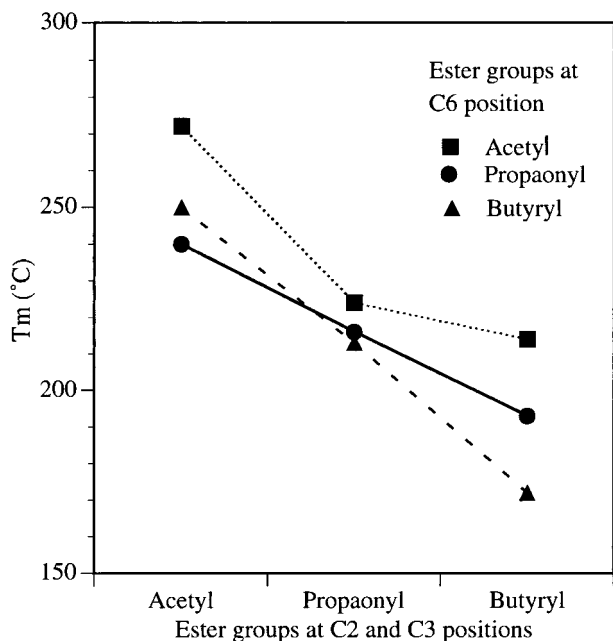


Figure 2 T_m of six kinds of regioselectively substituted cellulose heteroesters and three kinds of cellulose triesters.

of acetyl–propanoyl, propanoyl–butyryl, and acetyl–butyryl groups, the T_m values of the heteroesters having short-size acyl groups at C2 and C3 positions are higher than those having long-size acyl groups at the same positions. For example, in a set of acetyl–propanoyl group [Fig. 3(A)], the T_m value of CTA is closer to CPDA than that of CADP to give a steady decline of T_m values in the order of CTA > CPDA > CADP > CTP. This behavior is expected from the difference in the crystal structure of CPDA¹⁰ and CADP¹¹: CPDA adopted a 2-fold screw symmetry along the molecular axis¹⁰ similar to CTA,² whereas CADP had a 3-fold screw symmetry¹¹ like CTP.⁴ Recently, T_m values of nonselectively substituted cellulose acetate butanoate were reported by Glasser and associates.⁹ Two cellulose acetate butanoates with degrees of butanoate substitution at 0.8 and 1.77 were shown to display two melting transitions at 185 and 227°C, respectively, and a single melting transition at 214°C. Although these cellulose acetate butanoates correspond to the present CBDA and CADB when only the degree of acyl substitution was taken into consideration, both CBDA and CADB gave a single melting transition with much higher T_m values, 250 and 214°C, respectively. Since these discrepancies are attributable to the difference in DP and position of acyl substituents,

