Chapter 4: Submitted to *Carbohydrate Polymers*

Novel Cellulose Derivatives. VI. Preparation and Thermal Analysis Of Two Novel Cellulose Esters with Fluorine-Containing Substituents

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Abstract:

Two novel cellulose esters were prepared with fluorine (F)-containing substituents using homogeneous phase reaction chemistry in DMAc/LiCl. The partially substituted derivatives and their corresponding perpropionates proved to be thermoplastic polymers. The 2,2 difluoroethoxy and 2,2,3,3,4,4,5,5 octafluoropentoxy substituents were easily identified by ^1H and ^{19}F-NMR spectroscopy without disclosing their precise location on the anhydroglucose unit. Thermal analysis revealed modest or no crystallinity; glass transition temperatures between 53 and 113°C; and improved thermal stability, as compared to their F-free counterparts.

Introduction:

Increasingly, cellulosic materials are incorporated into multiphase polymer and material systems with synthetic materials[1-11]. Problems with compatibility, however, often limit the use of cellulosics in these systems. Compatibility problems arise from the fact that cellulosics are inherently more hydrophilic than their man-made counterparts due to their high level of oxygen.

The incorporation of hydrophobic moieties into cellulose was thought to increase the compatibility with synthetic polymers. Fluorine (F)-containing cellulose ethers were found to be thermoplastics with limited compatibility with polyesters[9]. The degree of compatibility depended on the amount of F in the sample suggesting that a variation in F-content might be exploited to increase miscibility of cellulosics and man-made polymers. The F-content of F-containing cellulose derivatives can be varied by changes in the degree of substitution with F-containing substituents (DS_F), the number of F-atoms in the F-substituent, and the type of fluorocarbon group. CF_2H-groups are known to be less hydrophobic than CF_3-groups due to the presence of an additional proton[12].

It was the goal of the present study to extend the range of F-containing cellulose derivatives with different degrees of F-content and hydrophobicity to derivatives having a single difluoroethoxy as well as an octafluoropentoxy substituent using the modification chemistry previously described[13].

Experimental:

Materials:

Cellulose was obtained from Whatman as cellulose powder designated CF-11. Its number average degree of polymerization was determined to be 190 by gel permeation chromatography[14]. DMAc, LiCl, chloroacetic acid, tosyl chloride and all solvents and reagents were obtained from Aldrich Chemical Company and used without further purification. 2,2-difluoroethanol and 2,2,3,3,4,4,5,5-octafluoropentanol were obtained from Lancester Chemical Company and used as received.

Methods

Synthesis of random copolymer: Random copolymers were synthesized in homogeneous solution using DMAc/LiCl and tosyl chloride as transesterification agent in accordance to Sealey *et al.*[13]. The procedure involves initially the synthesis of a so called free acid from the F-containing alcohols. A mixture of the respective F-containing alcohol and monochloroacetic acid (1:1 molar ratio) is refluxed for 24 h in an aqueous solution of NaOH according to Sealey *et al.*[13]. For the esterification, an amount of cellulose solution in DMAc/LiCl corresponding to 1 g of cellulose is placed in a three neck round bottom flask, stirred with a magnetic stirrer and held under nitrogen. After pyridine is added to the solution in a 3 to 1 molar ratio to tosyl chloride, the mixture is allowed to stir for 15 min before the free acid is added. The amount of free acid depends on the desired degree of substitution with the fluorinated ester group (DS_F). For a DS_F of 1.5, 0.75 mole equivalents of acid per OH group of cellulose is used. The acid is added slowly and allowed to stir for 5 min, before tosyl chloride, dissolved in DMAc to give a 50% solution, is added in a 1 to 1 molar ratio of chloride to free acid. The solution temperature is then raised to 40-50°C for 24 hours. Finally, the solution is precipitated into water, filtered and the isolated powderous random copolymer is dried in the vacuum oven over night.

Perpropionylation: The statistical F-esters may subsequently be perpropionylated. Typically, a 5% solution of the starting material is prepared in a 1:1 solution of acid and anhydride using a round bottom flask. Sodium alkanoate (0.3 eq M^{-1} of anhydride) is then added. The solution remains at room temperature while stirring, before it is heated to a boil for 2 hours. The mixture is then cooled to room temperature and precipitated into ten-fold excess of 0.1% HCl. The product is filtered, washed with water, and dried under vacuum.

NMR spectroscopy: ^{1}H and ^{19}F-NMR were recorded on a 400 Varian Instrument. A small amount of sample (approximately 20 μg) was dissolved in deuterated chloroform (1 ml) and measured in a 5 mm NMR tube. F-ester samples were characterized only by ^{19}F-NMR. In order to accurately determine peak shifts, all samples were run with the addition of 3-(trifluoro) methyl benzophenone as an internal standard, which has a chemical shift of -64.1 ppm.

Molecular weight determination: The molecular weights, polydispersity and Mark-Houwink exponential factor were determined by GPC with a differential viscosity detector (Viscotek Model No. 100) and a differential refractive index (concentration) detector (Waters 410) in sequence. The system was controlled by Viscotek software (Unical GPC software, Version 3.02). The materials were dissolved in THF and analyzed using a high pressure liquid chromatography system based on three Waters Ultrastyragel columns with pore sizes of 10^3, 10^4, and 10^6Å. Narrow molecular weight polystyrene standards were used to establish a universal calibration of the GPC columns.

