STRUCTURE-PROPERTY RELATIONSHIPS OF NOVEL CELLULOSE
ESTERS

by

Jason G. Todd

Thesis submitted to the faculty of Virginia Polytechnic Institute and State University in
partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved:

Wolfgang G. Glasser, Chair

Charles E. Frazier

Eva Marand
LD
5655
V855
1994
T633
c.2
STRUCTURE-PROPERTY RELATIONSHIPS OF NOVEL CELLULOSE ESTERS

by

Jason G. Todd

Wolfgang G. Glasser, Chairman

Department of Wood Science and Forest Products
Virginia Tech, Blacksburg, Virginia

(ABSTRACT)
Cellulose "waxy" (long-chain aliphatic) tri-esters of lauric (C_{12}), myristic (C_{14}), stearic (C_{18}), and eicosanoic (C_{20}) acids; mixed esters of lauric and acetic acids; and fluorinated mixed esters of 2,2,2-trifluoroethoxyacetic (TFEA) and acetic acids were synthesized in homogeneous DMAc/LiCl solution. Degree of substitution (DS) was conveniently controlled via stoichiometry, and fully-substituted cellulose derivatives were produced with little depolymerization. Thermal analysis of the C_{12} - C_{14} waxy tri-esters revealed separate melting transitions (T_{m,L} and T_{m,H}) for ester substituents and main cellulose chains, providing evidence for the existence of a separate (crystalline) phase formed by the ester substituents. Main-chain T_{m,s} of waxy esters converged with the melting transition of the side-chain phase and/or disappeared as substituent length reached C_{18}. The effectiveness of melting point depression at low DS of large substituents increased with increasing substituent length for n-alkyl substituents up to lauryl (C_{12}); at mid-DS of large substituent, increasing the substituent length had no further effect in melting point depression above a length of C_{6} (hexanoyl). The preferential sorption of ethanol from aqueous solution by cellulose (CE) and cellulose acetate trifluoroethoxyacetate (CATA) of varying DS was measured by liquid chromatography (LC); the preferential sorption of ethanol did not change when acetate substituents were replaced by trifluoroethoxyacetate substituents. The preferential sorption of ethanol by unmodified cellulose was stronger than the preferential sorption by cellulose acetate and trifluoroethoxyacetate esters.
ACKNOWLEDGMENT

The following individuals have contributed greatly to my success in this endeavor, and their contributions are acknowledged with gratitude: Jim Sealey, for getting me into this (mess), and for his contributions in synthesis and thermal analysis of cellulose esters; Bob Wright for many exciting, interesting, and educational pilot plant experiences; Dr. Chip Frazier for helpful advice and discussions; Jody Jervis for her diligent and timely analysis of samples, willingness to help whenever possible, and consistent enthusiasm; to Drs. Geza Ifju and Wolfgang Glasser for financial support, and for creating a good environment for graduate study in the Department; and to Dr. Glasser (my advisor) for much advice, ideas, and help throughout my career. Special thanks go to Gamini Samaranayake for his constant, patient help and teaching of chemistry and laboratory technique. Thank you very much to my family, and especially my mother, for the support, financial and otherwise, which made this possible. Thank you, too, to anyone I forgot to mention here.
# Table of Contents

1. Introduction ....................................................................................................................... 1
   1.1. Overview and Justification ......................................................................................... 1
   1.2. Conventional Cellulose Esters .................................................................................. 3
       1.2.1. Conventional Synthesis and Production .......................................................... 3
       1.2.2. Applications ......................................................................................................... 6
       1.2.3. Properties ............................................................................................................. 6
   1.3. Novel Cellulose Esters .............................................................................................. 9
       1.3.1. Homogeneous-Phase Esterification ................................................................... 9
       1.3.2. Waxy Ester Substituents .................................................................................. 11
       1.3.3. Fluorinated Ester Substituents .......................................................................... 12
   1.4. Cellulose Esters in Membrane Separation Processes ................................................. 12
       1.4.1. Theory and Types of Membrane Separations .................................................... 12
       1.4.2. Criteria for Selection of Membrane Materials .................................................. 16
   1.5. References ................................................................................................................ 18

2. Research Objectives .......................................................................................................... 20

3. Thermal Analysis of Waxy Esters of Cellulose ................................................................. 21
   3.1. Introduction ................................................................................................................ 22
   3.2. Experimental ............................................................................................................. 24
       3.2.1. General ............................................................................................................... 24
       3.2.2. Materials ............................................................................................................ 24
       3.2.3. Methods .............................................................................................................. 24
           3.2.3.1. Esterification Reaction .............................................................................. 25
           3.2.3.2. DSC .......................................................................................................... 25
           3.2.3.3. DMTA ...................................................................................................... 26
   3.3. Results and Discussion .............................................................................................. 26
       3.3.1. Synthesis ............................................................................................................ 26
       3.3.2. Thermal Analysis .............................................................................................. 29
       3.3.3. Melt Processability ............................................................................................ 38
   3.4. Conclusions ............................................................................................................... 38
   3.5. Acknowledgment ....................................................................................................... 40
   3.6. References ................................................................................................................ 40

4. Thermal Analysis of Mixed Esters with Lauric Acid ......................................................... 42
   4.1. Introduction ................................................................................................................ 42
   4.2. Experimental ............................................................................................................. 43
       4.2.1. Materials ............................................................................................................ 43
       4.2.2. Methods ............................................................................................................. 43
4.3. RESULTS AND DISCUSSION ................................................. 44
   4.3.1. Reactivity and Structure ......................................... 44
   4.3.2. Thermal Analysis ................................................. 46
     4.3.2.1. Cellulose Laurates (CL) .................................. 46
     4.3.2.2. Cellulose Acetate-Laurates (CAL) .......................... 53
4.4. CONCLUSIONS .............................................................. 60
4.5. ACKNOWLEDGMENT ........................................................ 61
4.6. REFERENCES ............................................................... 61

5. LC EXPERIMENTS WITH FLUORINATED CELLULOSE ESTERS ................. 63
   5.1. INTRODUCTION .......................................................... 63
   5.2. EXPERIMENTAL ......................................................... 70
     5.2.1. Materials .......................................................... 70
     5.2.2. Methods ........................................................... 70
   5.3. RESULTS AND DISCUSSION .......................................... 72
   5.4. CONCLUSIONS .......................................................... 79
   5.5. ACKNOWLEDGMENT .................................................... 79
   5.6. REFERENCES ........................................................... 79

6. OVERALL CONCLUSIONS ..................................................... 81

7. VITA ........................................................................... 83
LIST OF FIGURES

Figure 1.1. Molecular structure of cellulose, cellulose esters ................................................. 2
Figure 1.2 US Production of cellulose esters, 1972-1983: ..................................................... 4
Figure 1.3 Products and processing methods of cellulose organic esters ................................. 5
Figure 1.4 Melting Points of Commercial Cellulose Acetates and Acetate Butyrates ............. 8
Figure 1.5 Melting temperature versus aliphatic ester substituent length, cellulose triesters ................................................................. 10
Figure 1.6 Size range of permeating species in membrane processes .................................... 13
Figure 1.7 Mode of transport and mechanism of permselectivity as determined by membrane morphology ........................................................................ 14
Figure 3.1 Relationship between the melting points of cellulose triesters and acyl substituent size ........................................................................................................ 23
Figure 3.2 DSC thermograms for cellulose esters annealed at 140°C for 2-3 h......................... 28
Figure 3.3 DSC cooling curves of cellulose esters ................................................................. 30
Figure 3.4 Tm,l and Tm,h of cellulose esters, and Tm of corresponding methyl esters, as a function of ester substituent size for per-acetylated waxy esters of cellulose .................. 31
Figure 3.5 DSC scans showing annealing effect on Tm,l for C20 cellulose ester ..................... 32
Figure 3.6 DMTA scans of C12, C14, C18, and C20 esters ....................................................... 34
Figure 3.7 Relationship between substituent transitions Tg,L, Tm,L, Tc,L and no. of carbons in acyl substituent. Data from DSC and DMTA ....................................................... 35
Figure 3.8 DSC scans of the per-acetylated C14 cellulose mixed ester, DSmyr = 2.8 ............ 37
Figure 3.9 Dimensionally-accurate molecular model of cellulose eicosanoate (C20, DS 3.0) ........................................................................................................................................ 39
Figure 4.1 1H NMR spectrum of cellulose laurate of DS 2.9 .................................................. 45
Figure 4.2 DSC thermograms of cellulose laurates of DS 2.0 and 2.9 .................................... 48
Figure 4.3 Thermal transitions of cellulose laurate (CL) as measured by DSC, DMTA, and TMA ......................................................................................................................... 49
Figure 4.4 TMA thermogram of cellulose laurate of DS 1.3 ................. 51
Figure 4.5 DMTA thermograms of cellulose laurates of DS 1.3 and 2.0 ........ 52
Figure 4.6 Typical DSC thermograms of cellulose acetate laurate (CAL) of DS_{lu} 2.0 .... 55
Figure 4.7 Thermal transitions of cellulose acetate laurate (CAL) as measured by DSC, DMTA, and TMA .......................................................... 56
Figure 4.8 Comparison of melting points (T_m) of cellulose laurates (CL) and cellulose acetate laurates (CAL) ................................................................. 58
Figure 4.9 Comparison of T_m and Δ(T_m - T_g) data for CAB, CAH, and CAL ........ 59
Figure 5.1 Retention volume data for cellulose (CE); cellulose triacetate (CTA); and cellulose acetate trifluoroethoxyacetate (CATA) of DS_{F} 0.6 and 2.8 ........ 74
Figure 5.2 Surface excess volume of ethanol as a function of ethanol solution concentration for CE, CTA, DS_{F} - 0.6 CATA, DS_{F} - 2.8 CATA ......................... 75
Figure 5.3 LC system pressure drop versus solution ethanol concentration for empty column, CE, CTA, DS_{F} - 0.6 CATA, DS_{F} - 2.8 CATA .................................. 78
LIST OF TABLES

Table 1.1 Properties of Commercial Cellulose Ester Plastics .............................................. 7
Table 1.2 Solvents for Cellulose Acetate .................................................................................. 7
Table 1.3 Commercial Polymer Membranes .............................................................................. 17
Table 3.1 Thermal and Molecular Weight Data for Unacetylated Cellulose Esters .......... 27
Table 3.2 Thermal Data for Per-Acetylated Cellulose Esters .................................................. 36
Table 4.1 Degree of Substitution (DS) of Cellulose Laurate (CL) and Cellulose Acetate Laurate (CAL) Esters ........................................................................................................ 44
Table 4.2 Thermal Transitions of CL Esters .............................................................................. 47
Table 4.3 Thermal Transitions of CAL Esters .......................................................................... 54
Table 5.1 Summary of Published Ethanol/Water Pervaporation Results ......................... 66
Table 5.2 Structure of Cellulose Acetate Trifluoroethoxyacetates .......................................... 72
1. INTRODUCTION

1.1. Overview and Justification

The subject of this thesis, in its broadest scope, is the measurement and control of material properties of novel cellulose ester derivatives. A material property is defined as the factor that relates the response of a material to an applied field. Thus, knowledge of material properties allows us to predict how a material will behave in a particular application. Material properties are always defined, studied, and measured in the context of some intended application(s). The control of properties is sought so that one can optimize a material for a particular application.

In this case, the materials studied are cellulose esters generated using novel, homogeneous-phase synthesis. Cellulose esters are a commercially-important class of naturally-based, thermoplastic polymers. The thesis considers two separate topics: 1) thermal analysis of long-chain aliphatic ('fatty' or 'waxy') esters of cellulose, and 2) measurement of the preferential sorption of ethanol by cellulose acetate-trifluoroethoxyacetate esters. The first topic, thermal analysis, studies the effect of ester substituent length on the melting point (T_m) and glass transition (T_g) temperatures of the waxy cellulose esters; these properties are important for a very broad range of applications, including extruded and injection-molded parts, fiber spinning from the melt, and film drawing from the melt. T_g and T_m also define the temperature range over which a polymer may be used in a structural application. The second topic, preferential sorption, is more specific. It deals with the problem of how to increase the selectivity towards ethanol of a cellulose ester pervaporation membrane. Separation membranes are seen as promising high-value applications for cellulose esters prepared in homogeneous solution; high value is important because of the expected high cost of producing cellulose esters in this manner. (High cost is expected because a large amount of N,N-dimethylacetamide solvent is used).
Native Cellulose

Cellulose Ester

Anhydroglucose Repeat Unit
n = Degree of Polymerization (DP)

Hydroxyl (Unsubstituted)
\[ R = \text{--H} \]

Aliphatic Ester
\[ R = \text{--C} \left( \text{CH}_2 \right)_x \text{CH}_3 \]
\[ x = \]
0  Acetate (C$_2$)
1  Propionate (C$_3$)
2  Butyrate (C$_4$)
4  Hexanoate (C$_6$)
10  Laurate (C$_{12}$)
12  Myristate (C$_{14}$)
16  Stearate (C$_{18}$)
18  Eicosanoate (C$_{20}$)

2,2,2 - Trifluoroethoxyacetate Ester
\[ R = \text{--C} \text{CH}_2 \text{O} \text{CH}_2 \text{CF}_3 \]

Figure 1.1. Molecular structure of cellulose, cellulose esters, and possible ester substituents
A cellulose ester molecular structure, along with the substituents discussed in this work, is shown in Figure 1.1. An important parameter for describing cellulose derivatives is the degree of substitution (DS). Cellulose in its native state (ignoring stereochemistry) consists of anhydroglucose repeat unit with three hydroxyl groups. DS is defined as the number of hydroxyl groups substituted per anhydroglucose, averaged over all anhydroglucose units. DS ranges from 0 (unsubstituted) to 3 (fully substituted).

