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Surface Segregation Phenomena in Blends of Cellulose Esters

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Abstract:

The principle of surface segregation and subsequent self-assembly of mixtures of molecules has been utilized to create cellulosic films that have properties characteristic of smart materials. This has been achieved by solvent-casting a blend of cellulose propionate and an fluorine (F)-containing cellulose ester derivative. Evidence suggests that surface segregation of the F-containing species takes place spontaneously in cellulosic systems. Cellulose propionate films containing a small amount of F-containing cellulose derivative exhibit a much lower surface free energy (i.e. are more hydrophobic) than predicted by the rule of mixing, and this indicates surface segregation. The current research examined the influence of the chemistry of the fluorine-containing component (type of derivative and chemistry of the F-containing group) on the segregation process.

Introduction:

A smart material is defined as a structure "...having the following attributes: it senses the environment, it responds in a purposeful way through design or by means of a logic controller element" (1). The surface segregation and subsequent self-assembly observed in some multicomponent films can be classified as a smart process, and thus the resulting film is a smart material.

The principle of surface segregation (see below) allows constructing films with surface energetics distinctly different from the bulk phase. Natural polymers with hydrophobic surfaces can be created in this manner, although the bulk retains the usual hydrophilic nature which is due to a high oxygen content. This creates new opportunities for applications of natural polymers. For example, cellulose and its derivatives have achieved prominence in the biomedical field as kidney dialysis membranes. However, advancements in this field have been limited because of the limited surface energetics of cellulosic materials. As polymers of natural origin, cellulose and its derivatives are prime candidates as raw materials for biomedical implants because of their general biological compatibility and biodegradability. However, for an implant material to function at the interface with living cells and body fluids, characteristic surface requirements must be met which prevent the spontaneous formation of blood clots. The general ability of foreign materials to cause thrombosis constitutes one of the principal limitations of biomedical implant materials. While it is recognized that the process of blood clotting is initiated by the adsorption of proteins on the surface of the implants, consensus has not yet been reached over whether this process is aggravated by excessively hydrophilic or hydrophobic

surfaces (2,3). General agreement has, however, been reached over the issue of the importance of surface engineering in terms of polarity. Thus, the ability to engineer the critical surface free energy (γ_c) of implant materials is pivotal to the development of biomedical implants (4). Most studies indicate that thrombogenicity increases with increasing γ_c (5), and that simultaneously, clotting time decreases (6). This suggests that a more hydrophobic surface is less prone to thrombosis. It is therefore of interest to examine methods of engineering the surface characteristics of cellulose-based materials in terms of their surface free energy.

While fluorine plasma treatment represents the easiest and most widely practiced method of surface modification, negative toxicological effects have been noted from this method which result from the partial molecular breakdown and leaching of toxic degradation products into the surrounding medium (7). Utilizing the smart process of self-assembly, it is possible to create cellulose-based materials with hydrophobic surfaces for potential use as biomedical implant materials.

The Principle of Spontaneous Self-Assembly by Surface Migration

The principle of spontaneous segregation of blend components by migration of one component to the surface on the nano-scale has been employed for engineering bi-layered materials in the past. By mixing two incompatible polymers with each other in a blend, molecular composites with a distinct surface layer, which is different from the bulk phase, can be obtained.

Surface migration is a thermodynamically-driven process. Fundamental thermodynamics dictates that a system adopt the state of lowest possible total free energy under equilibrium conditions. In the case of a film consisting of at least two polymers, three quantities have to be taken into account: 1. entropy of mixing; 2. interaction energy between polymers; and 3. surface free energy (8). Quantities 1 and 2 are given by the composition of the system. At a given film composition, however, the surface free energy, which is the interfacial energy between the film and air (which is considered to be hydrophobic) can be subjected to changes. During film formation the system rearranges itself so that the lowest free energy component resides preferentially at the surface, and therefore the lowest free energy of the entire system is gained. Therefore, surface migration can be used to create a system with a low surface free energy, i.e. a hydrophobic surface.