Differential Scanning Calorimetry: DSC measurements were conducted on a Perkin Elmer model DSC4 with a Perkin Elmer Thermal Analysis Data Station. The temperature was scanned between -30°C and +270°C at a heating rate of 10°C/min. The samples were subjected to three heating and three cooling cycles. The glass transition temperatures (T_g) were taken as the mid-point of the step-function change in slope of the baseline and the melting transition was taken as the temperature corresponding to the maximum energy point of the endothermic peak.

*Thermogravimetric Analysis:*Thermogravimetric analysis was conducted using a Perkin-Elmer TSII Thermogravimetric Analyzer. A 10 mg (max.) sample was used without pre-drying. The analysis was carried out in air atmosphere, with a temperature rise of 10°C min^{-1} to 900°C.

Elemental analysis: The elemental analysis was provided by Quantitative Technologies Incorporated, New Jersey.

Results and Discussion:

The two fluoroalkoxy cellulose ester derivatives, having 2,2 difluoroethoxy and 2,2,3,3,4,4,5,5 octafluoropentoxy substituents, were prepared in accordance with the procedure of Sealey *et al.*[13] following the reaction scheme illustrated in Figure 1. The acetic acid derivatives were isolated as colorless liquids by distillation; and the esterification reaction was performed using the esterification reaction mediated by tosyl chloride. The difluoroethoxy and octafluoropentoxy derivatives were obtained with degrees of substitution of the F-substituent of 1.0 and 1.5, respectively, as was evident from elemental analysis (Table I).

The conversion of alcohol to alkoxy acetic acid is conveniently monitored using ^{1}H-NMR spectroscopy (Figures 2 and 3). Whereas the difluoromethyl group retains its peak at 3.8 ppm following ether formation, the OH-proton at 2.0 ppm vanishes and a new methylene peak appears at 4.3 ppm representing the methylene group of acetic acid. In addition, a carboxyl-H appears in the usual place (9-10 ppm) (Figure 2). Similar results are obtained for the octafluoropentoxy derivatives (Figure 3). Disappearance of the OH-signal at 2.3 ppm and appearance of a new methylene singlet and carboxyl-signal at 4.3 ppm and around 10 ppm, respectively testify to the successful synthesis of the fluoroalkoxy acetic acid (Figure 3). The downshift of the methylene and difluoromethyl-peaks representing the octafluoropentoxy species as compared to the difluoroethoxy species attests to the deshielding effect of the additional CF_2 moieties in the octafluoro derivatives.

^{19}F-NMR spectroscopy is a convenient method for analyzing fluorinated polymers. The two novel fluoroalkoxy cellulose ester derivatives having difluoroethoxy and octafluoropentoxy substituents proved to be no exception. The ethoxy derivative is characterized by a peak at –129 ppm corresponding to the CF_2H moiety (Figure 4). The pentoxy derivative shows peaks at -122, - 127, -132 and –140 ppm representing the fluorocarbon moieties (Figure 5). The peak patterns in the cellulose derivatives are analogous to the one found in the respective fluoro-alcohols (Table I), and the presence of fluorine in the cellulose esters indicates successful esterification.

A detailed peak assignment for both ^{1}H and ^{19}F-NMR spectroscopy of the various derivatives, alcohol, acid, and acetate, is given in Table II.

The chemical and molecular structure of the two novel fluorine-containing cellulose ester derivatives is also evaluated by molecular weight determination (by GPC) and thermal analysis (Table I). GPC data reveal surprisingly little depolymerization during the esterification reaction or the subsequent peracylation (Table I). The apparent decline in the Mark Houwink exponential factor (*a*), from nearly one to 0.5 in the novel derivatives is explained with the introduction of alkoxy acetate substituents along the backbone. N-alkyl esters of comparable dimensions do not show a similar decrease in a^{14}. The large degree of flexibility of the F-containing ester induced by the ether-linkage, as compared to alkyl esters, accounts for the apparent transformation of the cellulose derivative from a rod-like worm to a branched polymer.

Thermal analysis data by DSC reveal distinct glass transition temperatures for all derivatives, but faint melting transitions only for the perpropionylated difluoroethoxy cellulose derivative (Figure 6). A heat of fusion of only 0.7 J g^{-1} corresponds to only about 10% of that for comparable cellulose propionate. No other derivative studied revealed any sign of T_m. The glass transitions, which range between 53 and 113°C, are distinctly below that of cellulose propionate (Table I). The influence of the larger octafluoropentoxy group as compared to the difluoroethoxy group is revealed by the significant T_g-reduction by 13°C from 66°C to 53°C (see Table I). This agrees with similar results obtained for n-alkyl cellulose esters with increasing alkyl chain length[14].

The previously reported observation that OH substituted trifluoroethoxy cellulose derivatives had thermal transitions which were identical to those of the corresponding peracylated derivatives[13] was, however, not repeated. The OH-functional derivative had a T_g that was approximately 60°C higher than the corresponding peracylated derivative (Table I). This may possibly be explained with the difference in behavior between CF_3 and CF_2H terminal functionalities and their interaction with OH groups present. Related research on these derivatives has confirmed significant differences in intermolecular bonding behavior between the two types of fluorine-containing derivatives. Observations regarding solution behavior has pointed to a significant acidity of the difluoromethyl terminal group that has been explained with the presence of a lone proton surrounded by electron-withdrawing F-atoms[17]. Thus, differences in thermal behavior between OH-functional and peracylated derivatives are not entirely surprising. The increase in T_g in the OH-functional derivatives as compared to the peracylated products points to a strong influence of hydrogen bonding between OH and CF_2H on the molecular mobility.