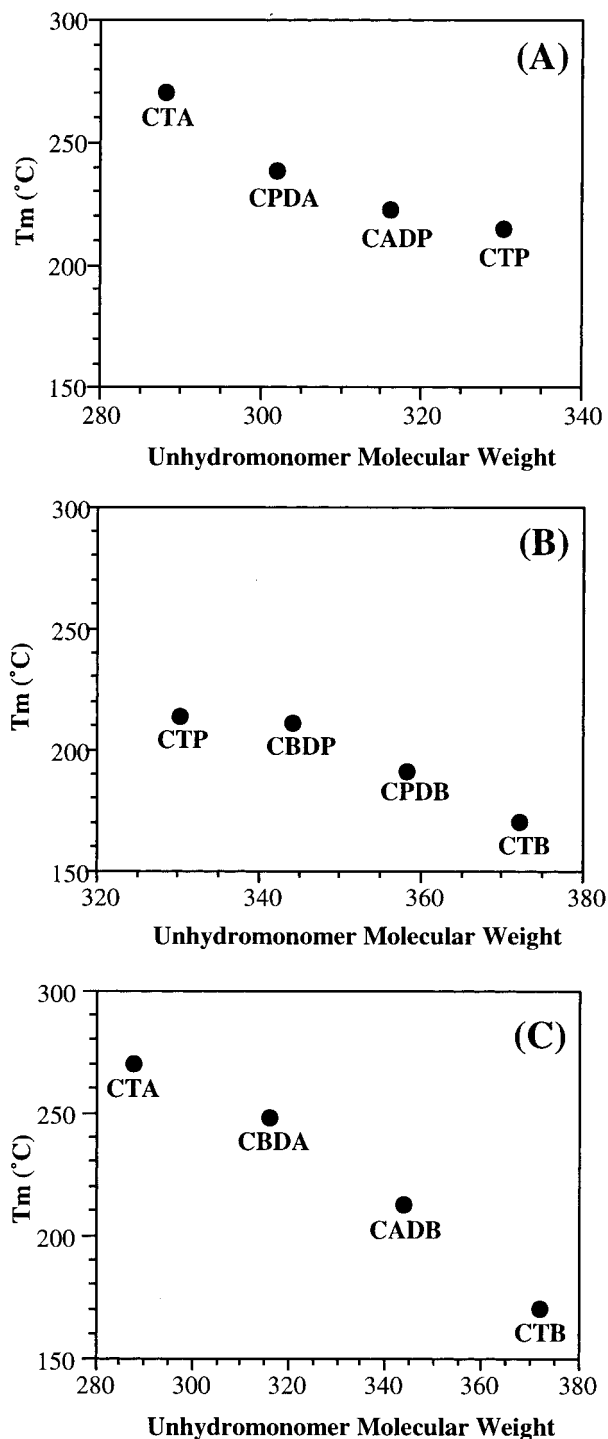


Figure 3 T_m of nine kinds of cellulose esters plotted against unhydromonomer molecular weights as revealed by three sets (A–C) of four different acylates: (A) acetate–propanoate series (CTA = 288, CPDA = 302, CADP = 316, CTP = 330); (B) propanoate–butanoate series (CTP = 330, CBDP = 344, CPDB = 358, CTB = 372); (C) acetate–butanoate series (CTA = 288, CBDA = 316, CADB = 344, CTB = 372).

the present results suggest the importance of uniformity of DP and regioselectivity of acylation for precise investigation of the effects of acyl substituents on thermal properties of cellulose. The present good connectivity of the T_m values with the unhydromonomer molecular weights and declining of the T_m values with increase in size of acylates at the secondary hydroxyl groups revealed that the length of acyl substituents at the two secondary hydroxyl groups at C2 and C3 positions has a dominating effect on thermal events of cellulose acylates. Based on our previous X-ray and electron diffraction analysis of CPDA,¹⁰ CADP,¹¹ and CBDA,^{17,18} we have concluded that the ester groups derived from two secondary hydroxyl groups at C2 and C3 positions play a decisive role in the molecular conformation and crystal structure of cellulose triesters. The present study further indicates the extensibility of our conclusion to the thermal behavior of cellulose heteroesters and triesters.

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REFERENCES

1. A. J. Stipanovic and A. Sarko, *Polymer*, **19**, 3 (1978).
2. E. Roche, H. Chanzy, M. Boudeulle, R. H. Marchessault, and P. Sandararajan, *Macromolecules*, **11**, 86 (1978).
3. H. Steinmeier and P. Zugenmaier, *Carbohydr. Res.*, **164**, 97 (1987).
4. Y. Shuto, K. Okamura, J. Azuma, F. Tanaka, and H. Chanzy, in *Cellulose: Structural and Functional Aspects*, J. F. Kennedy, G. O. Phillips, and P. A. Williams, Eds., Ellis Horwood Publishers, Chichester, England, 1989, pp. 283–288.
5. C. J. Malm, J. W. Mench, D. L. Kendall, and G. D. Hiatt, *Ind. Eng. Chem.*, **43**, 684 (1951).
6. C. J. Malm, J. W. Mench, D. L. Kendall, and G. D. Hiatt, *Ind. Eng. Chem.*, **43**, 688 (1951).
7. T. Morooka, M. Norimoto, T. Yamada, and N. Shiraishi, *J. Appl. Polym. Sci.*, **29**, 3981 (1984).
8. W. De Oliveira and W. G. Glasser, *Cellulose*, **1**, 77 (1994).
9. W. G. Glasser, G. Samaranyake, M. Dumay, and V. Davé, *J. Polym. Sci., Polym. Phys. Ed.*, **33**, 2045 (1995).
10. T. Iwata, K. Okamura, J. Azuma, and F. Tanaka, *Cellulose*, **3**, 91 (1996).
11. T. Iwata, K. Okamura, J. Azuma, and F. Tanaka, *Cellulose*, **3**, 107 (1996).
12. T. Iwata, J. Azuma, K. Okamura, M. Muramoto, and B. Chun, *Carbohydr. Res.*, **224**, 277 (1992).
13. E. J. Bourne, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).
14. E. J. Bourne, J. E. B. Randles, J. C. Tatlow, and J. M. Tedder, *Nature*, **168**, 942 (1951).
15. Y. Shuto, M. Murayama, J. Azuma, and K. Okamura, *Bull. Inst. Chem. Res., Kyoto Univ.*, **66**, 128 (1988).
16. T. Nishino, K. Takano, K. Nakamae, K. Saitaka, S. Itakura, J. Azuma, and K. Okamura, *J. Polym. Sci., Polym. Phys. Ed.*, **33**, 611 (1995).
17. T. Iwata, K. Okamura, J. Azuma, H. Chanzy, and F. Tanaka, *Cellulose*, **1**, 67 (1994).
18. T. Iwata, A. Fukushima, K. Okamura, and J. Azuma, *Mokuzai Gakkai-shi*, **42**, 289 (1996).