Since fluoro-carbon molecules are known to have low surface free energies, they are likely to migrate to the surface in a mixture of fluorine (F)-free and F-containing molecules. The goals of this study were to examine the surface migration effects of two types of novel F-containing cellulose derivatives in a blend with cellulose propionate. The first type of F-containing component was a mixed ester of cellulose propionate (CP) with fluoroalkoxy acetate groups whereby the F-containing substituents were randomly distributed, and the second type of component was a fluorine-terminated cellulose propionate oligomer with exactly one F-containing endgroup (ie, with a blocky type of architecture). Both F-containing species were expected to surface-segregate, but differences in migration behavior were expected depending on the difference in the

chemistry of the derivative and the type and the distribution of F-containing group. Two different F-containing groups were used, trifluoroethyl (with CF₃ terminus) and octafluoropentyl (with CF₂H terminus) substituents.

Energetic effects that stem from the presence of atoms other than hydrogen (X) in hydrocarbon containing molecules are the cause for the surface migration of F-containing molecules. These effects are described with nearest neighbor interactions. χ_s is defined as the difference between the adsorption energies (U_α) of the segments of the components ($\alpha = 1$ or 2 in a two component system),

$$\chi_s = U_1 - U_2 \quad (\text{equation 1}),$$

where

$$U_\alpha \equiv u_\alpha / k_B T \quad (\text{equation 2}),$$

and

$$u_\alpha \equiv \omega_{\alpha s} - 0.5\omega_{\alpha\alpha} \quad (\text{equation 3})$$

with k_B as the Boltzmann constant, T the temperature, $\omega_{\alpha\alpha}$ as the intracomponent interaction energy, and $\omega_{\alpha s}$ the surface interaction energy. u_α represents the difference in adsorption energies between the surface and the bulk (9). Thus χ_s is a measure for the adsorption energy difference between the segments of the two constituent chains, and this is a measure for the preference of one component to be at the surface over the other (10). In the case of a mixture at an energetically neutral surface (like air) the term simplifies to

$$\chi_s = - (\omega_{11} - \omega_{22}) / k_B T \quad (\text{equation 4})$$

with ω_{11} and ω_{22} as the interaction energy between the monomers in the bulk where ω_{11} is larger than ω_{22} . A positive χ_s is an expression for the fact that the system partitions the component with the relatively less favorable monomer interaction in the bulk, i.e. less attraction forces between the monomers, to the surface (11). This species experiences less energy loss due to the smaller number of neighbors at the surface than a species with a large interaction energy. In systems like C-H and C-F, possible interactions arise from London forces. The C-F bond has a high polarity, but at the same time, due to the high electronegativity of the fluorine atom, a low polarizability. London forces are proportional to polarizability. The C-F containing species has therefore weaker London forces and thus less interaction energy when compared to a C-H containing species. This results in a positive χ_s -parameter and it drives the partitioning of the fluorinated component to the surface. Altogether, the result is a lower surface free energy. The more F-atoms present, the weaker are the London forces. As a result, the χ_s parameter becomes more positive. This means that the driving force for surface migration increases.

The F-containing, randomly-substituted cellulose esters have more F-containing substituents per molecule than an F-terminated oligomer, which has exactly one F-containing substituent (Figure 1). Thus the driving force for the random copolymer is larger on a molecular basis. But at the same time, the F-containing groups of the terminated oligomers are independent from each other, whereas in the random copolymer many F-substituents are connected through the cellulose backbone. In addition the oligomers are more mobile and encounter fewer entanglements due to their smaller size.

Thus it is expected that the surface migration of the oligomers is more efficient when compared to the random copolymers on the basis of number of F-containing groups in the system. Consequently, blends containing F-terminated oligomers are expected to yield materials with lower surface free energy than blends with randomly substituted F-containing copolymers.