Polymer fluorination is a common method of adding thermal stability to materials[17]. The TGA results obtained with the F-containing cellulose derivatives reveal increased thermal stability for the F-containing derivatives (Figure 7). Whereas the cellulose propionate control revealed moisture loss at temperatures up to 120°C, and thermal degradation commencing at about 230°C, F-containing cellulose esters fail to reveal moisture loss (suggesting nonsorption), and the first signs of thermal degradation are delayed to about 300°C. Furthermore, the degradation isotherm was shifted to higher temperatures for F-containing cellulose esters and the increase was more pronounced for the octafluoropentoxy derivative as compared to the difluoroethoxy derivative, indicating that thermal stability increases with increased F-content of the sample.

Conclusions:

The formation of fluoroalkoxy acetates of cellulose that has previously been reported for trifluoroethoxy acetates, has apparent widespread applicability to other fluoro-alcohols. Cellulose esters with high concentrations of fluorine (octafluoropentoxy groups) as well as with lone difluoromethyl substituents are accessible using the homogeneous phase reaction chemistry in DMAc/LiCl in conjunction with tosyl chloride catalysis.

Fluorine content and type of F-containing ester group impact thermal mobility (glass transition temperature) and thermal degradation behavior.

High as opposed to low fluorine concentration in substituents contributes to increased thermal stability.

Hydroxyl as opposed to peracyl functionality in F-containing cellulose ester derivatives has an unexpected effect on T_g which was attributed to the hydrogen bonding potential of CF_2H-groups as opposed to CF_3-groups.

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Literature cited:

1. D. Aptel, I. Carbasso. J. Appl. Polym. Sci., 1980, 25, 1969
2. Y. Nishio, S.K. Roy, R.St.J. Manley. Polymer, 1987, 28, 1385
3. Y. Nishio, R.St.J. Manley. Macromolecules, 1988, 21, 1270
4. J.-F. Masson, R.St.J. Manley. Macromolecules, 1991, 24, 6670
5. J.-F. Masson, R.St.J. Manley. Macromolecules, 1991, 24, 5914
6. J. Lsun, I. Carbasso. Macromolecules, 1991, 24, 3603
7. A.-W. White, C.M. Buchanan, B.-G. Pearcy, M.D. Wood. J. Appl. Polym. Sci., 1994, 52, 525
8. T. Kondo, C. Sawatari, R.St.J. Manley, D.G. Gray. Macromolecules, 1994, 27, 210
9. C.E. Frazier, W.G. Glasser. J. Appl. Polym. Sci., 1995, 58, 1063
10. R.St.J. Manley, in Cellulose Derivatives – Modification, Characterization and Nanostructures. T.J. Heinze, W.G. Glasser, eds., ACS Symp. Ser. 688, 253 (1998)
11. M.F. Davis, X.M. Wang, M.D. Myers, J.H. Iwamiya, S.S. Kelley. in Cellulose Derivatives – Modification, Characterization and Nanostructures. T.J. Heinze, W.G. Glasser, eds., ACS Symp. Ser. 688, 283 (1998)
12. R.A.L. Jones, E.J. Kramer, Polymer, 34 (1), 1993, 115
12. J.E. Sealey, C.E. Frazier, G. Samaranayake, W.G. Glasser. Manuscript submitted
13. A. Wallis, R. Evans. J. Appl. Polym. Sci. 1989, 37, 2231
14. V. Davé, W.G. Glasser. Polymer, 1997, 38, 2121
15. J.E. Sealey, G. Samanaranayake, J.G. Todd, W.G. Glasser. J. Polym. Sci.: Pt B, 1996, 34, 1613

16. U. Becker, J.G. Todd, W.G. Glasser. In Cellulose Derivatives – Modification, Characterization and Nanostructures. T.J. Heinze, W.G. Glasser, eds., ACS Symp. Ser. 688, 315 (1998)

17. R.G. Bauer, J. Fire Retard. Chem., 1978, 5, 200

Table I: Molecular weight and thermal characteristics of novel F-containing cellulose esters