It is necessary to first discuss some of the possible applications of cellulose esters in order to understand what properties are important and why we want to control them.

1.2. Conventional Cellulose Esters

1.2.1. Conventional Synthesis and Production

Commercial cellulose ester production is dominated by cellulose acetate (Figure 1.2). Lesser amounts of cellulose acetate butyrate and acetate propionate make up the remainder of organic ester production. Almost all cellulose acetate is produced via a heterogeneous-phase reaction with acetic anhydride, using sulfuric acid as a catalyst in a glacial acetic acid solvent. In a typical process, cellulose (usually obtained as bleached Kraft pulp) is fed to a large batch reactor after being pretreated to improve accessibility by means such as mechanical fluffing and presoaking in acetic acid. Sulfonation as well as acetylation occurs in the reaction. The sulfuric acid-acetic anhydride reagent reacts with the more accessible amorphous regions of cellulose first, and acetylated cellulose dissolves in the acetic acid-acetic anhydride solvent as the reaction progresses. Transesterification reduces sulfate content and increases acetyl content; a small amount of water (0.5%) in the reaction mixture is found to aid desulfation. Cellulose acetate produced by this method is almost completely substituted (DS = 2.8 out of a maximum of 3); it is referred to as cellulose triacetate or primary cellulose acetate. Partial hydrolysis of ester groups is employed to yield cellulose diacetate (secondary acetate, DS = 2.4). Cellulose acetate butyrate (CAB) and acetate propionate (CAP) mixed esters are produced via the same process, substituting butyric or propionic anhydride for some of the acetic anhydride. The
Figure 1.2 US Production of cellulose esters, 1972-1983: (A), total cellulose esters production; (B), cellulose acetate flake; (C), other cellulose esters, i.e. cellulose nitrate, cellulose acetate butyrate, and cellulose acetate propionate. Source: Ref. 1.
Figure 1.3 Products and processing methods of cellulose organic esters. Source: Ref.1, p. 132
ratio of acetate to other ester substituents is controlled by varying the ratio of acetic to other anhydrides in the reaction mixture.\textsuperscript{1,4}

1.2.2. Applications

Cellulose esters are thermoplastic and exhibit useful solubility properties in organic solvents, so they find a wide range of commercial application in product categories such as plastics, fibers, and films.\textsuperscript{1} Cellulose acetate fiber production is primarily accomplished by spinning from acetone solutions of secondary acetate. The most important commercial use of cellulose acetate fiber is in cigarette filter tow, with 339,000 metric tons produced in 1982. Cellulose acetate is the second-oldest synthetic textile fiber and is still important, with 260,000 metric tons produced worldwide in 1982.\textsuperscript{1} A wide range of plastic products are manufactured from cellulose esters by extrusion and solvent casting (Figure 1.3).

A focal point of this work is the application of cellulose esters in separation membranes. The first commercially-viable reverse osmosis membranes were made from cellulose acetate, and cellulose acetates and other esters continue to be used in large volume as reliable materials for microfiltration, ultrafiltration, reverse osmosis, gas separation, and dialysis membranes.

1.2.3. Properties

The properties of cellulose esters which are most important for fiber, film, and plastics applications include thermal properties such as melting point, glass transition, and flow temperature; solubility in organic solvents; and moisture absorption (Table 1.1). Since the properties of a material determine its suitability for a particular end use, it is desirable to be able to control these properties in order to find the best possible material for the job.
Table 1.1 Properties of Commercial Cellulose Ester Plastics


<table>
<thead>
<tr>
<th>Property</th>
<th>Cellulose Acetate</th>
<th>Cellulose Acetate Butyrate</th>
<th>Cellulose Acetate Propionate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow temperature (°C)</td>
<td>130-180</td>
<td>130-175</td>
<td>155-190</td>
</tr>
<tr>
<td>Molding qualities</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Compression molding temp. (°C)</td>
<td>171-188</td>
<td>121-182</td>
<td>138-193</td>
</tr>
<tr>
<td>Injection molding temp. (°C)</td>
<td>188-227</td>
<td>154-210</td>
<td>182-221</td>
</tr>
<tr>
<td>Refractive index at 25°C</td>
<td>1.46-1.50</td>
<td>1.46-1.49</td>
<td>1.46-1.48</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.27-1.34</td>
<td>1.15-1.22</td>
<td>1.19-1.23</td>
</tr>
<tr>
<td>Water absorption, 24 h, %</td>
<td>2.0-6.5</td>
<td>1.0-4.0</td>
<td>1.0-3.0</td>
</tr>
</tbody>
</table>

Table 1.2 Solvents for Cellulose Acetate

*Source*: Ref. 10, p.368.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CA Solubility Range (DS&lt;sub&gt;Acetyl&lt;/sub&gt;)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>2.3-2.7</td>
</tr>
<tr>
<td>Dioxane</td>
<td>&lt;1.9-2.7</td>
</tr>
<tr>
<td>Pyridine</td>
<td>&lt;1.9-2.7</td>
</tr>
<tr>
<td>Dimethyl Formamide</td>
<td>&lt;1.9-2.7</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>2.5-2.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> Cellulose Acetate (Secondary Acetate) DS = 2.4;
Cellulose Triacetate (Primary Acetate) DS = 2.8
Figure 1.4 Melting Points of Commercial Cellulose Acetates and Acetate Butyrates. (□) CAB, (■) CTA (DS 2.8), (O) CA (DS 2.4). Source: Ref. 10. p.368.
Cellulose acetate and cellulose triacetate are often seen as two separate polymers because their properties are so different. Cellulose triacetate is highly crystalline in comparison to secondary acetate; this leads to decreased solubility\textsuperscript{4,10} (Table 1.2) and increased melting point\textsuperscript{10} (Figure 1.4) for cellulose triacetate. Increased crystallinity is attributed to a higher degree of regularity for triacetate.\textsuperscript{4,10} The melting temperature of acetate-butyrate mixed esters can be controlled by varying the ratio of acetyl to butyryl substituents; $T_m$ declines with increasing butyryl content (Figure 1.4). Other properties such as moisture sorption and solution properties may be controlled in the same manner. For example: Cellulose esters are capable of forming anisotropic (liquid-crystalline) solutions in organic solvents; in one study, the critical solution concentration at which an anisotropic phase formed was seen to decrease with increasing butyryl content for CAB solutions in DMAc.\textsuperscript{11}

Material properties important for separation membrane applications may be broken down into two categories: those properties responsible for the separating ability of the membrane, and those properties related to the stability of the membrane in its use environment.\textsuperscript{10} The stability-related properties include oxidation resistance, hydrolysis resistance, fouling resistance, thermal stability, structural stability, and anything else that may degrade performance over time. The stability properties are secondary in consideration to the separating-ability properties. The properties that determine separating ability will be discussed in detail in the section on membranes.

1.3. Novel Cellulose Esters

1.3.1. Homogeneous-Phase Esterification

Partial esterification of cellulose in heterogeneous phase leads to derivatives with an uneven distribution of substituents along the cellulose backbone. Amorphous regions of cellulose are reacted before crystalline regions, so if the reaction is stopped before complete esterification is achieved, a "blocky" derivative will result, with highly-substituted (amorphous) and unsubstituted (crystalline) regions present.\textsuperscript{14} This is why
Figure 1.5 Melting temperature versus aliphatic ester substituent length, cellulose triesters.

Source: Adopted from data of Malm et al. (Ref. 16), and Morooka et al. (Ref. 17)
cellulose acetates of less-than-fully-substituted DS are conventionally produced by hydrolysis of triacetate ester.

Esterification in homogeneous solution allows the synthesis of cellulose esters of low DS with uniform distribution of ester substituents along the cellulose chain, since all regions of the polymer are accessible in solution.\textsuperscript{12,13} Reaction in solution also allows modification via reagents that are not practical in heterogeneous reactions due to problems such as solubility, low reactivity, or tendency to degrade cellulose.\textsuperscript{4,14}

The solvent system used in this work is N,N-dimethylacetamide (DMAc)/LiCl.\textsuperscript{13} Acylation is accomplished via a novel p-toluenesulfony chloride/free acid reagent system.\textsuperscript{15} These methods are discussed in further detail in the Experimental sections of this paper.

1.3.2. Waxy Ester Substituents

As seen with commercially-produced CAB esters, incorporation of ester substituents of longer chain length lowers the T\textsubscript{m} of the material. Although not commercially-produced, cellulose triesters with substituent chain lengths longer than butyryl have been synthesized in the laboratory. Data on melting transitions of these derivatives are available in the literature.\textsuperscript{16,17} The T\textsubscript{m} is seen to decline sharply with increasing substituent length up to a length of about six carbon atoms (C\textsubscript{6}, hexanoyl); at this point, the T\textsubscript{m} levels off and begins to rise slightly with increasing substituent length (Figure 1.5). Thus it is possible to control T\textsubscript{m} over a wide range (90-290°C) by choice of ester substituent.

This study attempts to answer the following questions: Why does the T\textsubscript{m} of cellulose triesters reach a minimum at C\textsubscript{6} and then begin to increase with increasing ester substituent length? What happens to other transitions such as T\textsubscript{g} as substituent length increases? What happens to the thermal transitions as DS of the large substituent decreases?

Long-chain (C\textsubscript{12+}) aliphatic substituents are similar in structure to paraffin wax; therefore, they are deemed “waxy” esters. Cellulose waxy esters of C\textsubscript{12}, C\textsubscript{14}, C\textsubscript{18}, and C\textsubscript{20} can be synthesized in homogeneous solution, and DS can be controlled stoichiometrically.
1.3.3. Fluorinated Ester Substituents

Perfluoroalkyl alcohols can be reacted with chloroacetic acid to form perfluoroalkoxyacetic acids, which can then react with cellulose in homogeneous solution to yield fluorinated cellulose esters. Fluorine content of the cellulose ester can be varied by varying the length of the perfluoroalkyl chain or by varying DS of fluorinated substituents. Fluoroalkane polymers (e.g. polytetrafluoroethylene) are well known for their hydrophobic nature. Addition of fluorinated substituents to cellulose is expected to increase the hydrophobicity of cellulose.\textsuperscript{18} The synthesis of cellulose 2,2,2-trifluoroethoxyacetate and the effect of fluorinated substitution on thermal properties is the subject of a separate publication.\textsuperscript{19}

1.4. Cellulose Esters in Membrane Separation Processes

1.4.1. Theory and Types of Membrane Separations

Membrane separation processes employ a selectively-permeable barrier to achieve separation of two or more feed components. Membrane processes are classified primarily by the sizes of the species to be separated, which range in size from macroscopic particles and colloids all the way down to gas molecules (Figure 1.6). Membrane structure (morphology) is another important classification. Membrane structure may be either porous or nonporous; the membrane structure in combination with molecular sizes of separated species determines the mode of transport and the basis of selectivity (Figure 1.7).

There are four basic modes of transport in membrane processes: viscous flow, Knudsen diffusion, ultramicroporous molecular sieving, and solution/diffusion.\textsuperscript{23} For porous membranes with large (> 1 μm) pore size (i.e. simple filtration), transport is by viscous flow, and separation is achieved when particles which are too large to fit in the pores are retained. Knudsen diffusion occurs in porous membranes with pore sizes too small to accommodate viscous flow (i.e. ultrafiltration), and separation is based on differences in diffusion rates of solutes (typically macromolecules). For Knudsen diffusion
Figure 1.6  Size range of permeating species in membrane processes. Source: Ref.20.
Figure 1.7  Mode of transport and mechanism of permselectivity as determined by membrane morphology. Source: Ref. 20.
separation of two solute species "A" and "B", selectivity can be related to the inverse square root ratio of the molecular weights of A and B.\textsuperscript{23} Ultramicroporous molecular sieving involves membranes with very small pore sizes on the order of molecular dimensions (ca. 1 nm), and separation of a liquid feed (i.e. reverse osmosis, pervaporation). Transport is by diffusion of molecules in the pores, and selectivity favors the smallest molecules, which have the highest diffusion rates. For the case of separation of solutes of similar size, differences in sorption of solutes by the membrane may govern separation. Finally, separation of gas mixtures by nonporous membranes is described by the solution/diffusion mechanism, in which transport is by diffusion and selectivity is determined by differences in solubility and diffusivity of permeants. Diffusivity selectivity favors the smallest molecule, while solubility selectivity favors the most condensable component.\textsuperscript{23}

The performance of a process is defined in terms of flux and selectivity. Flux is defined as the amount of material per unit area per unit time that moves from one side of the membrane to the other. The driving force for flux is a chemical potential gradient across the membrane. There is a resistance to transport across the membrane; it is a difference in resistances between different components that is responsible for selectivity.\textsuperscript{21} In the case of dense (nonporous) membranes, transport is by diffusion; the basic transport equation for this process is Fick's Law, which relates flux $J_i$ of component $i$ to driving force and resistance:

$$J_i = P_i \frac{\Delta \mu_i}{l} \quad (1)$$

where $\Delta \mu_i$ is the difference in chemical potential of component $i$ from one side of the membrane to the other, $l$ is the thickness of the membrane, and $P_i$ is the permeability of component $i$ in the membrane. (The permeability is the reciprocal of the resistivity). Selectivity is defined in terms of a separation factor $\alpha$:

$$\alpha_A = \frac{y_A / y_B}{x_A / x_B} \quad (2)$$
where \( y_A, y_B \) are concentrations of components \( A \) and \( B \) in the permeate, and \( x_A \) and \( x_B \) are concentrations of components \( A \) and \( B \) in the feed. Permeability, a material property which is a function of both the permeating species and the polymeric membrane, is the most important property in membrane separation since differences in permeabilities of individual components determine the selectivity of the membrane. The permeability of a component (in nonporous membranes) is determined by a product of two factors: the diffusivity of the component in the membrane, and the solubility of the component in the membrane.\(^{21}\) Diffusivity of components differs primarily on the basis of molecular size, while solubility depends on solute-solute interactions and solute-membrane interactions.\(^{21,22}\)

Pervaporation is a process employing a dense or ultramicroporous membrane in which a liquid feed in contact with the membrane is vaporized as it passes through the membrane. The pervaporation process can be described by the same solution/diffusion mechanism as the gas diffusion process, with one important difference: in gas diffusion, solubility is determined by the condensability of the solute, which is a function of the strength of interactions between individual solute molecules or atoms (interactions between solute gas molecules and membrane polymer are small), whereas, in pervaporation, solubility may be strongly influenced by polymer-solute and solute-solute interactions.\(^{22}\) Therefore, the chemical nature (composition) of the membrane polymer becomes important in determining selectivity in membrane processes in which the membrane is in contact with a liquid phase, such as pervaporation or reverse osmosis.