Comparing the F-containing substituents alone shows two effects depending on the chemistry of the substituent. First, the χ_s parameter increases with increasing number of F-atoms in the group. In the case of an energetically neutral surface, the value of χ_s can be deduced from the cohesive energy density (CED) since the CED is proportional to $\omega_{\alpha\alpha}$ (12). For polymers, the CED can be calculated through group contribution as the sum of the molar attraction constants, F, for the group (13). For every proton that is replaced by a fluorine atom, the interaction energy decreases. Therefore, the more H-atoms are replaced by F-atoms, the lower is the interaction energy of the species. Consequently, χ_s increases. As χ_s represents the driving force for the surface segregation, a larger value of χ_s indicates a stronger “pulling force” for the surface segregation and the equilibrium state is expected to be reached in a shorter time. Accordingly, derivatives containing the octafluoropentyl group are expected to show a larger degree of surface segregation and therefore a more hydrophobic surface when compared to the trifluoroethyl-containing derivative of the same type.

The overall objectives of this study were to synthesize novel types of F-containing cellulosic derivatives and to examine their surface segregation properties in relation to

fluorine content and polymer architecture. The F-containing components were either randomly-substituted cellulose esters with variable F-content and with either CF₂H- or CF₃-terminal groups, or they were F-terminated cellulose propionate oligomers.

Experimental

Materials.

Micro-crystalline CF-11 cellulose was purchased from Whatman Chemicals. Cellulose propionate was obtained from Eastman Chemical Co. All solvents were obtained from Fisher Scientific and used as received, except tetrahydrofuran for the synthesis of the F-terminated oligomers, which was used freshly distilled over sodium. P-toluene-sulfonyl chloride (TsCl) , toluene diisocyanate (TDI), and other reagents were obtained from Aldrich Chemical Co. and used as received.

Methods

Statistical F-ester synthesis. Cellulose mixed esters with fluorine-containing substituents randomly-distributed along the cellulose backbone (statistical F-ester) were synthesized via homogeneous phase reaction of cellulose solution in dimethylacetamide / lithium chloride (DMAc/LiCl). This reaction is described in detail elsewhere (14). Briefly, a fluorinated acid was reacted with cellulose in solution via a mixed anhydride intermediate formed with p-toluene sulfonyl chloride (TsCl). The fluorinated acids used were trifluoroethoxy acetic acid and octafluoropentoxy acetic acid. The acids were synthesized by reaction of either 2,2,2-trifluoroethanol or 2,2,3,3,4,4,5,5-octafluoropentanol, respectively, with chloroacetic acid in water under reflux with strong alkali. Pyridine,

followed by fluorinated acid, and finally TsCl, were added to cellulose in DMAc/LiCl solution. The reaction mixture was stirred overnight at 40-60°C. The resulting randomly-substituted fluorinated cellulose esters had a degree of substitution of fluorinated substituent (DSF) of approximately 1.5 (by NMR and/or elemental analysis). The remaining cellulose hydroxyl groups were subsequently acylated via reaction with acetic or propionic anhydrides, resulting in cellulose mixed esters with a random distribution of fluorinated and unfluorinated ester substituents. Molecular weight distributions of the random mixed esters were determined by GPC.

Fluorine-terminated cellulose propionate segments were prepared using monofunctional (OH-terminated) cellulose esters of variable degree of polymerization and coupled with fluorine-containing alcohols. In brief, the procedure involves first the degradation of cellulose propionate into CP oligomers of various degrees of polymerization (DP) as described elsewhere (15). The resulting segments were endcapped with toluene diisocyanate according to deOliveira and Glasser (16). The isocyanate terminated oligomers were immediately coupled with a fluorinated alcohol. Typically, 3 grams of the predried endcapped oligomer were placed in a 250 ml three neck round bottom flask with 0.01 ml of stannous octanoate as a catalyst. Two necks of the flask were closed with rubber septa, then the flask was placed in a polycarbonate desiccator with rubberseal and connected to a vacuum pump overnight. The flask was then connected to a condenser and flushed with prepurified nitrogen gas. Subsequently, 60 ml of freshly distilled THF were introduced into the flask using syringe and needle. The flask was put into an oilbath and heated to 50°C. At that time, a 5 molar excess of the F-containing

alcohol was added via syringe. The flask was stirred at 50°C for 24 hours under nitrogen. After that, it was allowed to cool to room temperature. The product was precipitated in petroleum ether under vigorous stirring. The precipitate was filtered and washed several times with petroleum ether. The product was dried and kept until further use in a small polypropylene container.