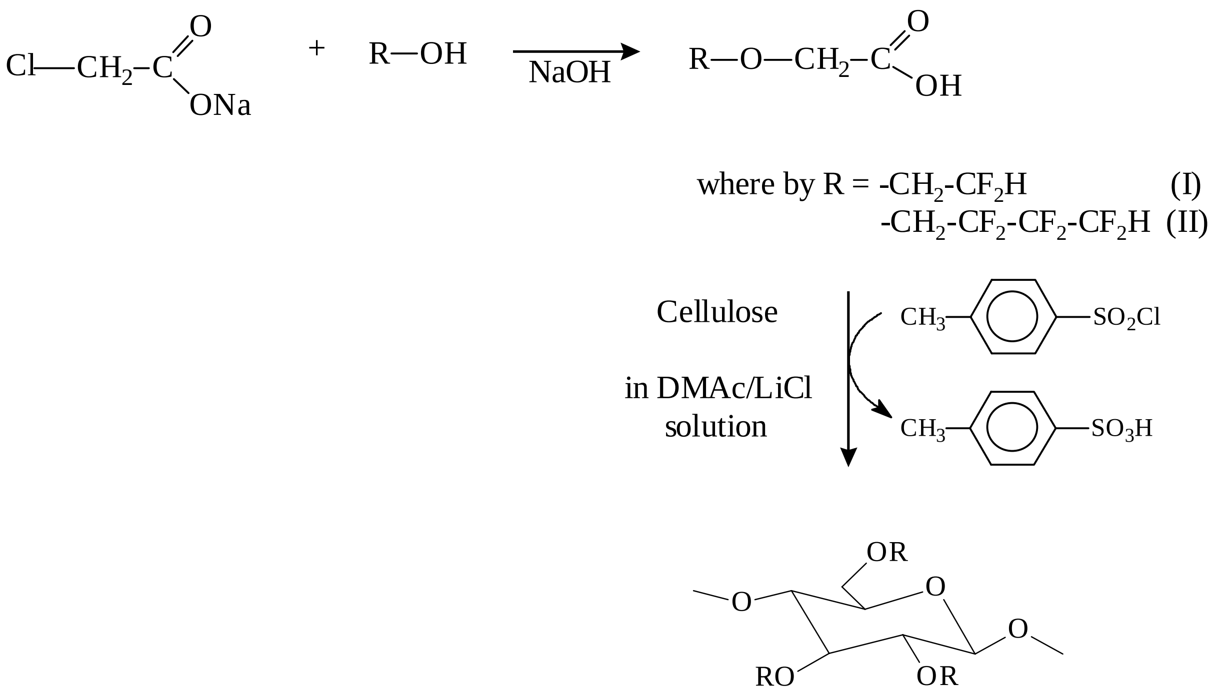
Sample	DS_F[1]	DS_{pr}[2]	F-content, %[3]	DP_n[4]	Mw/Mn[4]	a[5,4]	T_g, °C	T_m,°C
CP	n/a	2.6	0	350	1.6	0.9	130	215
Cellulose difluoroethoxy acetate	1.0	0	11.5	n/a				
Cellulose propionate difluoroethoxy acetate	1.0	2.0	12.9	187	1.3	0.7	66	211
Cellulose octafluoropentoxy acetate	1.5	0	39	194	1.8	0.5	113	no T_m observed
Cellulose propionate octafluoropentoxy acetate	1.5	1.5	30.1	181	1.4	0.6	53	no T_m observed

[1] degree of substitution with the F-containing substituent
[2] degree of substitution with propionyl substituent
[3] by elemental analysis
[4] from GPC data
[5] Mark-Houwink exponential factor *a*

Table II: Peak assignment for alcohols, acids and esters in NMR-spectra

Substituent species	F-Species	
	Difluoroethyl group	Octafluoropentyl group
Alcohol - ^{1}H-NMR		
CH_2	3.8 (tt)[a]	4 (tt)
CHF_2	5.85 (tt)	6.0 (tt)
OH	2.0 (s)	2.3 (s)
- ^{19}F-NMR		
CF_2H	-129 (s)	-122 (s) -127 (s) -132 (s) -140 (s)
Acid - ^{1}H-NMR		
CH_2 (a)	3.8 (tt)	4.1 (tt)
CH_2 (b)	4.3 (s)	4.3 (s)
CO_2H	9.3 (s)	10.4 (s)
CHF_2	5.95 (tt)	6.0 (tt)
- ^{19}F-NMR		
CF_2H	-65	
Ester - ^{19}F-NMR		
CF_2H	- 129 (s)	-122 (s) -127 (s) -132 (s) -140 (s)

[a] *s* signifies singlet, *d* represents a doublet and *t* a triplet



where by R = $-CH_2-CF_2H$ (I)
$-CH_2-CF_2-CF_2-CF_2H$ (II)

where R = $CO-CH_2-O-CH_2CF_2H$ (III)
= $CO-CH_2-O-CH_2CF_2CF_2CF_2CF_2H$ (IV)

with DS of 1-2, remaining R = H

With:
I: 2,2 difluoroethoxy acetic acid
II: 2,2,3,3,4,4 octafluoropentoxy acetic acid
III: cellulose 2,2 difluoroethoxy acetate
IV: 2,2,3,3,4,4 octafluoropentoxy acetate

Figure 1:
Reaction scheme for homogeneous phase esterification in accordance with the procedure of Sealey *et al*. [12].