### 1.4.2. Criteria for Selection of Membrane Materials

A successful membrane polymer must meet the following general requirements:

1. It must possess an appropriate chemical nature so that interactions between polymer and solutes enhance selectivity (in cases where polymer-solute interactions are important, i.e. separation of liquid feeds, as in pervaporation and reverse osmosis).\(^{10,21,22}\)
<table>
<thead>
<tr>
<th>Material</th>
<th>Abbrev</th>
<th>Processes(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose acetate</td>
<td>CA</td>
<td>MF, UF, RO, D, G</td>
</tr>
<tr>
<td>cellulose triacetate</td>
<td>CTA</td>
<td>MF, UF, RO, G</td>
</tr>
<tr>
<td>CA–triacetate blend</td>
<td></td>
<td>RO, D, G</td>
</tr>
<tr>
<td>cellulose esters, mixed</td>
<td></td>
<td>MF, D</td>
</tr>
<tr>
<td>cellulose nitrate</td>
<td>MF</td>
<td></td>
</tr>
<tr>
<td>cellulose, regenerated</td>
<td>MF</td>
<td></td>
</tr>
<tr>
<td>gelatin</td>
<td>MF</td>
<td></td>
</tr>
<tr>
<td>polyamide, aromatic</td>
<td>MF, UF</td>
<td></td>
</tr>
<tr>
<td>polyamide</td>
<td>MF</td>
<td></td>
</tr>
<tr>
<td>polybenzimidazole</td>
<td>PBI</td>
<td>RO</td>
</tr>
<tr>
<td>polybenzimidazolone</td>
<td>PBIL</td>
<td>RO</td>
</tr>
<tr>
<td>polyacrylonitrile</td>
<td>PAN</td>
<td>UF, D</td>
</tr>
<tr>
<td>PAN–poly(vinyl chloride) copolymer</td>
<td>PAN-PVC</td>
<td>MF, UF</td>
</tr>
<tr>
<td>PAN–methallyl sulfonate copolymer</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>polysulfone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(dimethylphenylene oxide)</td>
<td>PVO</td>
<td>UF, G</td>
</tr>
<tr>
<td>polycarbonate(^b)</td>
<td>MF</td>
<td></td>
</tr>
<tr>
<td>polyester(^c)</td>
<td>MF</td>
<td></td>
</tr>
<tr>
<td>polytetrafluoroethylene</td>
<td>PTFE</td>
<td>MF</td>
</tr>
<tr>
<td>poly(vinylidene fluoride)</td>
<td>PVF(_2)</td>
<td>UF, MF</td>
</tr>
<tr>
<td>polypropylene</td>
<td>PP</td>
<td>MF</td>
</tr>
<tr>
<td>polyelectrolyte complexes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(methyl methacrylate)(^d)</td>
<td>PMMA</td>
<td>UF, D</td>
</tr>
<tr>
<td>polydimethylsiloxane</td>
<td>PDMS</td>
<td>G</td>
</tr>
</tbody>
</table>

\(^a\) MF = microfiltration, UF = ultrafiltration, RO = reverse osmosis, D = dialysis, and G = gas separation.

\(^b\) Tack-etched.

\(^c\) Stereotropic complexes.

1. It must be capable of forming membranes with appropriate structure for the separation in mind. This requires either solubility in organic solvents or melt processability. The goal is to create a high-flux membrane while maintaining high selectivity.\(^{10,21}\)

2. It must withstand deterioration or change in structure under the normal operating conditions of the separation process.\(^{10}\)
Cellulose acetates have been widely used as membrane materials because they meet the above requirements for a wide range of applications (Table 1.3). Cellulosic polymers in general are attractive membrane materials because they combine convenient chemical modification ability with solubility in a wide range of solvents, good film-forming ability, good mechanical properties, good thermal, mechanical, and chemical stability, and thermoplasticity. A wide range of cellulosic substituents via homogeneous-phase reaction chemistry is possible, so the ability to control the material properties of cellulose derivatives to fit a wide range of separation applications exists and is very attractive.

1.5. References

18. Youngs et. al. (need reference - fluorinated cellulose?)
2. RESEARCH OBJECTIVES

The objectives of this study were:

1. To determine the effect of ester substituent size on the thermal behavior (melting point, glass transition, crystallization) of waxy cellulose tri-esters.

2. To determine the effects of DS and substituent type (hydroxyl, acetyl, lauryl, or mixtures of lauryl and either hydroxyl or acetyl) on the thermal behavior of cellulose laurate and cellulose acetate laurate esters.

3. To determine the effects of DS and substituent type (hydroxyl, acetyl, or 2,2,2-trifluoroethoxyacetyl) on the preferential sorption behavior of ethanol/water solutions by cellulose acetate trifluoroethoxyacetate esters.
3. THERMAL ANALYSIS OF WAXY ESTERS OF CELLULOSE

ABSTRACT

Cellulose esters with acyl substituents ranging in size from C\textsubscript{12} (lauric acid) to C\textsubscript{20} (eicosanoic acid) were prepared in homogeneous solution (DMAc/LiCl) using a novel synthetic method based on the use of a mixed p-toluenesulfonic/carboxylic acid anhydride. Waxy cellulose esters with C\textsubscript{12}, C\textsubscript{14}, C\textsubscript{18}, and C\textsubscript{20} acyl substituents, with high degree of substitution (DS) between 2.8 and 2.9, and high degree of polymerization (DP), were synthesized. Thermal analysis by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermo-mechanical analysis (TMA) revealed a series of transitions that represented motion by both ester substituents and the cellulosic main chain. A separate crystalline morphology of substituent chains was detected, with crystallization (T\textsubscript{c}) and melting (T\textsubscript{m}) events recorded in the range between -19 and +53°C; these T\textsubscript{c} and T\textsubscript{m} events were exceptionally broad, covering a temperature range of between 40 and 80°C. The T\textsubscript{m} and T\textsubscript{c} transition temperatures increased by 10°C per carbon atom in the ester substituent. A main chain T\textsubscript{m} was detected for C\textsubscript{12} and C\textsubscript{14} derivatives, and it was found to converge with the substituent T\textsubscript{m} as substituent chain length approached C\textsubscript{20}.

*This chapter is adopted from a draft manuscript entitled, "Novel Cellulose Derivatives. IV. Preparation and Thermal Analysis of Waxy Esters", and authored by James E. Sealey, Gamini Samaranayake, Jason G. Todd, and Wolfgang G. Giesser; Department of Wood Science and Forest Products and Biobased Materials Center, Virginia Tech. My contribution to this work consisted of: per-acetylation of the cellulose laurate (C\textsubscript{12}) derivative, DMTA analysis of the C\textsubscript{18} and C\textsubscript{20} cellulose esters, and significant interpretation of results and preparation of figures. Synthesis, NMR analysis, DSC analysis, and DMTA analysis of C\textsubscript{12}, C\textsubscript{14}, C\textsubscript{18}, and C\textsubscript{20} cellulose esters: per-acetylation of C\textsubscript{14} ester; and DSC analysis of per-acetylated C\textsubscript{12} and C\textsubscript{14} esters; was contributed by James E. Sealey. Per-acetylation and DSC analysis of C\textsubscript{18} and C\textsubscript{20} esters was performed by Gamini Samaranayake. Molecular weight analysis (by GPC) was skillfully performed by Jody Jervis."
3.1. Introduction

Cellulose esters represent a class of commercial polymers with excellent fiber and film-forming characteristics and with melt processability. Cellulose esters are conventionally produced by heterogeneous-phase reaction chemistry involving short-chain acids, acid anhydrides, and acyl chlorides. Although cellulose esters of long-chain fatty acids have been reported\(^1\), only those cellulose esters having acyl groups as large as C\(_4\) (butyryl) are commercially available. Cellulose esters with larger substituents are apparently difficult to prepare using heterogeneous-phase reaction chemistry\(^2\).

Several novel cellulose solvent systems employing combinations of organic and inorganic reagents have been reported within the past twenty-five years\(^3\). These solvents make it possible to produce, in homogeneous phase, cellulose esters with bulky and/or multifunctional acyl substituents that are (a) uniformly distributed along the cellulose backbone, and (b) that may cover all or only a portion of the available OH groups. In a series of n-alkyl esters of cellulose, it was observed that as the size of the substituent chain length increased, the \(T_m\) decreased, until about C\(_8\) before leveling off\(^4,5\). Above C\(_{12}\), a slight increase is noted again (Figure 3.1). The \(T_g\) has been shown to follow the same trend but \(T_g\) and \(T_m\) converge as the chain length increases\(^5\).

The previous report\(^6\) of this publication series dealt with thermal transitions of cellulose mixed esters having butyryl and hexanoyl\(^7\) functionality in addition to acetyl groups. It was of interest in this study to explore the nature of the thermal transitions of cellulose esters having alkyl substituents in the range of C\(_{12}\) to C\(_{20}\). Another objective of this study was to test the reactivity of a p-toluenesulfonic acid/carboxylic acid mixed anhydride with cellulose in homogeneous phase, dissolved in DMAc/LiCl. Fully-substituted esters of bulky “waxy” acids were to be synthesized using novel reaction
Figure 3.1 Relationship between the melting points of cellulose triesters and acyl substituent size. Data taken from visual observation (+) (Malm et al., ref. 4), and from DMTA analysis (▲) (Morooka et al., ref. 5).
considerations and the resulting cellulose derivatives were to be examined in terms of their thermal characteristics in relation to acyl substituent size.

3.2. Experimental

3.2.1. General

$^1$H NMR spectra of the cellulose esters were recorded at ambient temperature in CDCl$_3$/2% trifluoroacetic acid with TMS as the internal standard, on a Varian 400 MHz NMR spectrometer. A Varian 3700 gas chromatograph with a Hewlett Packard Model 3394A integrator and an OV-17 packed-glass column was used for GC analysis in accordance with earlier work.$^8$ Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-4 instrument with TADS software package. DMTA and TMA experiments were carried out with Polymer Laboratories DMTA and Perkin-Elmer TMS-2 instruments respectively, using Polymer Laboratories Plus V software package. Molecular weights of the materials were determined by Gel Permeation Chromatography (GPC) as described elsewhere.$^7, 8$

3.2.2. Materials

Cellulose: Whatman CF-11 (Whatman Chemicals, Hillsboro, OR) microcrystalline cellulose was used in all reactions. Cellulose solutions of approximately 4% solids content were prepared in DMAc/LiCl (9 wt.%).$^7$

Solvents and Reagents: P-toluenesulfonyl chloride (TsCl); lauric (C$_{12}$), myristic (C$_{14}$), palmitic (C$_{18}$), and eicosanoic (C$_{20}$) acids; solvents; and other reagents were obtained from Aldrich Chemical Company (Milwaukee, WI) and used as received.

3.2.3. Methods
3.2.3.1. Esterification Reaction

Pyridine (1 eq/TsCl) was added dropwise to 100 mL of a 4% cellulose solution in DMAc/LiCl. To the magnetically-stirred solution under a nitrogen atmosphere was added dropwise a solution (in DMAc) of alkanoic acid (2 eq/cellulose OH) followed by a solution (in DMAc) of p-toluenesulfonyl chloride (2 eq/OH). The reaction temperature was raised to 50°C and held there for 24 h. The products were isolated as white powders by precipitation into 50/50 methanol/H2O. The precipitates were vacuum-dried at 60°C and ca. 29 in. Hg vacuum for 18 h.