Characterization. Characterization involved ^1H and ^{19}F -NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and solubility studies. The molecular weight and the distribution of hydroxyl-terminated CP oligomers 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 CP oligomers were dissolved in THF and analyzed using a high pressure liquid chromatography system. The calculations were based on an universal calibration curve using polystyrene standards.

^{19}F -NMR spectra were recorded on a Varian 400 MHz spectrometer. The samples were dissolved in protonated THF and run without lock. In order to accurately determine peak shifts, all samples were run with the addition of 3-(trifluoro)methyl benzophenone as an internal standard (at -64.15 ppm).

^1H -NMR was used to determine the degree of polymerization through endgroup determination. The analysis was conducted on a Varian 400 MHz instrument with deuterated chloroform as the solvent. In order to increase the detection sensitivity of the hydroxyl proton, the oligomers were silylated at the lone terminal hydroxyl group using

chlorotriethylsilane as the silylation agent as described elsewhere (17). The DP was calculated as a ratio of the peak areas for the silyl protons to the cellulose backbone protons.

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 point of the endothermic peak.

The solubility of the F-containing samples was tested in various solvents. Typically a small amount of the sample was transferred into a 4 ml glass vial and solvent was added. If completely dissolved, the resulting solution had a concentration of about 0.5-1%. The vial was equipped with a magnetic stir bar and stirred overnight. At that point solubility was determined visually.

3. Blend Preparation. Cellulose propionate/F-containing cellulose propionate (CP/CP-F) blends were prepared volumetrically. This involved initially the preparation of stock solutions of CP and CP-F in THF. Blends were prepared by mixing these solutions to the desired content of F-containing species. The total solids content of all solutions was 5% w/v.

4. Contact Angle Measurements. Cellulose ester and cellulose ester blend films were characterized by contact angle (CA) measurements. This was based on a modified

Wilhelmy Plate method. Microscope cover slides were cleaned thoroughly in hexanes, dried and subsequently dip-coated with the respective solutions. The solvent was evaporated at 4°C over night and all films were stored for three days before the contact angle measurements. Great care was taken to ensure that all films were prepared in the same fashion. The contact angle measurements were conducted with deionized water as the wetting medium using a CAHN Analyzer, controlled both manually and by CAHN control software DCA2d Version 2.0. The instrument recorded the force depending on the immersion depth, and the water contact angle was calculated using the force and the surface free energy of water. Six measurements were performed per sample.

Results and Discussion

1. Synthesis.

The synthesis of F-containing statistical esters and terminated CP segments is schematically illustrated in Figure 2. Monofunctional, OH-terminated cellulose propionate segments with variable degree of polymerization were prepared by partial degradation with HBr under esterification conditions.

The molecular weights of the cellulose propionate segments were determined by GPC and NMR spectroscopy (Table I). The two methods are mutually supportive. For NMR, the signal of the one OH end group was enhanced by reaction with chlorotriethylsilane. The 15 ethylsilane protons show a characteristic and easily distinguished proton peak at 0.55 ppm. Integration of this peak and the peaks associated with the cellulose backbone protons is used to calculate the degree of polymerization. At high

block sizes (large DP), the enhanced ethylsilane signal becomes less distinct and block size determination by NMR becomes less accurate. A comparison of DP determinations by NMR and GPC (Figure 3) reveals that NMR and GPC produce almost identical results at low DP-values whereas at high block sizes (large DP), the determination by NMR yields a higher DP value. At higher molecular weights, a complete reaction of the chlorotriethylsilane becomes more difficult. This accounts for the fact that the DP values obtained by NMR are higher than those found by GPC.