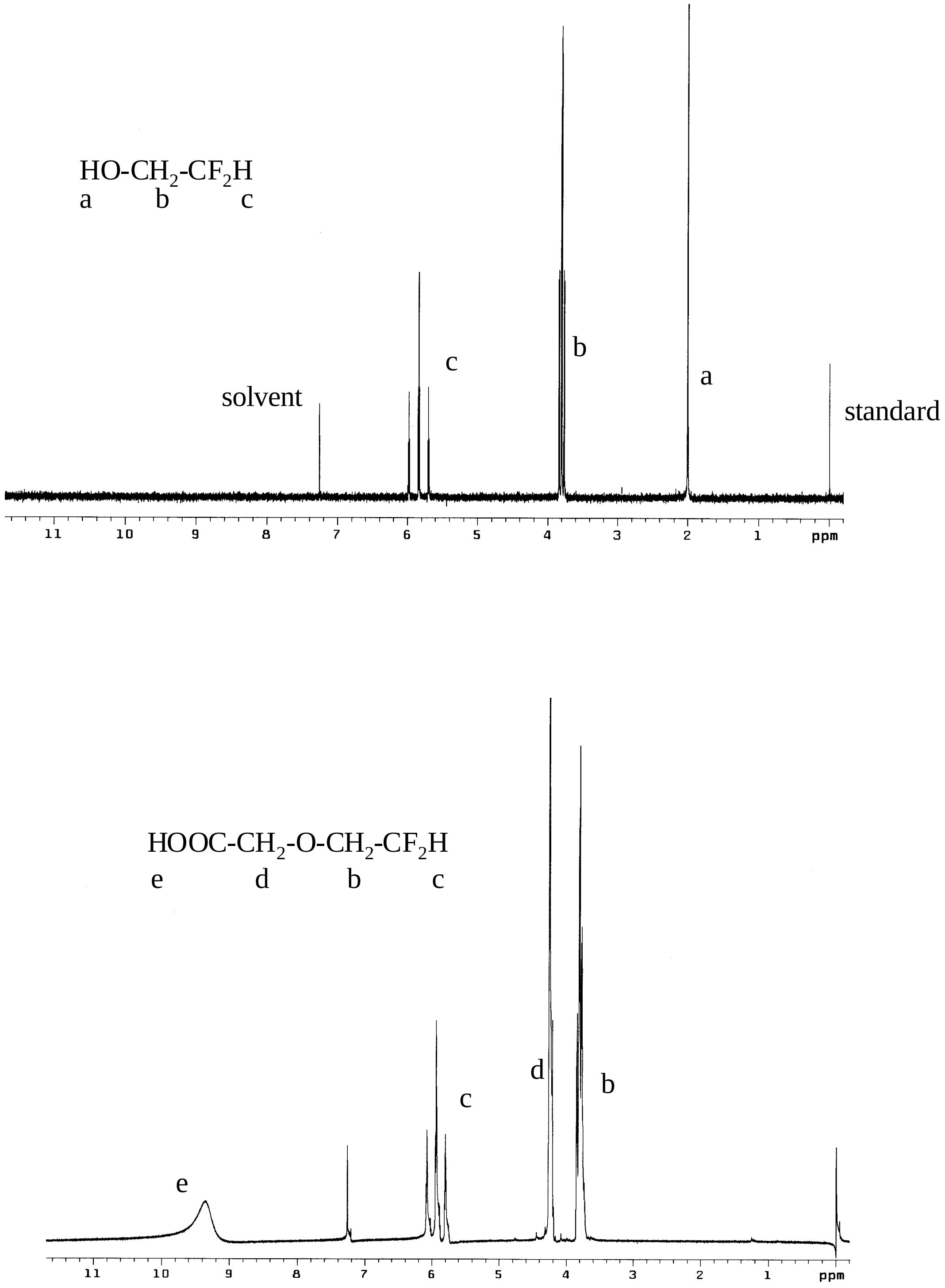


Figure 2:
^{1}H-NMR spectra of difluoroethanol (top) and difluoroethoxy acetic acid (bottom). The solvent is deuterated chloroform and the internal standard is trimethyl silane (TMS).