All esters (C₁₂, C₁₄, C₁₈, and C₂₀) had degree of substitution (DS) between 2.8 and 2.9 as determined by proton NMR and gas chromatography. Molecular weight data are given in Table 3.1. All esters had similar ¹H NMR spectra. Typically, the following signals were recorded (all δ-scale in ppm): alkanoyl chain, 0.9 (a group of triplets, CH₃), 1.3 (multiplet, -CH₂-), 1.5 (multiplet, β-CH₂), 2.0-2.5 (multiplet, α₉₅-CH₂); cellulose main chain, 3.3-5.3 (multiplet 1, 2, 3, 4, 5, & 6 ring protons). Characteristic FTIR absorptions were (λmax, cm⁻¹): 1720-1740 (carboxyl group), 3200-3800 (hydroxyl groups and moisture).

3.2.3.2. DSC

The samples were used in powder form or as films prepared on a heated hydraulic press (Fred S. Carver Inc., WI). Average weight was 10 mg per sample, which was placed into an aluminum DSC pan and typically heated at 10°C/min and cooled at 5°C/min for 3 consecutive scans between -50 and 180°C. Similarly, three heating scans were performed with quick cooling (320°C/min) between each scan. After the second scan, the samples were held at 140°C for 2-4 h and then reheated from -30 to 180°C. Finally, the samples were heated to 250°C to determine whether there were any melting transitions at high temperature. The melting point temperatures (Tm) by DSC were defined as the peaks of the melting endotherms as seen on the third heating scan after annealing at 150°C. Melting point and decomposition temperatures were determined visually in a MELT-
TEMP II apparatus (Laboratory Device, Holston, MA). The temperature at which a sample becomes visibly discolored was taken as the onset of decomposition. For these samples the average decomposition temperature was 250°C.

3.2.3.3. DMTA

Most samples were tested from -120°C to the onset of flow. The samples were pressed into thin films on the heated Carver press at 140°C. The films were allowed to cool slowly in the press to room temperature (allowing approximately 30 minutes to cool); they were then cut into rectangular test specimens. Flat-edge clamps were used in single-cantilever bending at a frequency of 1 Hz. One ft-lb of torque was used for clamping. Relaxation transitions \( \alpha \) and \( \beta \) were defined as the maxima of tan-\( \delta \) or loss modulus peaks. The highest-temperature transition was designated as \( \alpha \), while \( \beta \) was the designation for the lower-temperature transition.

3.3. Results and Discussion

3.3.1. Synthesis

Relatively non-polar aliphatic carboxylic acids are insoluble in the polar DMAC/LiCl solvent mixture. In the presence of tosyl chloride,\(^9\) however, these acids dissolve immediately indicating the formation of soluble mixed p-toluenesulfonic/carboxylic acid anhydrides. Derivatives with DS between 2.8 and 2.9 for C\(_{12}\), C\(_{14}\), C\(_{18}\), and C\(_{20}\) acids were obtained using a stoichiometric ratio of 2 equivalents of acid per cellulose hydroxyl. Compared to other published cellulose esterification techniques, this is a highly reactive and efficient method for the synthesis of long-chain aliphatic cellulose esters.
Table 3.1 Thermal and Molecular Weight Data for Unacylated Cellulose Esters.

<table>
<thead>
<tr>
<th>Ester Length</th>
<th>Substituent</th>
<th>Main Chain</th>
<th>Molecular Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DPₙ</td>
</tr>
<tr>
<td>C₁₂</td>
<td>2.9</td>
<td>-54</td>
<td>-19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-39 to +20)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[5 J/g]</td>
<td></td>
</tr>
<tr>
<td>C₁₄</td>
<td>2.8</td>
<td>-39</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-29 to +50)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[17 J/g]</td>
<td></td>
</tr>
<tr>
<td>C₁₈</td>
<td>2.8</td>
<td>-15</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(+4 to +61)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[48 J/g]</td>
<td></td>
</tr>
<tr>
<td>C₂₀</td>
<td>2.9</td>
<td>4</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(+20 to +82)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[66 J/g]</td>
<td></td>
</tr>
</tbody>
</table>

¹ DMTA ² DSC

Elemental analysis of these derivatives established that no significant tosylate or chlorination had taken place. It is important, however, to keep the reaction temperature below 70°C, rapid degradation of cellulose was observed above 70°C. Molecular weight data (by GPC, Table 3.1) suggest that no significant depolymerization had occurred except for the C₂₀ derivative, which had to be heated to 65°C (instead of the normal 50°C) to dissolve the C₂₀ acid.
Figure 3.2 DSC thermograms for cellulose esters annealed at 140°C for 2-3 h. (A) C₁₂, DS 2.8; (B) C₁₄, DS 2.8; (C) C₁₈, DS 2.9; and (D) C₂₀, DS 2.9.
3.3.2. Thermal Analysis

The thermal characterization of the waxy esters presents a number of complexities that give rise to different responses by DSC, DMTA, and TMA.

Several distinct transitions were observed in DSC analysis of cellulose waxy esters. A broad melt endotherm at low temperature (designated \( T_{m,L} \)) increased in temperature linearly with increasing substituent size from -19°C for \( C_{12} \) to 53°C for \( C_{20} \) (Table 3.1, Figure 3.2). A corresponding crystallization exotherm (\( T_{c,L} \)) on cooling scans was seen for each sample, 5 to 10° below \( T_{m,L} \) (Figure 3.3). The \( T_{m,L} \) endotherms could be reproduced after heating at temperatures above 100°C, so they are not attributed to enthalpy relaxation or moisture interactions. A plot of melting temperatures of the methyl esters of \( C_{12} \) to \( C_{20} \) acids (from literature) reveals good agreement between the methyl ester \( T_{m} \)'s and the cellulose ester \( T_{m,L} \)'s (Figure 3.4); therefore, \( T_{m,L} \) is attributed to melting of a waxy-ester substituent crystalline phase. DSC scans of \( C_{20} \) ester samples that were annealed at room temperature, at 140°C, and at 40°C indicated that significant morphological reorganizations occurred during annealing, as reflected by a sharpening of \( T_{m,L} \) at low temperature (Figure 3.5).

DSC scans of \( C_{12} \) and \( C_{14} \) cellulose esters revealed second-order transitions at 100 and 110°C respectively (Figure 3.2); these transitions are attributed to the glass transition temperature (\( T_g \)) of the main (cellulose) chain. Main chain glass transitions were not detected by DSC analysis of \( C_{18} \) and \( C_{20} \) derivatives; however, these \( T_g \)'s may be hidden by the broad \( T_{m,L} \) endotherms. The \( C_{14} \) ester revealed a sharp endotherm above 200°C; this \( T_{m,H} \) is attributed to melting of main-chain crystalline structure (Figure 3.2). No other ester sample exhibited a \( T_{m,H} \) endotherm.

The DMTA thermograms for the \( C_{12} \) to \( C_{20} \) ester derivatives (Figure 3.6) reveal tan-δ peaks with maxima that increase linearly with increasing substituent size from -54°C for \( C_{12} \) to -4°C for \( C_{20} \). This transition is attributed to motion of the ester substituent chain and is designated \( T_{g,L} \); however, the \( T_{g,L} \) transition as seen by DMTA may be a
Figure 3.3 DSC cooling curves of cellulose esters. (A) C\textsubscript{12}, DS 2.8; (B) C\textsubscript{14}, DS 2.8; (C) C\textsubscript{16}, DS 2.9; and (D) C\textsubscript{20}, DS 2.9.
Figure 3.4  $T_{m,L}$ and $T_{m,H}$ of cellulose esters, and $T_m$ of corresponding methyl esters, as a function of ester substituent size for per-acetylated waxy esters of cellulose.
Figure 3.5  DSC scans showing annealing effect on $T_{mL}$ for $C_{20}$ cellulose ester. Annealing temperature ($T_a$): room temperature (ROOM), 140°C, and 40°C (pressed film).
manifestation of the $T_{m,L}$ melting transition as seen by DSC. It is inconclusive whether $T_{g,L}$ and $T_{m,L}$ represent separate thermal transitions.

The following observations are made regarding the $T_{m,L}$ and $T_{c,L}$ transitions: $T_{m,L}$ and $T_{c,L}$ increase with increasing ester substituent length, and the increase of both $T_{m,L}$ and $T_{c,L}$ amounts to 10°C per carbon atom (Figure 3.7). $T_{m,L}$ endotherms and $T_{c,L}$ exotherms (DSC) become more energetic as substituent length increases (Figures 3.2 & 3.3). These observations lead to the conclusion that an independent side-chain crystalline morphology exists, and that the degree of side-chain crystallinity is increasing with increasing substituent length. This apparent contribution of the olefinic ester substituent to the thermal transitions of cellulose esters is consistent with corresponding observations made with poly($\gamma$-alkyl-glutamates)$^{10}$ and cellulose (oligo-oxymethylene) acylates$^{11}$ having ester substituents of increasing size. This also agrees with an independent observation that ester substituents of greater than 12 carbon-atom length are capable of creating their own independent morphology.$^{12}$

Further DSC experiments were conducted with peracetylated cellulose waxy esters (the samples described in Table 3.1 were peracetylated). Previous work$^6$ indicated that the presence of free (unmodified) hydroxyl groups in cellulose esters created difficulties in thermal analysis due to moisture interactions. Acetylation reactions were performed on the C_{12}, C_{14}, C_{18}, and C_{20} cellulose esters in order to substitute any remaining free hydroxyls. Following acetylation, the C_{12} sample revealed a melting transition at 96°C (Table 3.2); the melting point of the C_{14} derivative declined from 225 to 84°C in response to acetylation (Figure 3.2, Figure 3.8). The C_{18} and C_{20} derivatives failed to reveal $T_{m,H}$ endotherms after acetylation; however, they exhibited $T_g$'s at 99 and 110°C, respectively. For all derivatives, the low-temperature endotherm ($T_{m,L}$) remained unchanged following peracetylation, indicating that $T_{m,L}$ is independent of main chain morphology.
Figure 3.6  DMTA scans of C_{12}, C_{14}, C_{18}, and C_{20} esters. Shown are tan δ and loss modulus (E'') curves.
Figure 3.7 Relationship between substituent transitions $T_{g,L}$, $T_{m,L}$, $T_{c,L}$ and no. of carbons in acyl substituent. Data from DSC and DMTA. (▲) $T_{m,L}$; (▲) $T_{c,L}$; (O) $T_{g,L}$. 
Table 3.2 Thermal Data for Per-Acetylated Cellulose Esters

<table>
<thead>
<tr>
<th>Ester Length</th>
<th>Substituent</th>
<th>Main Chain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{m,l}$ ($°C$) (range)</td>
<td>$T_{m,H}$ ($°C$)</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>-19 (-39 to -20)</td>
<td>96</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>5 (-12 to +30)</td>
<td>84</td>
</tr>
<tr>
<td>C$_{18}$</td>
<td>34 (-2 to +65)</td>
<td>-</td>
</tr>
<tr>
<td>C$_{20}$</td>
<td>59 (+20 to +78)</td>
<td>-</td>
</tr>
</tbody>
</table>

If the main-chain melt transition of the (peracetylated) derivatives is assumed to be a linear function of the size of the substituent (Figure 3.4), the main-chain melting points of the C$_{18}$ and C$_{20}$ cellulose esters may be estimated by extrapolation. These hypothetical melting points would be located in close proximity to the side-chain melting points. It may therefore be speculated that the C$_{18}$ and C$_{20}$ derivatives display only a single melting transition, and that this represents the coordinated melting endotherm of both main chain and substituents. It seems likely, however, that main chain crystallization becomes increasingly difficult as ester substituents become larger, inhibiting packing of the cellulose ester molecules into a crystal lattice. A dimensionally-accurate molecular model that assumes that the long aliphatic chains are arranged in an all-anti conformation stipulates that a superior chain arrangement of the ester substituents may exist, and that this is
Figure 3.8  DSC scans of the per-acetylated C₁₄ cellulose mixed ester, DS$_{myr}$ = 2.8. (A) Heat 1; (B) Heat 2; (C) Heat 3 annealed at 80°C for 4 h; (D) Heat 4 annealed at 5°C for 1.5 h; (E) Cooling curve.
responsible for a distinct olefinic phase. Crowding along the backbone obviously enhances the propensity for side-group crystallization (Figure 3.9).

3.3.3. Melt Processability

The large drop in $T_{m,H}$ of the C$_{14}$ ester observed upon peracetylation (Figure 3.2) demonstrates that strong hydrogen bonding (and therefore a high melting point) may occur with less than 10% of hydroxyls unsubstituted. Interchain hydrogen bonding of free hydroxyls may also inhibit crystallization by restricting the translational mobility of cellulosic chains; this effect may be responsible for the absence of a $T_{m,H}$ transition for the un-acetylated C$_{12}$ ester, which then displayed a $T_{m,H}$ endotherm following peracetylation. Difficulties in melt processing of cellulose esters arise when the $T_m$ (or $T_g$ in the case of an amorphous material) lies too close to the decomposition temperature; therefore, control of $T_m$ becomes critical when melt processability is desired.

Injection-molding experiments were performed with the C$_{18}$ and C$_{20}$ (un-acetylated) derivatives. Although DSC showed the melting points of these derivatives to lie well below 100°C, the materials remained in the state of a viscous wax and did not become completely liquid until heated above 200°C. This suggests that they actually melt at or around $T_{m,L}$ but there is still some hydrogen bonding that must be overcome by thermally-induced molecular motion before a melt-processable fluid state is achieved.