The OH-terminated segments were subsequently end-capped with toluene diisocyanate resulting in a monofunctional terminated oligomer. The resulting NCO-terminated cellulose propionate oligomer was immediately (to avoid degradation of the remaining isocyanate groups) reacted with F-containing alcohols in which both F-content and terminal functionality (CF_2H versus CF_3) vary (Figure 1). The alcohols were trifluoroethanol (CF_3 -terminus) and octafluoropentanol (CF_2H -terminus). The reaction of the F-containing alcohols and the cellulose propionate segment was confirmed by ^{19}F -NMR spectroscopy. As a result of the formation of a terminated segments, the CF_3 -peak in the ^{19}F -NMR spectrum shifted downfield from -14.4 ppm to -11.5 ppm (Figure 4). All ^{19}F -NMR samples were run with an internal standard (3-(trifluoro)methyl benzophenone). This was necessary because ^{19}F -resonances often shift, consequently, the shifts can only be accurately measured when the CF_3 -peak position is observed in relation to a standard peak. The F-containing cellulose derivatives used in this study are summarized in Table II.

2. Characterization of F-containing cellulose derivatives.

The characteristics of random and block copolymers containing fluorinated substituents involve solubility testing and thermal analysis. The solution characteristics of F-derivatives in various solvents are shown in Table III. The results reveal significant differences between the statistical F-ester and the terminated segments. Among the statistical F-esters, differences in solution behavior depended on the nature of the F-containing substituent. F-esters containing a substituent with a CF_3 -terminus were soluble in non-polar organic solvents like chloroform and dichloromethane, as well as in acetone. In contrast, F-esters with an F-containing group with a CF_2H -terminus are not only soluble in these solvents but also in such alcohols as methanol and ethanol. This behavior is attributed to the lone proton of the CF_2H -terminus. This proton is covalently linked to a carbon to which two F-atoms are attached. Due to the high electronegativity of the F-atoms, the carbon has a strong positive partial charge. This charge increases the negative inductive effect of the carbon onto the hydrogen atom. Altogether, the proton becomes very electron deficient and as such is able to engage in secondary interaction, like for example hydrogen bonding, with the hydroxyl-groups of the alcohols. These interactions lead to the dissolution of the copolymer in alcoholic solvents.

The end-terminated segments, on the other hand, do not exhibit a solubility behavior that depends on the chemistry of the F-containing endgroup. All segments were formed turbid solutions in all tested solvents and at all concentrations, and did not settle out in several weeks. This behavior also did not depend on the molecular weight of the cellulose propionate segments or the type of F-containing endgroup.

Consistent with the solution behavior of other amphiphilic substances, it is at this point hypothesized that this behavior reflects the formation of micelles where the F-containing endgroups form the core, and the corona consists of cellulose propionate residues (Figure 5).

The examination of thermal properties of copolymers by DSC produces results consistent with the generic architecture of the different derivatives (Figure 6). Whereas the F-esters revealed a gradual, transitionless decline in T_g and T_m with increasing content of fluorinated substituents, the terminated segments revealed thermal transitions that were identical to those of the parent cellulose propionate. The fluorinated end groups in the segments, constituting only a minor part of the molecule, proved to have an insignificant influence on the thermal copolymer properties.

3. Contact angle measurements of blended films.

Films prepared from blends of cellulose propionate and fluorinated cellulose derivatives were characterized by contact angle measurements. Preliminary results revealed that water contact angles varied between approximately 75 and 110°, and the degree of variation from the CP control depended on fluorine content, substituent type, and polymer architecture in a significant way (Figure 7). The pure F-ester film with a CF_2H -terminus achieves a maximum advancing water contact angle of 110°. This angle is lower than values found in the literature for fluorinated surfaces (18). However, the literature values describe surfaces with CF_3 -groups, and the present case examines a surface containing CF_2H -groups. The lower contact angle is again explained by the

presence of the lone proton at the CF₂H-terminus which can engage in hydrogen bonding with the water molecules in the same fashion as outlined above.

The F-ester shows an exponential increase in contact angle at low blend contents of F-containing component. This behavior represents a deviation from the rule of mixing which validates the segregation phenomenon of the F-containing species at the surface.

The terminated segments, however, show a linear increase of contact angle with increasing amount of CP-F in the blend. In this case the rule of mixing is followed. The apparent lack of surface enrichment is explained by micelle formation. The F-containing endgroups are “locked” into the core of the micelles and are therefore prevented from orienting themselves to the surface. This also explains the fact that the segments are less effective in increasing the water contact angle when compared to the F-ester. The pure segment with a CF₂H-terminus achieves a water contact angle of only 93°.