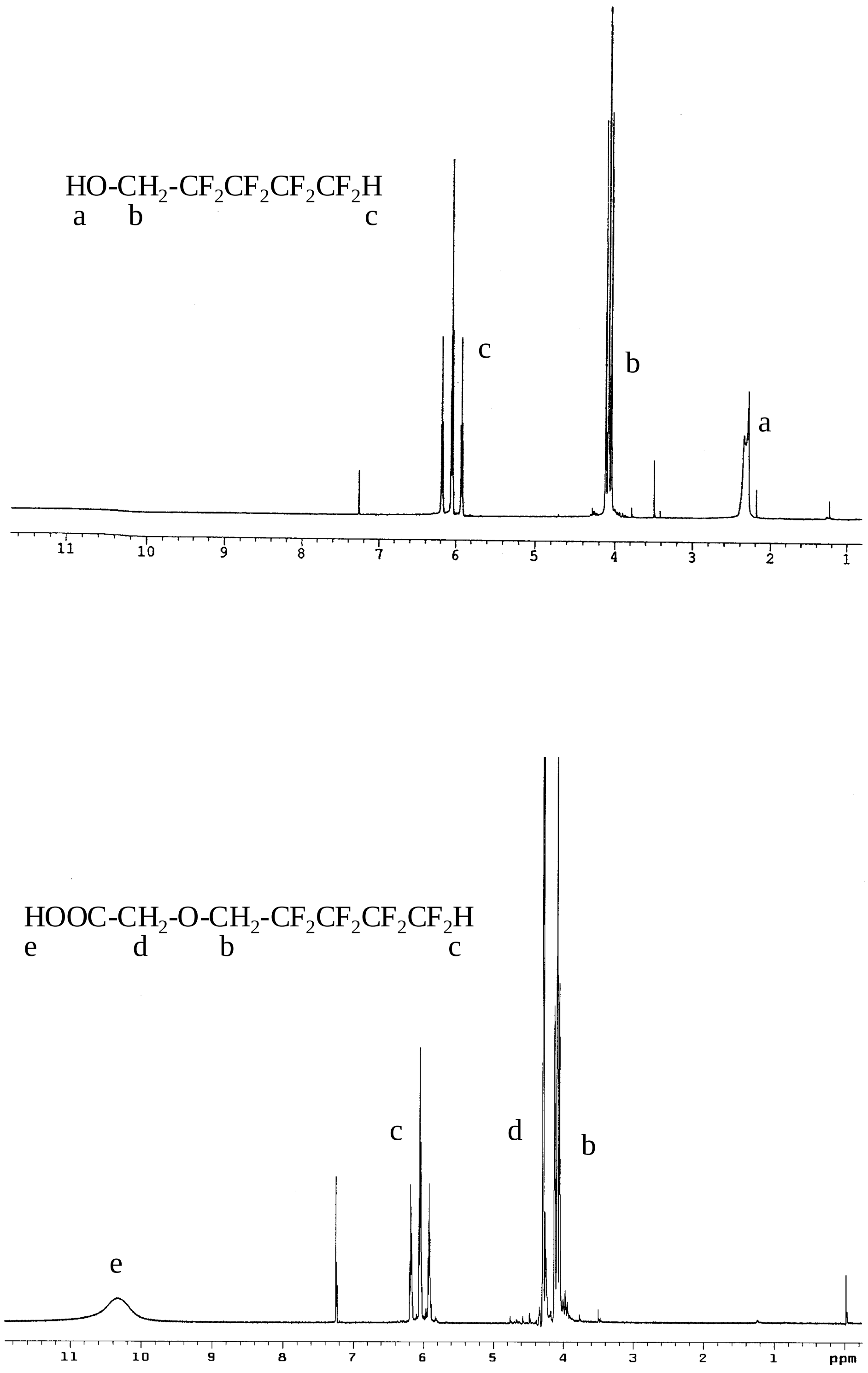


Figure 3:
^{1}H-NMR spectra of octafluoropentanol (top) and octafluoropentoxy acetic acid (bottom). Solvent and standard are the same as in Figure 3.

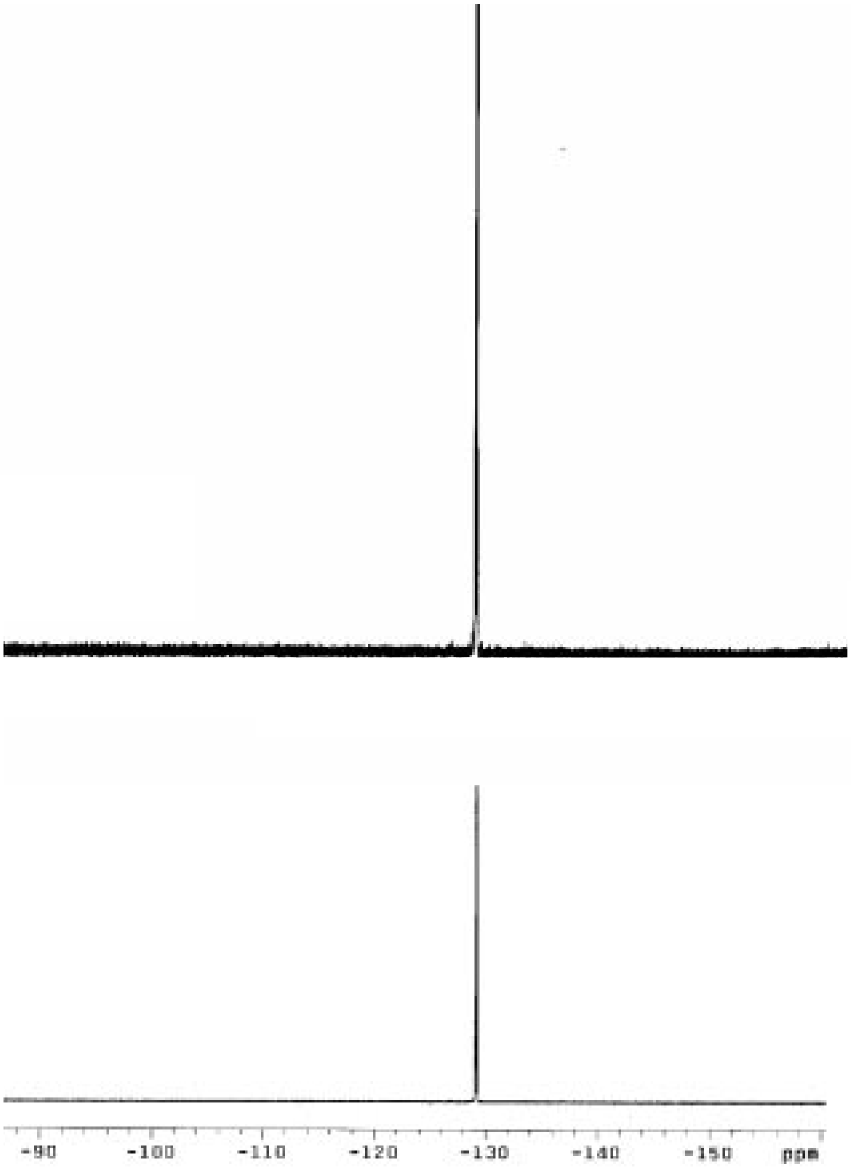


Figure 4:
^{19}F-NMR spectra of difluoroethanol (top) and cellulose difluoroethoxy acetate (bottom). The internal standard is 3 (trifluoromethyl) benzophenone at -64 ppm.