3.4. Conclusions

1. The esterification of cellulose in homogeneous phase using mixed anhydrides consisting of p-toulenesulfonic and carboxylic acids is highly effective. Waxy ester derivatives with high DS and undiminished degree of polymerization can be produced.
2. The thermal transitions exhibited by the waxy ester derivatives reveal an independent side-chain crystalline morphology when substituent length is 12 carbon atoms or greater.
Figure 3.9 Dimensionally-accurate molecular model of cellulose eicosanoate (C_{20}, DS 3.0). Black hexagons represent gluco-pyranose rings in cellulose chain, the acyl groups are drawn in all-anti conformation.
3. The melting point \( (T_{m,L}) \) of side-chain crystals increases linearly, at a rate of 10°C per carbon atom, as the length of substituents increases from \( C_{12} \) to \( C_{20} \); \( T_{m,L} \) increases from -19°C for \( C_{12} \) to 53°C for \( C_{20} \).

4. Main-chain \( T_m \)'s of peracetylated waxy esters of cellulose converge with the melting transition of the olefinic (side-chain) phase and/or disappear as substituent length reaches \( C_{18} \).

5. Main chain \( T_f \) and \( T_m \) transitions are greatly influenced by the presence of a small number (<10%) of free hydroxyls.

6. The side-chain melting transition is independent of main-chain morphology.

3.5. Acknowledgment

This study was financially supported, in part, by a grant from AKZO Research America, Inc., Dobbs Ferry, New York. This is acknowledged with gratitude.

3.6. References


4. THERMAL ANALYSIS OF MIXED ESTERS WITH LAURIC ACID* 

ABSTRACT

Cellulose laurates (CL) and cellulose acetate laurates (CAL) prepared by homogeneous-phase reaction in DMAc/LiCl, were found to be derivatives with undiminished molecular weight and with distinct melting and melt flow behavior that was related to substitution pattern. For CL (with free OH-groups) the $T_m$ declined from 220 to 170°C as $DS_{lau}$ increased from 0.6 to 2.5, and $T_g$ declined from 155 to 105°C as $DS_{lau}$ increased from 0.6 to 2.9. Thermal transitions attributed to substituent motion at -50°C and substituent crystallization at -20°C were detected. For CAL esters, $T_m$ declined by 25°C per DS unit, from 170 to 95°C, as $DS_{lau}$ rose from 0.6 to 2.9. Viscous flow was recorded at or below $T_m$. The propensity of CAL to crystallize when cooled from the melt was not hindered by the proximity of $T_g$ to $T_m$, which was less than 50°C. CLs and CALs are found to be cellulose derivatives which combine crystalline character with melt-processability.

4.1. Introduction

The previous papers* in this series reported on the relationship between chemical structure and thermal properties of several cellulose ester derivatives. Glass and melting

* This chapter is adopted from a draft manuscript entitled, "Novel Cellulose Derivatives. VI. Thermal Analysis of Mixed Esters with Lauric Acid", and authored by James E. Sealey, Jason G. Todd, Gamini Samaranayake, and Wolfgang G. Glasser, Department of Wood Science and Forest Products, and Biobased Materials Center, Virginia Tech. My contribution to this work consisted of synthesis and NMR analysis of DS-1.3 and 2.0 cellulose laurate (CL) esters; per-acetylation of all CL esters; DSC analysis of DS-0.6, 1.3, and 2.0 CL esters; DMTA analysis of DS-1.3 and DS-2.0 CL esters; and TMA analysis of DS-0.6, 1.3, and 2.0 CL esters. Synthesis, NMR analysis, DSC analysis, DMTA analysis, and TMA analysis of DS-0.6, 2.5, and 2.9 CL esters; as well as NMR, DSC, and TMA analysis of all CAL derivatives was contributed by James E. Sealey.
point transitions, \( T_g \) and \( T_m \), respectively, were found to reflect both substituent type and degree of substitution (DS). Ester derivatives with low DS, therefore having underivatized hydroxyl groups remaining on the polymer backbone, were found to present insurmountable difficulties during thermal analysis, which could be attributed to moisture problems\(^\text{13}\). Whereas unmixed tri-esters have, according to the literature\(^4^5\), \( T_m \)s which often lie extremely close to \( T_g \)s, mixed acetate esters with butyric and hexanoic acid, by contrast, were found to have distinct glass transition and melting temperatures, which decrease as the degree of substitution with respect to the bulkier substituent increases.\(^1\) The \( \Delta(T_m - T_g) \) values were found never to fall below 40°C.

It is the aspect of crystallization in relation to the glassy and melt state which is of interest because it determines melt processability and eventual material properties. It was therefore the goal of the present study to examine structure-thermal property relationships in mixed cellulose esters that have an even larger alkanoic substituent, lauric acid (\( C_{12} \)).

4.2. Experimental

4.2.1. Materials

Cellulose: Whatman CF-11 (Whatman Chemicals, Hillsboro, OR) microcrystalline cellulose was used in all reactions. Cellulose solutions of approximately 4 wt. % cellulose content were prepared in DMAc/LiCl (9 wt. % LiCl).\(^1^6^7\)

Lauric (\( C_{12} \)) acid, p-toluenesulfonyl chloride, solvents, and other reagents were obtained from Aldrich Chemical Company (Milwaukee, WI) and used as received.

4.2.2. Methods

The synthesis of cellulose esters in homogeneous solution has been the subject of prior publications\(^1^2^7\). Briefly, in a typical reaction, cellulose (4% solution in DMAc/LiCl, diluted to 2% with additional DMAc) was reacted with a mixed anhydride of p-toluenesulfonic acid and lauric acid generated in situ\(^2\). The DMAc solution of cellulose
and mixed anhydride was allowed to stir for 24 hours before being precipitated in water. The CL precipitates were purified by soxhlet-extraction with methanol and dried at 60°C and 29 in. Hg vacuum in a vacuum oven. The CAL derivatives were prepared by subsequent acetylation of CL remaining OH groups with acetic anhydride, in pyridine solution, followed by precipitation in water and then soxhlet extraction with methanol and vacuum drying as with the CL precipitates.

Spectroscopic and thermal analyses were conducted in accordance with prior publications.\textsuperscript{1,7}

4.3. Results and Discussion

4.3.1. Reactivity and Structure

The degree of substitution (DS) of cellulose esters prepared homogeneously is conveniently controlled via stoichiometry as was described previously\textsuperscript{1,7}. Cellulose laurate esters had $D_{\text{la}}$ values between 0.6 and 2.9 (Table 4.1). The DS was determined quantitatively by $^1\text{H}$ NMR spectroscopy as the relative ratio of the integrated signals of substituent protons to cellulose protons (Figure 4.1). For reactions conducted at 50°C or

<table>
<thead>
<tr>
<th>$D_{\text{la}}$ of CL, CAL</th>
<th>$D_{\text{ac}}$ of CAL</th>
<th>Total DS of CAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>2.5</td>
<td>3.1</td>
</tr>
<tr>
<td>1.3</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>2.8</td>
</tr>
<tr>
<td>2.5</td>
<td>0.4</td>
<td>2.9</td>
</tr>
<tr>
<td>2.9</td>
<td>0.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>

\textsuperscript{1} DS values from integration of $^1\text{H}$-NMR spectra.
Figure 4.1  $^1$H NMR spectrum of cellulose laurate of DS 2.9.
lower, no significant depolymerization was observed, as determined by gel permeation
cromatography (GPC). This is in contrast to reports by Shimizu and Hayashi\textsuperscript{9} who
detected significant depolymerization during the reaction with tosyl chloride and cellulose
under heterogeneous reaction conditions at 80°C; however, it is in accord with another
study also employing homogeneous-phase conditions (previous chapter of this thesis).

4.3.2. Thermal Analysis

4.3.2.1. Cellulose Laurates (CL)

CLs with low DS, and with free OH functional groups, reveal several thermal
events by DSC, DMTA, and TMA (Table 4.2). Thermal analysis of cellulose esters may be
hindered by the strong interaction of OH groups with moisture, especially at low DS.\textsuperscript{1,3}

DSC indicates broad melting transitions at temperatures of 170°C for CL of DS
2.5, increasing with decreasing DS\textsubscript{m} to 220°C for CL of DS 1.3 (Figures 4.2, 4.3). These
melt endotherms were detected on first heating scans; after cooling at 10°C/min to 0°C, the
endotherms were not detected, but the endotherms reappeared on the third heating scans
after annealing at 40°C below the initial T\textsubscript{m} for 2 hours. T\textsubscript{m} values reported here are
defined as the peak of the melt endotherm as seen on the third heating scans; third-scan T\textsubscript{m}
values agreed with those from the first scans. The CL of DS 0.6 showed a melt event
which coincided with thermal decomposition of the sample at 220°C. Broad, weak
-crystallization exotherms were detected during cooling from the melt at temperatures of
160 and 185°C for CL samples of DS 1.3 and 2.0, respectively. No melting transition was
observed for the CL of DS 2.9; however, it exhibited a broad T\textsubscript{s} from about 70 to 120°C
(Figure 4.2). In accordance with the observations by Hsu at al.\textsuperscript{11} and Daly et al.\textsuperscript{12}, weak
crystallization and melt events at -20 and -25°C, respectively, which could be attributed to
substituent organization, were detected for the DS 2.5 CL and 2.9 CL, and the DS 1.3,
2.0, and 2.9 CAL derivatives. C\textsubscript{12} substituents are reported to be capable of forming a
separate crystalline morphology in comb-like polymers. As discussed in the previous

46
### Table 4.2  Thermal Transitions of CL Esters

<table>
<thead>
<tr>
<th>DS&lt;sub&gt;last&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>β-relaxation (°C)</th>
<th>(T_{g,\text{high}}) (°C)</th>
<th>Onset of Flow (°C)</th>
<th>(T_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR</td>
<td>DMTA</td>
<td>TMA</td>
<td>DMTA</td>
<td>DSC</td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
<td>-46</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.3</td>
<td>-48</td>
<td>-40</td>
<td>74</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>-45</td>
<td>-50</td>
<td>76</td>
<td>-</td>
</tr>
<tr>
<td>2.5</td>
<td>-</td>
<td>-50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.9</td>
<td>-</td>
<td>-55</td>
<td>-</td>
<td>87</td>
</tr>
</tbody>
</table>

<sup>a</sup> Remaining positions (i.e., balance to 3.0) present as OH-groups.

<sup>b</sup> Sample decomposed during melting.
Figure 4.2  DSC thermograms of cellulose laurates of DS 2.0 and 2.9. (A) DS 2.0; (B) DS 2.9.
Figure 4.3  Thermal transitions of cellulose laurate (CL) as measured by DSC, DMTA, and TMA. (▼) $T_m$ (DSC); (+) $T_g$ (TMA); (O) Flow temp. (TMA); (□) $T_g$ (DSC); (●) $T_{m,L}$ (DSC); (▲) $T_{g,L}$ (TMA); (♦) $T_{g,L}$ (DMTA).
chapter of this thesis, the existence of a separate morphology for the long-chain alkyl
groups in cellulose esters of C_{12} to C_{20} acids has been clearly identified.

Thermograms by TMA (Figure 4.4) revealed two separate relaxation or glass
transitions for all CL derivatives. The first transition, referred to as $T_{g\text{L}}$, was detected as
an increase in the slope of film expansion near -50°C; it is attributed to molecular motion
of the substituent (laurate) group. $T_{g\text{L}}$ did not vary appreciably with DS; this is a good
indication that this relaxation is associated with the substituent and not the main
(cellulose) chain. The $T_{g\text{L}}$ transitions as seen by TMA may be another manifestation of the
$T_{m\text{L}}$ event detected by DSC; it is inconclusive whether $T_{g\text{L}}$ represents a separate
transition. A second transition, seen (for TMA samples thicker than 0.4 mm) as an
increase in the slope of film expansion, may be assigned to the $T_g$ of the main (cellulose)
chain. This high-temperature $T_g$ declined from 155 to 105°C as DS increased from 0.6 to
2.9 (Figure 4.3). TMA samples less than 0.4 mm thick exhibited penetration of the probe
into the film as a result of viscous flow; the onset of flow was approximately 15°C above
$T_g$ (Figure 4.3).

The mechanical behavior of CL in relation to temperature is illustrated by DMTA
thermograms of DS 1.3 and 2 derivatives (Figure 4.5). Below -50°C, the material exists in
a glassy state, with high storage modulus. A distinct damping (tan $\delta$) peak with
accompanying drop in modulus at -50°C confirms the existence of $T_{g\text{L}}$ detected by TMA,
but again, this transition may not be independent but may be associated with the $T_{m\text{L}}$
substituent melting transition. The modulus remains relatively constant from -30°C until
the onset of a broad damping transition at 40°C. This relaxation event, with a weak
decline in storage modulus and corresponding loss modulus peak at 75°C, is attributed to
plasticization of the samples by moisture; broad $T_g$-like transitions observed by DSC
during first heating scans were not seen on subsequent scans; DMTA thermograms shown
here are first scans. The $T_g$ of the cellulose chain is marked by a rapid decline of storage
modulus beginning at 130°C with corresponding tan $\delta$ peak.
Figure 4.4  TMA thermogram of cellulose laurate of DS 1.3.
Figure 4.5  DMTA thermograms of cellulose laurate of DS 1.3 and 2.0.  (A) DS 1.3, log ($E'$); (B) DS 2.0, log ($E'$); (C) DS 1.3, tan $\delta$; (D) DS 2.0, tan $\delta$.  