The effect of the nature of the F-containing group is examined in two terminated segments having an octafluoropentyl and a trifluoroethyl endgroup, respectively. The octafluoropentyl group is comparatively F-rich and is expected therefore to result in a higher contact angle; but preliminary results show that the oligomer with the trifluoroethyl endgroup has a higher contact angle. This behavior is again explained by the secondary interaction of the lone proton with water. The expected increase in water contact angle in the F-rich octafluoropentyl terminated segment is off-set by the interactions of the proton of the CF₂H-terminus.

Conclusions:

Surface engineering of cellulose ester derivatives by blending with fluorine containing cellulose derivatives appears to follow expectations within the following framework.

The nature of the terminus on the F-containing substituent, CF_2H versus CF_3 , substantially determines surface characteristics. The observed differences are explained with the presence of an electron deficient proton in the CF_2H -terminus which readily engages in secondary interactions, like for example hydrogen bonding. This overshadows any effects that stem from the difference in atomic F-density per substituent.

The type of copolymer architecture, statistical versus terminal design, has a significant impact on both, solubility and surface character. The observations are consistent with the view that end-fluorinated segments can form micelles of the type shown in Figure 5. The micelles are thought to consist of a fluorine-rich core with a cellulose propionate corona. They are virtually insoluble in all common solvents, and they form stable colloids in solution and in solid state. This accounts for the observed modest influence of the segments on contact angle. Statistical F-esters cannot form micelles because of the delocalized distribution of the F-containing groups. Therefore they are both soluble in appropriate solvents and more effective in increasing the contact angle.

Acknowledgment

This study was financially supported by a grant from the U. S. Department of Agriculture, CSREES Contract #96-35103-3835. This support is acknowledged with

gratitude. Thanks is also given to Ms. Jody Jervis, Dep. WSFP, for the help with the molecular weight determination.

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Table I. Molecular weight characteristics of cellulose propionate segments

Segment Designation	Molecular Weight (Mn)		Molecular Weight Distribution (MWD)
	by GPC ²⁾	by H-NMR ³⁾	
CP-7 ¹⁾	2375	2150	1.4
CP-14	4480	5000	1.6
CP-28	9380	11250	1.5
CP-70	24100	26300	1.4

¹⁾ The number behind B- denotes the DP of the segment.

²⁾ Using THF as solvent and a universal calibration curve.

³⁾ Following OH-modification with chloro-triethyl silane (see Experimental Section).

Table II. Identification of F-containing derivatives used in this study

Designation	Description
T30-CF ₃	segment with DP = 30, terminated with trifluoroethyl group
T30-CF ₂ H	segment with DP = 30, terminated with octafluoropentyl group
S-CF ₃	statistical F-ester with trifluoroethoxy acetate substituent (DSF = 1.5), peracylated
S-CF ₂ H	Statistical F-ester with octafluoropentoxy acetate substituent (DSF = 1.5), peracylated

Table III. Solution behavior of fluorinated cellulose derivatives; sample designation is as outlined in Table II.

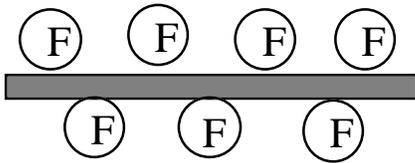
sample	solvent				
	acetone	dichloromethane	chloroform	ethanol	methanol
T30-CF3	T	T	T	T	T
T30-CF2H	T	T	T	T	T
S-CF2H	++	+	+	++	++
S-CF3	++	+	+	-	-