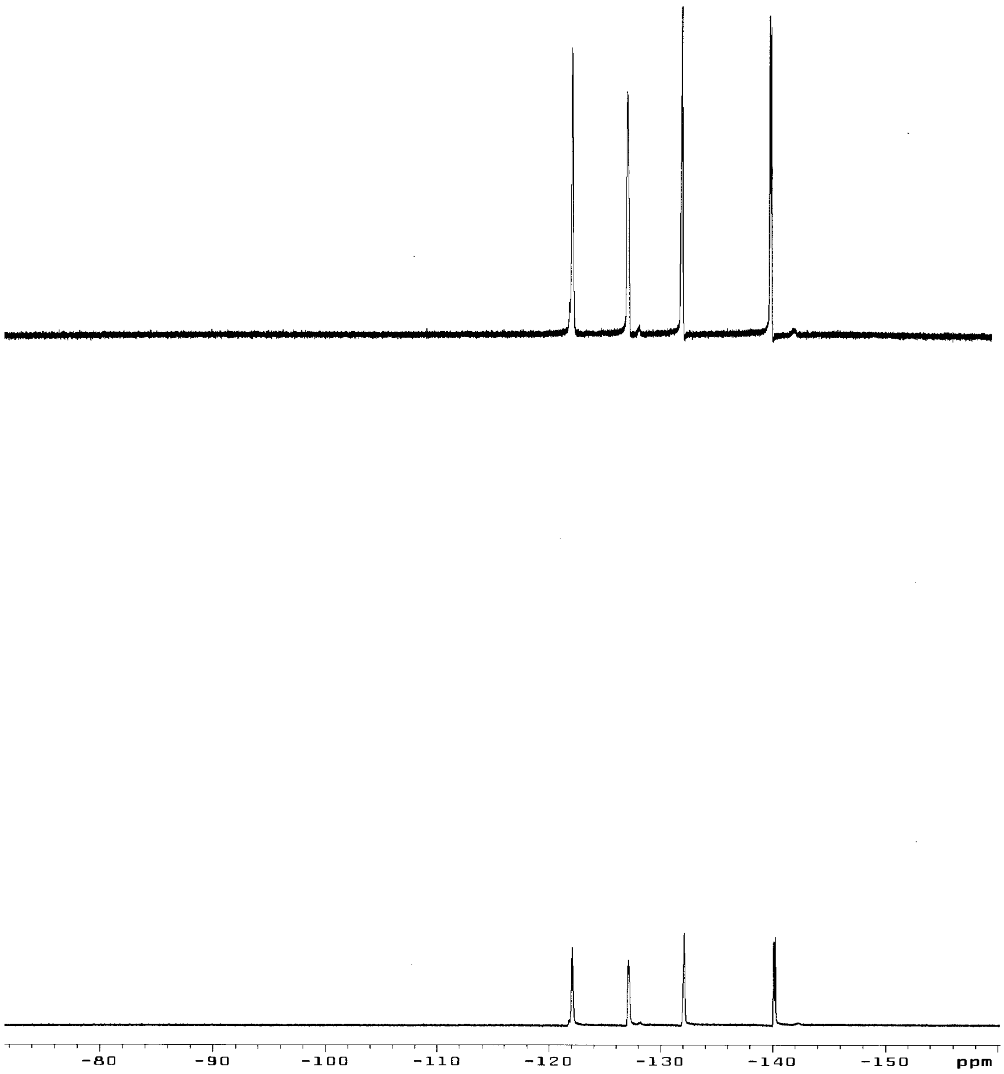


Figure 5:
^{19}F-NMR spectra for octafluoropentanol (top) and cellulose octafluoropentoxy acetate (bottom). The spectrum is referenced to 3-(trifluoromethyl) benzophenone at -64 ppm.