52
$T_m$ declines more rapidly than $T_g$ as $DS_{lauro}$ increases; therefore, the interval between them, $\Delta(T_m - T_g)$, converges from 75°C at DS of 0.6 to 45°C at DS of 2.5. No melting transition was observed at DS of 2.8. A curve fit of $T_m$ data predicts that the value of $T_m$ at DS 2.8 would lie very close to $T_g$; therefore, crystallization would be very difficult for this sample (Figure 4.3). The value of $T_m$ is determined by the thermodynamics of crystallization. Thermal energy ($k_B T$) is required to overcome the lattice energy of a crystal in order for melting to occur; as the lattice energy increases, $T_m$ increases. Interchain hydrogen bonding makes a large contribution to the lattice energy of cellulosic crystals. As $DS_{lauro}$ increases, fewer cellulosic hydroxyl groups are available for hydrogen bonding, causing $T_m$ to decrease. The incorporation of bulky C$_{12}$ substituents also decreases the lattice energy by causing an increase in entropy, but entropic effects are likely to be small compared to enthalpic effects (due to hydrogen bonding). The melting point of unmodified cellulose (strongly hydrogen-bonded) is unobservable since it lies above the thermal decomposition temperature ($T_d$) of cellulose. The $T_m$ of DS 0.6 CL, 230°C, coincides with $T_d$. The $T_g$ of cellulosic chains is increased by intrachain hydrogen bonding, which stiffens the chain by inhibiting rotation about bonds; the $T_g$ of unmodified cellulose is reported to occur near 230°C. 13

4.3.2.2. Cellulose Acetate-Laurates (CAL)

CALs, with a uniformly-distributed mixture of laurate and acetate groups along the backbone, exhibited thermal characteristics by DSC that are typical of highly-ordered, highly-crystalline linear polymers with median $T_m$s (Table 4.3). $T_m$s are observed to lie very close to $T_g$s, making $T_g$s very difficult to distinguish (by DSC) in most cases. Despite the close proximity of $T_m$ to $T_g$, CALs are capable of rapid crystallization, which manifests itself in sharp $T_m$ and $T_c$ events during heating and cooling (Figure 4.6). The $T_m$ of CALs is found to decline from 170 to 95°C as $DS_{lauro}$ rises from 0.6 to 2.9 (Figure 4.7). The 2.9-$DS_{lauro}$ value for $T_m$ agrees with results reported by Malm$^5$ and Morooka et al.$^6$ $T_c$ parallels $T_m$ behavior approximately 10°C below $T_m$ (not shown in Figure 4.7). Since crystallization cannot occur below $T_g$ (due to lack of mobility of polymer chains), $T_g$ may
be assumed to lie near \( T_{c,\text{min}} \), which is defined as the lowest extent of the crystallization exotherm on a DSC thermogram. Following the above assumption, the \( \Delta(T_m-T_g) \) of CAL remains fairly steady, declining slightly from 48°C at \( DS_{\text{luu}} \) 0.6 to 36°C for \( DS_{\text{luu}} \) 2.9. A similar behavior was observed for cellulose acetate hexanoate (CAH): at \( DS_{\text{hex}} \) below 1, \( \Delta(T_m-T_g) \) has a large value; it decreases progressively with increasing \( DS_{\text{hex}} \) until leveling off at 40-45°C in the \( DS_{\text{hex}} \) range of 1-3.\(^1\)

CAL samples crystallized much faster than CL samples; annealing above \( T_g \) for at least 1 hour was required to restore CL melting endotherms after the first heating scan, while CAL melting endotherms could not be suppressed even by quench-cooling from the melt. CAL would be expected to crystallize less rapidly than CL based on the broader \( \Delta(T_m-T_g) \) seen for CL over most of the \( DS_{\text{luu}} \) range. This apparent contradiction is explained by the relative lack of interchain hydrogen bonding in CAL (nearly all hydroxyls are substituted) compared to CL, where the translational motion required to pack polymer chains into a crystal lattice is severely hindered by interchain hydrogen bonds.

### Table 4.3 Thermal Transitions of CAL Esters

<table>
<thead>
<tr>
<th>( DS_{\text{luu}} )</th>
<th>( DS_{\text{ac}} )</th>
<th>( \beta)-Relax.</th>
<th>( T_{m,\text{low}} )</th>
<th>( T_{c,\text{low}} )</th>
<th>Onset of Flow</th>
<th>( T_m )</th>
<th>( T_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR</td>
<td>NMR</td>
<td>TMA</td>
<td>DSC</td>
<td>DSC</td>
<td>TMA</td>
<td>DSC</td>
<td>DSC</td>
</tr>
<tr>
<td>0.6</td>
<td>2.5</td>
<td>-70</td>
<td>-</td>
<td>-</td>
<td>110</td>
<td>165</td>
<td>131</td>
</tr>
<tr>
<td>1.3</td>
<td>1.5</td>
<td>-40</td>
<td>-20</td>
<td>-25</td>
<td>138</td>
<td>153</td>
<td>143</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>-65</td>
<td>-20</td>
<td>-25</td>
<td>110</td>
<td>142</td>
<td>132</td>
</tr>
<tr>
<td>2.5</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>125</td>
<td>112</td>
</tr>
<tr>
<td>2.9</td>
<td>0.2</td>
<td>-60</td>
<td>-20</td>
<td>-25</td>
<td>120</td>
<td>97</td>
<td>90</td>
</tr>
</tbody>
</table>
Figure 4.6  Typical DSC thermograms of cellulose acetate laurate (CAL) of DS_{lu} 2.0. (A) Heat 1; (B) Cooling curve; (C) Heat 2.
Figure 4.7  Thermal transitions of cellulose acetate laurate (CAL) as measured by DSC, DMTA, and TMA. (▲) $T_m$ (DSC); (△) Flow temp. (TMA); (○) $T_{c,\text{min}}$ (DSC); (＋) $T_{m,L}$ (DSC); (□) $T_{g,L}$ (TMA).
Comparison of $T_m$ values for CAL versus CL (Figure 4.8) illustrates the large contribution to the lattice energy of hydrogen bonding between free hydroxyls. A large drop in $T_m$, 45-67°C, results when CL free hydroxyls are acetylated to yield CAL. The decline in $T_m$ with increasing $DS_{lu}$ shows that introduction of a bulky substituent hinders packing of cellulosic chains into a crystal lattice, increasing the entropy of the crystal lattice, resulting in the formation of crystals which melt at a lower temperature. The relatively gradual decline of $T_m$ with increasing $DS_{lu}$ below $DS_{lu}$ of 2.0 for CL indicates that only 1 out of 3 hydroxyls needs to be unsubstituted in order to get strong hydrogen bonding; this observation is important when manipulating DS in order to optimize properties for applications where mechanical strength is important, such as fibers, films, etc.

Comparing the thermal transition data for CAB (from a previous publication\textsuperscript{1} and literature\textsuperscript{15}) and CAH (from a previous publication\textsuperscript{1}) with those of CAL indicates that $T_m$ declines as the DS of the larger substituent rises from 0 to 3 (Figure 4.9). (CAH and CAL samples were treated in a similar manner; they were both synthesized from low-DP Whatman CF-11 cellulose, and reported $T_m$s are defined as the peak of the melting endotherm form the second heating scan on DSC. CAB $T_m$'s are average values reported from commercial samples, and the exact method of $T_m$ determination is not known). The slope of $T_m$ decline ($T_m$ loss gradient) is steep at low DS (of large substituent) but levels off at medium DS. The initial $T_m$ loss gradient increases with increasing substituent length, from approximately 78°C per DS unit for CAB ($C_4$), to 160°C per DS unit for CAH ($C_6$), to 217°C per DS unit for CAL ($C_{12}$). The point at which the $T_m$ loss gradient levels off decreases with increasing substituent length, from 1.5 DS for CAB, to 0.9 DS for CAH, to 0.6 DS for CAL. This supports the conclusion that the effectiveness of melting point depression at low DS of large substituents increases with increasing substituent length for n-alkyl substituents up to lauryl ($C_{12}$). The effect of adding a bulky substituent is to increase the distance between polymer chains, reducing intermolecular attractive forces in the crystallite, thus lowering $T_m$. (It is assumed that entropic effects caused by the addition
Figure 4.8  Comparison of melting points ($T_m$) of cellulose laurates (CL) and cellulose acetate laurates (CAL).  (♦) CL; (■) CAL.
Figure 4.9  Comparison of $T_m$ and $\Delta(T_m - T_g)$ data for CAB (▼), CAH (□), and CAL (○). (—) $T_m$, (-----) $\Delta(T_m - T_g)$. 
of bulky substituents are small compared to the enthalpic effects). The leveling off of the \( T_m \) loss gradient at mid DS suggests that once a certain number of large substituents are added, the interchain distance reaches a fixed value, and this distance is characteristic of the substituent size. It is interesting to note that the \( T_m \) at mid DS is higher for CAB while the \( T_m \)s for CAH and CAL at mid DS are nearly the same; this indicates that above C₆, increasing the characteristic interchain spacing has no further effect on melting point depression.

4.4. Conclusions

1. Cellulose laurate (CL) esters prepared in homogeneous (DMAc/LiCl) solution exhibit high reactivity without significant depolymerization, and DS is conveniently controlled over the entire DS range (0 to 3) via stoichiometry.

2. The \( T_m \) of CL esters declines with increasing \( DS_{lau} \), decreasing from 220°C for CL of DS 0.6 and DS 1.3 to 170°C for CL of DS 2.5. The CL of DS 2.9 exhibits no melting transition; however, a \( T_g \) is observed from 70 to 120°C. Crystallization of CL esters is slow.

3. The \( T_g \) of CL declines from 155 to 105°C as \( DS_{lau} \) increases from 0.6 to 2.9.

4. The interval \( \Delta(T_m - T_g) \) for CL converges from 75°C at DS of 0.6 to 45°C at DS of 2.5.

5. Weak crystallization and melting events attributed to substituent-chain crystallization are seen in the range of -25 to -20°C.

6. The \( T_m \) of cellulose acetate-laurates (CAL) declines from 170 to 95°C as \( DS_{lau} \) rises from 0.6 to 2.9. Crystallization of CALs is rapid compared to CL esters.

7. The \( \Delta(T_m - T_g) \) interval for CALs declines slightly from 48 to 36°C over the \( DS_{lau} \) of 0.6 to 2.9.

8. The effectiveness of melting point depression at low DS of large substituents increases with increasing substituent length for n-alkyl substituents up to lauryl (C₁₂).
9. At mid-DS of large substituent, increasing the substituent length has no further effect in melting point depression above a length of C₆ (hexanoyl).

4.5. Acknowledgment

This study was financially supported by a grant from AKZO America Research, Inc., Dobbs Ferry, NY, and this support is gratefully acknowledged. The authors are indebted to Paul S. Vail, Laboratory analysis, for his skillful assistance with thermal analysis.

4.6. References


5. **LC EXPERIMENTS WITH FLUORINATED CELLULOSE ESTERS**

**ABSTRACT**

Novel fluorine-containing cellulose mixed esters of 2,2,2-trifluoroethoxyacetic acid and acetic acid were prepared in homogeneous (DMAc/LiCl) solution. The degree of substitution with the fluorinated substituent (DS\textsubscript{F}) ranged from 0.6 to 3. The effect of DS\textsubscript{F} on preferential sorption of ethanol from ethanol/water solutions by cellulose (CE), cellulose triacetate (CTA), and cellulose acetate-trifluoroethoxyacetate (CATA) was studied by liquid chromatography (LC). The LC method measured the polymer surface excess volume of ethanol as a function of bulk solution ethanol concentration. Preferential sorption of ethanol was found to not be affected by DS\textsubscript{F}. Preferential sorption of ethanol was strongest for unmodified cellulose.

5.1. **Introduction**

Separations of organic solvents from mixtures of organic solvents and from water are traditionally accomplished by distillation. The degree of separation possible by distillation is often limited by the existence of azeotropes, and distillation often requires large amounts of energy since the entire process stream to be separated must be vaporized. Much research attention is currently focused on the production of ethanol by fermentation as a means of conversion of biomass to energy. The ethanol concentration in the aqueous product stream from a fermentation process is very dilute (ca. 10 wt.%), so

* This chapter is adopted from a draft manuscript entitled, “LC Measurement of the Preferential Sorption Behavior of Ethanol/Water Solutions by Fluorinated Cellulose Esters”, and authored by Jason G. Todd and Wolfgang G. Glasser, Department of Wood Science and Forest Products, and Biobased Materials Center, Virginia Tech. Jody Jervis (Biobased Materials Center) performed molecular weight analysis (by GPC) of the cellulose esters. All other work in this chapter is my own original contribution.
vaporization of a large amount of water is necessary to obtain a usable ethanol product when distillation is employed.

Pervaporation is a membrane separation process which may have advantages over distillation. The membrane employed is selectively permeable toward certain components of the mixture. The feed side of the membrane is kept in contact with the liquid feed solution. The permeate side of the membrane is at a reduced pressure so that a phase change to vapor occurs across the membrane. Since the separation is not dependent on the vapor-liquid equilibria (VLE) of the mixture, but rather on the relative permeabilities of components in the membrane, the limitations imposed on product purity by azeotrope formation in distillation do not apply to pervaporation.

In the case of organic liquid-water separations, the membrane may be selective for either water or the organic liquid. Hydrophilic membranes, such as polyvinyl alcohol (PVA), are used commercially to selectively permeate water from organic liquid mixtures; e.g. dehydration of azeotropic (95 vol.%) ethanol. Hydrophobic membranes may be used to remove organics from dilute water solutions.\(^1\)

Separation performance of a pervaporation process is defined in terms of the separation factor \(\alpha_A\) which is defined as

\[
\alpha_A = \frac{y_A}{x_A} \frac{x_B}{y_B}
\]  

(1)

where \(y_A\) and \(x_A\) are the mole fractions of component \(A\) in the permeate and feed, respectively; and \(y_B\) and \(x_B\) are mole fractions of component \(B\) in the permeate and feed, respectively.

The driving force for transport is the difference in chemical potential, \(\Delta\mu_i\), across the membrane. The generic expression relating the flux of component \(i\), \(J_i\), to driving force \(\Delta\mu_i\), is

\[
J_i = P_i \frac{\Delta\mu_i}{l}
\]

(2)

where \(P_i\) is the permeability of component \(i\) and \(l\) is the thickness of the membrane.
The permeability of component \( i \) in the membrane is a function of two parameters: 1) diffusivity of component \( i \) in the membrane and 2) solubility of component \( i \) in the membrane.\(^1\)

In the case of gas separations, the interaction between gas molecules and the membrane polymer is small, and the contribution of solubility toward the permeability favors the most condensible gas. In the case of pervaporation, where the membrane is in contact with liquid and condensible vapors, the interaction between membrane polymer and solutes may be much higher. Plasticization (an increase in segmental mobility) of the polymer may occur. In the case of separating a binary mixture of A and B, if the affinity of the membrane polymer for component A is higher than that for component B, then the effect will be to increase the permeability of component A relative to component B.\(^8\) Diffusivity favors permeation of the smaller molecule, so the effects of solubility and diffusivity may act either in concert or opposition in pervaporation. As shown by a summary of ethanol/water pervaporation experiments (Table 5.1), some polymer membranes are selective for water, while others are selective for ethanol; this suggests that the interactions between polymer and solutes have a strong effect on the results of ethanol/water pervaporation, since the affinity of the membrane for ethanol (relative to water) varies according to the chemical structure of the polymer.\(^8\)
<table>
<thead>
<tr>
<th>Membrane Polymer</th>
<th>Membrane Structure</th>
<th>Feed ETOH Conc. (wt.%)</th>
<th>Permeate ETOH Conc. (wt%)</th>
<th>Separ. Factor $\alpha_{ETOH}$</th>
<th>Total Flux (g/m²h)</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>-</td>
<td>50</td>
<td>0.002</td>
<td>12</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>Dense</td>
<td>10</td>
<td>1</td>
<td>0.09</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>PC</td>
<td>Asymmetric</td>
<td>10</td>
<td>1</td>
<td>0.09</td>
<td>800</td>
<td>9</td>
</tr>
<tr>
<td>PA-TFMA</td>
<td>Dense</td>
<td>10</td>
<td>1</td>
<td>0.09</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>CA</td>
<td>Asymmetric</td>
<td>50</td>
<td>0.24</td>
<td>700</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>PTMSP</td>
<td>-</td>
<td>50</td>
<td>3.3</td>
<td>120</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>PTMSP</td>
<td>Asymmetric</td>
<td>5</td>
<td>30</td>
<td>8.1</td>
<td>450</td>
<td>4</td>
</tr>
<tr>
<td>PTMSP</td>
<td>Dense</td>
<td>8</td>
<td>49.3</td>
<td>11.2</td>
<td>11.5</td>
<td>5</td>
</tr>
<tr>
<td>PDMS</td>
<td>-</td>
<td>50</td>
<td>3.3</td>
<td>70</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>PDMS</td>
<td>Dense</td>
<td>8</td>
<td>48.4</td>
<td>10.8</td>
<td>25.1</td>
<td>5</td>
</tr>
<tr>
<td>PDMS-TFEA</td>
<td>Composite</td>
<td>8</td>
<td>58.6</td>
<td>16.3</td>
<td>9.5</td>
<td>5</td>
</tr>
<tr>
<td>PDMS-HdFDA</td>
<td>Composite</td>
<td>8</td>
<td>72.6</td>
<td>30.5</td>
<td>14.1</td>
<td>5</td>
</tr>
</tbody>
</table>

**Polymer Abbreviations:**

CA: cellulose acetate
HdFDA: graft copolymer of styrene-2-(4-nitrophenylcarbonyloxy)ethylmethacrylate and 3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecy acrylate
PA-TFMA: polyacrylene with trifluoromethylated heterocyclic substituents
PAN: polycrylonitrile
PC: polycarbonate
PDMS: polydimethylsiloxane
PTMSP: poly [1-(trimethylsilyl-1-propyne)]
PVC: poly (vinyl chloride)
TFEA: graft copolymer of styrene-2-(4-nitrophenylcarbonyloxy)ethylmethacrylate and 2,2,2-trifluoroethyl acrylate
In the case of selective permeation of ethanol from dilute water solutions, a membrane polymer with a high affinity for ethanol is needed. The ethanol molecule is slightly larger than the water molecule, so diffusivity is not expected to favor ethanol permeation; however, the evaluation of diffusivities is more complicated because of the potential for clustering of ethanol and water molecules through hydrogen bonding (i.e. flow coupling). Hydrophobic membranes have been employed in laboratory ethanol-water separations with varying results (Table 5.1). The majority of the membranes studied fall into one of two categories: 1) dense, nonporous films made from evaporation of solvent from a solution of polymer in a volatile solvent, with typical film thickness of 50-100 μm, or 2) asymmetric films, with a thin (ca. 1-2 μm), dense surface layer supported by a highly-porous understructure. Typical permeation rates for dense films were in the range of 7 to 25 g/m²h, while permeation rates between 450 and 800 g/m²h were achieved with asymmetric membranes, indicating that the resistance to mass transfer is much less for asymmetric membranes. Preferential sorption of ethanol was reported in dense polystyrene and poly(vinyl chloride) membranes; however, these membranes preferentially permeated water in pervaporation experiments. Dense membranes made from polyacetylene substituted with trifluoromethylated heterocyclic groups showed a high hydrophobic character as manifested in a critical surface tension of 22 dyn/cm (similar to polytrifluoroethylene); however, water was preferentially permeated, suggesting a higher diffusivity of water in the membrane.

Membranes made from the silicon-containing polymers poly[1-(trimethylsilyl-1-propyne)] (PTMSP) and polydimethylsiloxane (PDMS) demonstrated preferential permeation of ethanol in all reported cases (Table 5.1). PTMSP and PDMS are known for their high permeabilities in gas separations, due to an open, poorly-packed structure of rigid polymer chains. An asymmetric PTMSP membrane and a dense PTMSP membrane exhibited similar performance in terms of separation factor, with α_{ETOH} of 8.1 and 11.5 reported for the asymmetric and dense membranes respectively; however, flux of
the asymmetric membrane, 450 g/m²h, was much greater than that of the dense membrane, 11.2 g/m²h.

Ishihara et. al.⁵ created composite membranes consisting of a styrene-fluoroalkyl acrylate (St-FAA) graft copolymer cast in a dense, 20 μm-thick layer on top of a 100 μm-thick, dense PDMS membrane. Separation factor in comparison to the original PDMS membrane increased with increasing fluorine content in the St-FAA copolymer. Separation factor increased threefold with the styrene heptadecafluorodecyl acrylate (St-HdFDA) copolymer (Table 5.1). This suggests that incorporation of a fluorocarbon chain into the polymer structure increases the relative permeability of ethanol (relative to water) in the membrane, due most likely to an increased affinity for ethanol relative to water. Therefore, the creation of a successful membrane for selective permeation of ethanol from dilute aqueous solutions involves two independent requirements: 1) a material with a high affinity for ethanol and 2) appropriate membrane polymer morphology (open, permeable structure).

The affinity of a polymer for a particular solute is demonstrated by the degree of preferential sorption of that solute by the polymer. Preferential sorption behavior of membrane polymers may be measured by liquid chromatography (LC) experiments.⁶,⁷ This method measures the surface excess of a particular solute by comparing the retention volumes of individual solutes in a polymer-packed column. The surface excess of a solute is the amount of that solute in excess of bulk solution concentration that is adsorbed at a surface; it is related to the preferential sorption of a component at the polymer surface. In light of the observation with PTMSP membranes that a 2 μm-thick dense layer is all that is required for separation, it seems likely that preferential sorption at or near the polymer surface is what determines separation behavior; therefore, surface excess concentration as measured by LC should be a good indication of potential separating ability.

For the case of ethanol-water separations, the method is applied as follows:⁷ An ethanol-water solution of the concentration of interest is pumped at constant flow rate through a column packed with powdered polymer that has been size-adjusted by sieving.
A pulse of pure water is injected into the mobile phase ethanol-water stream ahead of the column, and its retention time in the column is recorded by a differential refractometer connected to the column effluent. A pulse of pure ethanol is then injected and its retention time is recorded. Retention volumes are calculated by multiplying retention times by the mobile phase flow rate. The preferentially-sorbed component will have a greater retention volume, since it interacts more with the column packing, spending more time adsorbed to the polymer surface. For a binary mixture of components A and B, the surface excess volume of component A, which is the product $\Gamma_A A_p \bar{V}_A$, of surface excess concentration $\Gamma_A$, surface area of packing $A_p$, and molar volume $\bar{V}_A$, is calculated as follows:

$$\Gamma_A A_p \bar{V}_A = \frac{X_{A,b} X_{B,b} \bar{V}_A \bar{V}_B}{\left(X_{A,b} \bar{V}_A + X_{B,b} \bar{V}_B \right)^2 \left(V_A^R - V_B^R \right)}$$

(3)

where $X_{A,b}$ and $X_{B,b}$ are bulk (mobile-phase) mole fractions of components A and B, $\bar{V}_A$ and $\bar{V}_B$ are molar volumes of components A and B, and $V_A^R$ and $V_B^R$ are retention times of components A and B, respectively.

Cellulose acetate esters are well known and widely utilized for their good membrane-forming properties, but they do not exhibit sufficient preferential permeation of ethanol to be useful as ethanol-selective pervaporation membranes. Novel cellulose esters containing a fluorinated alkoxy ester substituent, 2,2,2-trifluoroethoxycacetate (TFEA), were synthesized in our laboratory; their synthesis was the subject of a previous publication\textsuperscript{10}. The addition of fluorinated substituents is predicted to increase the hydrophobicity of the cellulose ester and therefore increase the affinity of the polymer for ethanol (relative to water). The objective of the current study is to determine the effect of degree of substitution with the fluorinated substituent (DS$_F$) of cellulose on the preferential sorption of ethanol, using the previously-described LC method.\textsuperscript{6,7}
5.2. Experimental

5.2.1. Materials

Cellulose: Whatman CF-11 (Whatman Chemicals, Hillsboro, OR) microcrystalline cellulose was used in all reactions. Cellulose was solvent-exchanged with N,N-dimethylacetamide (DMAc) prior to dissolution. Cellulose solutions of approximately 4 wt.% solids content were prepared in DMAc/LiCl (9 wt.%).

Reagents and solvents: All other solvents and reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received.

5.2.2. Methods

Synthesis of 2,2,2-trifluoroethoxyacetic acid (TFEAA): TFEAA was synthesized as described in a prior publication.\textsuperscript{10} Briefly, 2,2,2-trifluoroethanol was reacted with chloroacetic acid in aqueous NaOH solution at 80°C for 24 h. The resulting solution was acidified with HCl; TFEAA was precipitated by addition of NaCl and then purified by vacuum distillation.

Cellulose esterification: Cellulose trifluoroethoxyacetate (TFA) was synthesized in homogeneous solution as described in previous work.\textsuperscript{10} Briefly, cellulose in DMAc/LiCl solution was reacted with a mixed anhydride of p-toluenesulfonic acid and TFEAA generated \textit{in situ}.\textsuperscript{11} DS\textsubscript{F} was conveniently controlled via stoichiometry by varying the ratio of cellulose to mixed anhydride. Remaining free cellulosic hydroxyls were substituted with acetate ester in a subsequent peracetylation reaction with acetic anhydride in THF/pyridine solution. DS\textsubscript{F} and DS\textsubscript{Ac} were determined by \textsuperscript{19}F and \textsuperscript{1}H NMR. Molecular weight data was obtained by GPC.

Preferential Sorption Measurements by LC: Cellulose ester powders were size adjusted using brass sieves to a particle size of 53-180 μm. The powders were packed into a liquid chromatography column (glass, 1.0 cm inside diameter, height adjustable approx.
25-30 cm, Pharmacia). The columns were packed by slurrying the powders in water with a small amount of ethanol (<5%) to improve wetting of the particles.

The packed column was connected to a Waters LPLC pump, and the initial solvent (usually 10 vol.% ethanol) was pumped through the column at 1.0 mL/min. After an hour, the column was connected to a refractive index (RI) detector, and the flow rate was reduced to 0.1 mL/min. The solvent was pumped at 0.1 mL/min for 20 h to allow the column and RI detector to reach equilibrium with the solvent.