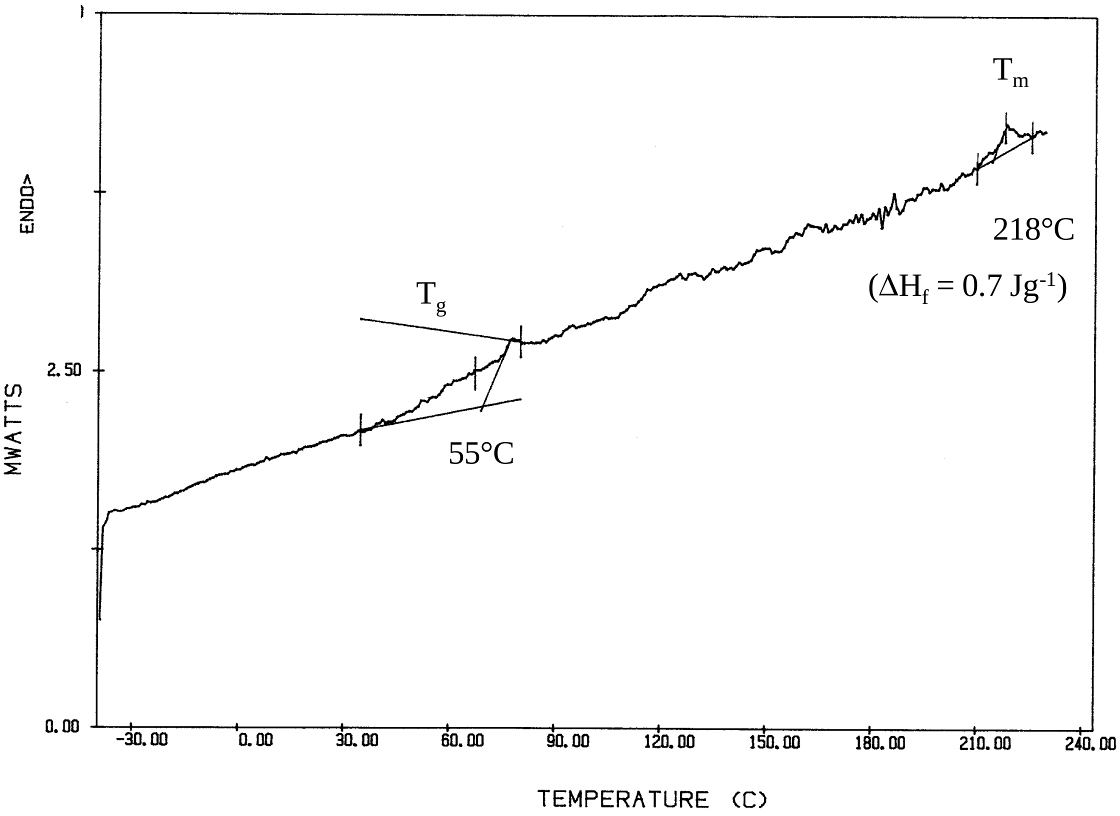


Figure 6:
DSC thermogram for cellulose propionate difluoroethoxy acetate (7.2 mg).

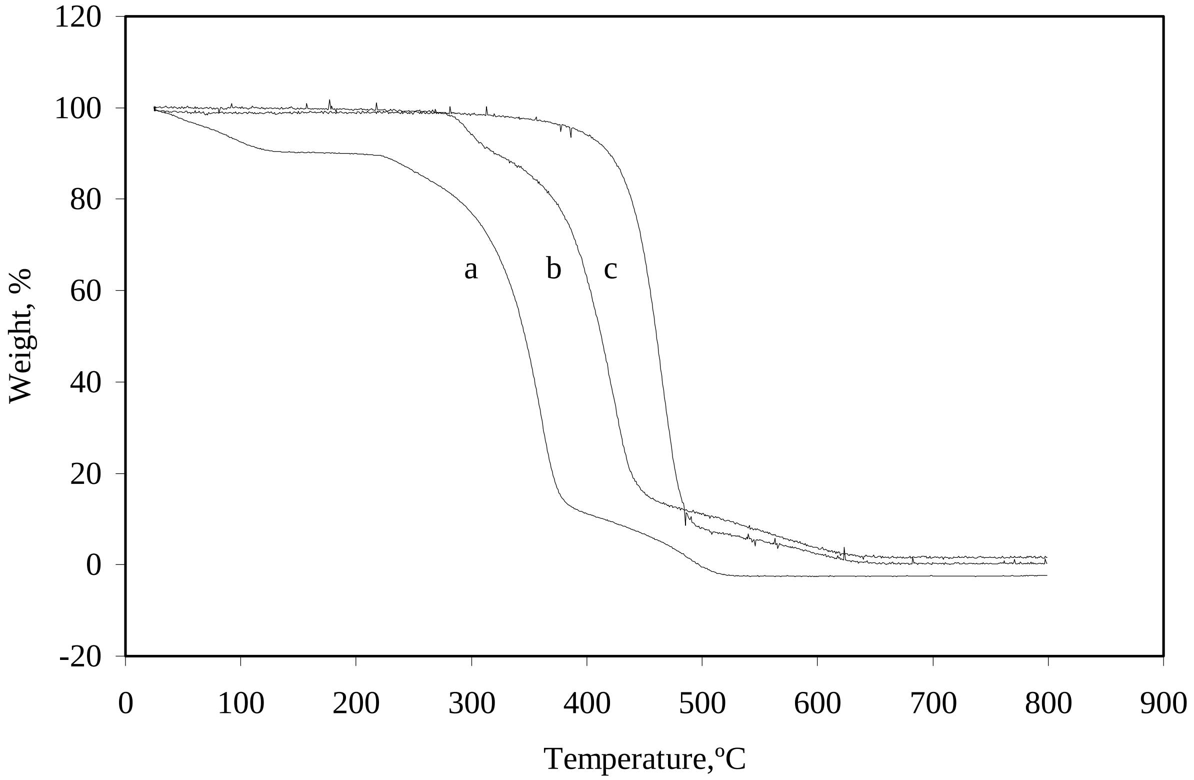


Figure 7:
TGA thermogram for cellulose propionate and F-containing esters. a: cellulose propionate, b: cellulose propionate difluoroethoxy acetate, c: cellulose propionate octafluoropentoxy acetate.