After the initial equilibration period, the flow rate was increased to 1.0 mL/min, and about 30 min. was allowed for the system to stabilize at the higher flow rate. At this point, a series of injections of pure water and pure ethanol was initiated. For each injection, the sample loop, calibrated to deliver a 26.5 μL pulse, was loaded with either water or 100% (absolute) ethanol. The loaded sample was then injected into the column, automatically starting a timer. The injected sample passed through the column and appeared as a peak on the RI detector. The retention time for the pulse was recorded as the time at which the peak was at its maximum intensity. This procedure was repeated for a total of three water injections and three 100%-ethanol injections, alternating water and ethanol injections, for each mobile-phase ethanol concentration studied.

The solvent (mobile phase) was then switched to the next (higher) ethanol concentration and the system was allowed to equilibrate for 20 h as previously described. The series of alternating water and 100% ethanol injections was repeated for each mobile-phase ethanol concentration studied.
Table 5.2 Structure of Cellulose Acetate Trifluoroethoxyacetates

<table>
<thead>
<tr>
<th>Stoichiometry (Eq. TFEAA/AHG)</th>
<th>DS_F (Eq. TFEA/AHG)</th>
<th>DS_Ac (Eq. Ac/AHG)</th>
<th>Total DS</th>
<th>Molecular Wt. M_w x 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.8</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>0.6</td>
<td>2.0</td>
<td>2.6</td>
<td>1.2</td>
</tr>
<tr>
<td>2.3</td>
<td>1.0</td>
<td>1.7</td>
<td>2.7</td>
<td>3.3</td>
</tr>
<tr>
<td>4.5</td>
<td>3.2</td>
<td>0</td>
<td>3.2</td>
<td>1.8</td>
</tr>
<tr>
<td>7.5</td>
<td>2.8</td>
<td>0</td>
<td>2.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

5.3. Results and Discussion

Cellulose TFEA/acetate esters were prepared in homogeneous solution; degree of substitution with the fluorinated ester substituent (DS_F) ranged from 0 to 3 (3 is the maximum, indicating that all three hydroxyl groups on the cellulose repeat unit are substituted). Degree of substitution (DS) and molecular weight data are shown in Table 5.2. Total DS reported (by NMR) ranged from 2.6 to 3.2; the accuracy of NMR determination of DS is accepted to be ± 0.2 units of DS, so it is possible that a few hydroxyl groups were left unsubstituted, particularly in the sample with DS_F of 0.6, total DS of 2.6. Molecular weight data shows that moderate depolymerization of cellulose may occur in these reactions, but this is assumed to be unimportant for the present study.

LC experiments were conducted with unmodified CF-11 microcrystalline cellulose, cellulose triacetate (CTA), and cellulose acetate/trifluoroethoxyacetate (CATA) derivatives with DS_F of 0.6 and 2.8. Mobile-phase ethanol concentration was varied from 10 vol.% to 95 vol.% (0.03 to 0.85 mole fraction ethanol). Retention volume
measurements were repeated three times for each mobile-phase ethanol concentration, and the variation in retention volumes between repeated measurements was typically less than 0.05 mL, indicating good accuracy of the measurement. Retention volume data are shown in Figure 5.1. The retention volumes followed the same general trend for each polymer studied. The retention volume of ethanol was initially higher than that of water, then both retention volumes fell as ethanol concentration increased; at some point, the ethanol retention volume fell below the retention volume of water, then both retention volumes began rising again with further increase in ethanol concentration (Figure 5.1). The point at which water and ethanol retention volumes intersect is the point of zero surface excess.

Surface excess volumes were calculated from the retention volume data; surface excess volumes versus mole fraction of ethanol for each polymer are plotted in Figure 5.2. Note that these results are calculated for the total amount of polymer in the column; no correction is made for differences in specific surface area between polymers. Surface area measurement using a p-nitrophenol adsorption method was attempted, but the method did not yield any useful results due to difficulty in wetting of the cellulose ester samples in the 10 vol.% ethanol-water solutions used in the analysis. Therefore, caution is advised in comparing absolute values of surface excess volume between different polymers.

The surface excess volume (Figure 5.2) followed the same basic trend for each polymer sample, starting with a positive surface excess of ethanol (indicating preferential sorption of ethanol) at low ethanol concentrations. The surface excess of ethanol then decreased with increasing ethanol concentration, reaching a value of zero at some point, indicating no preferential sorption of either ethanol or water at that ethanol concentration. The surface excess of ethanol then became negative when ethanol concentration increased further, indicating preferential sorption of water. Little difference in behavior was seen between CTA, DSF 0.6-CATA, or DSF 2.8-CATA. These three esters demonstrated a slight preferential sorption of ethanol at low ethanol concentrations; then, all three surface excess curves intercepted the zero axis near 0.20 mole fraction ethanol. In contrast, the ethanol surface excess volume for the CF-11 cellulose sample was an order of magnitude
Figure 5.1  Retention volume data for cellulose (CE); cellulose triacetate (CTA); and cellulose acetate trifluoroethoxyacetate (CATA) of DS$_F$ 0.6 and 2.8. Retention volumes of (□) water and (■) ethanol.
Figure 5.2 Surface excess volume of ethanol as a function of ethanol solution concentration for (●) CE, (△) CTA, (○) DS$_F$ - 0.6 CATA, (+) DS$_F$ - 2.8 CATA.
greater than those of the ester samples in the low-concentration range. It is possible that the cellulose sample had a larger surface area than the ester samples, causing the surface excess to be magnified. However, note that the cellulose surface excess curve intercepts the zero axis at 0.38 mole fraction ethanol, in contrast to 0.20 for the ester samples, indicating that ethanol preferential sorption was retained at a higher ethanol concentration for the cellulose sample relative to the three ester samples. Therefore, it is concluded that ethanol preferential sorption was strongest for the unmodified cellulose.

A graph of LC system pressure drop versus mobile-phase ethanol concentration (Figure 5.3) for empty and packed columns shows that the pressure drop increases with increasing ethanol concentration up to a certain point where it reaches a maximum value and then declines. The empty-column pressure drop reaches a maximum at 0.24 mole fraction ethanol, indicating that a maximum in viscosity of the ethanol/water solution occurs at this composition; this phenomenon indicates that the interaction between ethanol and water in solution is highest at this point. The pressure drop curves for packed columns follow the same increasing-then-decreasing trend; the maximum of each curve is observed to correspond to the point at which the ethanol surface excess reaches zero for that polymer. Therefore, at this critical solution composition, there is no tendency for either solution component to be preferentially sorbed; below the critical composition (solution more polar), ethanol sorption is favored, and above the critical composition (solution less polar), water sorption is favored.

The strong (in relation to CTA and CATA esters) preferential sorption of ethanol by unmodified cellulose is an unexpected result, but it may be explained in terms of the chemical structures of ethanol and cellulose. Ethanol is a short-chain alcohol containing a two-carbon-long aliphatic chain with an attached hydroxyl group; the cellulose repeat unit is an aliphatic ring with pendant hydroxyls. Ethanol may adsorb to cellulose in such a way that its hydroxyl group is hydrogen-bonded to a cellulose hydroxyl, while its aliphatic “tail” is at the same time adsorbed to the aliphatic part of cellulose, making for a strong interaction.
Based on the results of this work, the addition of fluorine to cellulose in the form of trifluoroethoxyacetate substituents does not increase the preferential sorption of ethanol. This is seemingly in conflict with the results of Ishihara et al.\textsuperscript{5} (Table 5.1), where ethanol selectivity was observed to increase with increasing fluorine content in pervaporation experiments with a styrene-fluoroalkyl acrylate graft copolymer membrane. It may be that the increase in hydrophobicity that is expected to occur due to the presence of the perfluoro group in the trifluoroethoxyacetate substituent is offset by the hydrogen-bonding ability of the ethoxy ether linkage. Better results with cellulose derivatives may be possible by increasing fluorine content with ester substituents containing longer fluoroalkane chain segments (e.g. pentafluoropropoxyacetate and heptadecafluorodeoxyacetate).

Mulder et al. have shown that polymer-solute affinity is the factor that determines selective transport in pervaporation.\textsuperscript{8} Other results suggest that component mobilities (diffusivities) may dominate selectivity if the affinity effects are not strong enough.\textsuperscript{23,9} Therefore, it is concluded that the LC preferential sorption-measurement method employed in this work is not capable of quantitative prediction of pervaporation membrane performance, since it does not consider diffusivity effects. This method is very useful, however, for quick comparative screening of polymers for a particular application, allowing selection of polymers with high affinity for the desired component(s) prior to membrane development.

Based on data reported by Mulder et al.\textsuperscript{8} (Table 5.1) on the ethanol/water-pervaporation performance of a cellulose acetate membrane (which preferentially permeated water), and the similarity in preferential sorption behavior of CATA to CTA discovered in our work, it is predicted that pervaporation membranes made from cellulose trifluoroethoxyacetate esters would not preferentially permeate ethanol from aqueous solutions.
Figure 5.3  LC system pressure drop versus solution ethanol concentration for (□) empty column, (■) CE, (○) CTA, (+) $D_{SF} = 0.6$ CATA, (▲) $D_{SF} = 2.8$ CATA.
5.4. Conclusions

1. Preferential sorption of ethanol by a fully-substituted cellulose acetate ester does not change when acetate substituents are replaced by 2,2,2-trifluoroethoxyacetate (TFEA) substituents.

2. The preferential sorption of ethanol by unmodified cellulose is stronger than the preferential sorption by cellulose acetate and trifluoroethoxyacetate esters.

3. Ethanol is preferentially sorbed by cellulose and cellulose acetate and trifluoroethoxyacetate esters below a critical bulk solution ethanol concentration. Above this critical concentration, water is preferentially sorbed. This critical concentration was 38 mol.% ethanol for cellulose and approximately 20 mol.% ethanol for cellulose acetate and trifluoroethoxyacetate esters.

4. Pervaporation membranes made from cellulose trifluoroethoxyacetate esters are predicted not to preferentially permeate ethanol from aqueous solutions.

5.5. Acknowledgment

The authors are indebted to James E. Sealey and Charles E. Frazier for their pioneering work with fluorinated cellulose derivatives, and to Jody Jervis for her skillful and timely assistance with molecular weight determinations. One of the authors (JGT) would like to thank Gamini Samaranayake for providing invaluable advice and assistance in chemical synthesis and purification.

5.6. References


6. **OVERALL CONCLUSIONS**

Cellulose esterification in homogeneous solution using mixed anhydrides consisting of p-toluenesulfonic acid and carboxylic acids is highly effective. Esterification with long-chain aliphatic acids and fluorinated alkoxyacetic acids is readily accomplished, producing fully-substituted derivatives with minimal depolymerization of cellulose. DS is conveniently controlled by varying the ratio of mixed anhydride to cellulose. Full substitution is achieved with as little as 1.5 molar equivalents of mixed anhydride per cellulosic hydroxyl.

Waxy esters of cellulose, with n-alkyl ester substituent length of C\textsubscript{12} or greater, exhibit separate thermal transitions (melting and glass transitions) for ester substituents and main cellulose chains. This indicates that waxy ester substituents form a separate phase from the cellulose backbone. The melting point ($T_{m,L}$) of side-chain crystals increases linearly, at a rate of 10°C per carbon atom, as the length of substituents increases from C\textsubscript{12} to C\textsubscript{20}; $T_{m,L}$ increases from -19°C for C\textsubscript{12} to 53°C for C\textsubscript{20}. Main-chain $T_m$s of peracetylated waxy esters of cellulose converge with the melting transition of the olefinic (side-chain) phase and/or disappear as substituent length reaches C\textsubscript{18}.

Material properties important to melt processability (i.e. $T_m$, $T_g$, rate and degree of crystallization) can be effectively controlled by varying the types and DS of substituents (hydroxyl groups, acetyl groups, and larger aliphatic ester substituents of varying chain length). The effectiveness of melting point depression at low DS of large substituents increases with increasing substituent length for n-alkyl substituents up to lauryl (C\textsubscript{12}). At mid-DS of large substituent, increasing the substituent length has no further effect in melting point depression above a length of C\textsubscript{6} (hexanoyl). When substituent length reaches C\textsubscript{18}, the melting points of ester substituent and cellulose phases converge, and the melting point of the ester phase determines the melting point of the entire derivative.

Incorporation of trifluoroethoxyacetyl substituents into cellulose acetate esters does not appreciably affect the preferential sorption of ethanol from aqueous solutions;
therefore, cellulose trifluoroethoxyacetate membranes are not expected to selectively permeate ethanol in pervaporation of aqueous ethanol solutions. Cellulose (with free hydroxyls) unexpectedly exhibits the highest preferential sorption of ethanol (compared to acetate and trifluoroethoxyacetate esters); this is probably due to the high similarity in chemical functional group composition between cellulose and ethanol.
Jason G. Todd was born in 1970 in Cincinnati, Ohio. His family moved around the eastern US several times, living in Kentucky, New Jersey, Tennessee, and Virginia for varying lengths of time. He attended Tabb High School in Yorktown, VA before moving to Blacksburg, VA to enter classes at Virginia Tech in August, 1988. Jason completed a Bachelor of Science degree in Chemical Engineering at Virginia Tech in December of 1992. He had been working for about a year under Dr. Glasser as a lab technician for the Biobased Materials Center, working on projects such as isolation of cellulose from steam-exploded yellow poplar and pilot-scale synthesis of cellulose esters in homogeneous solution. Jason was accepted into graduate school in the Department of Wood Science and Forest Products and began study for a Master of Science degree in January of 1993.