T = turbid solution

+ = soluble with some difficulty

++ = rapidly soluble

- = insoluble



Statistical F-ester

high molecular weight
high molar F-density



F-terminated segment
("blocky" structure)

low molecular weight
low molar F-density

Figure 1:
Schematic illustration of F-containing cellulose ester options

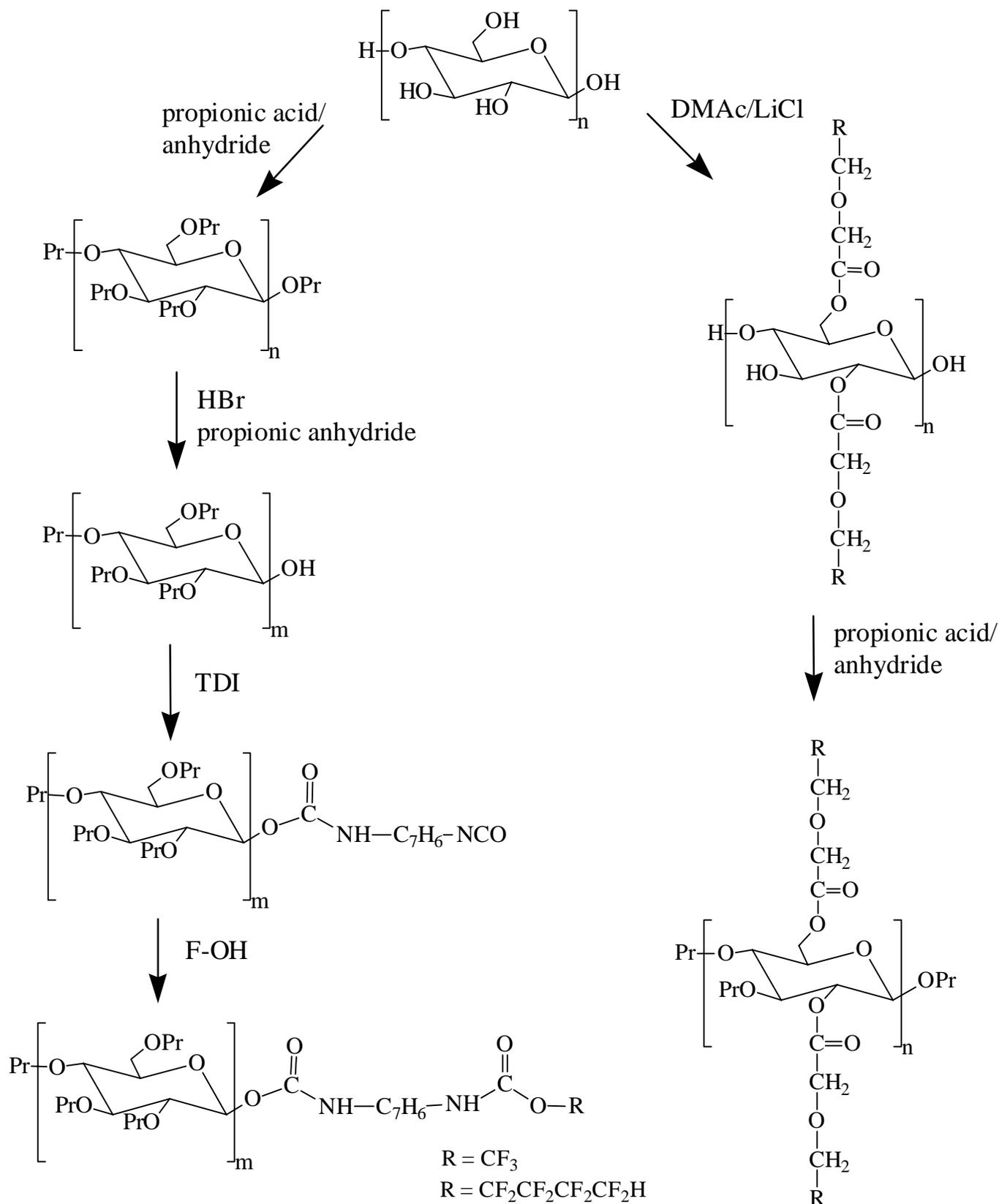


Figure 2:

Reaction schemes for F-terminated segments (left) and statistical F-esters (right); n indicated the high degree of substitution of polymerization (DP) of cellulose propionate, which is maintained in the F-ester, whereas m indicated the reduced DP in the segments which is achieved by hydrolytic degradation

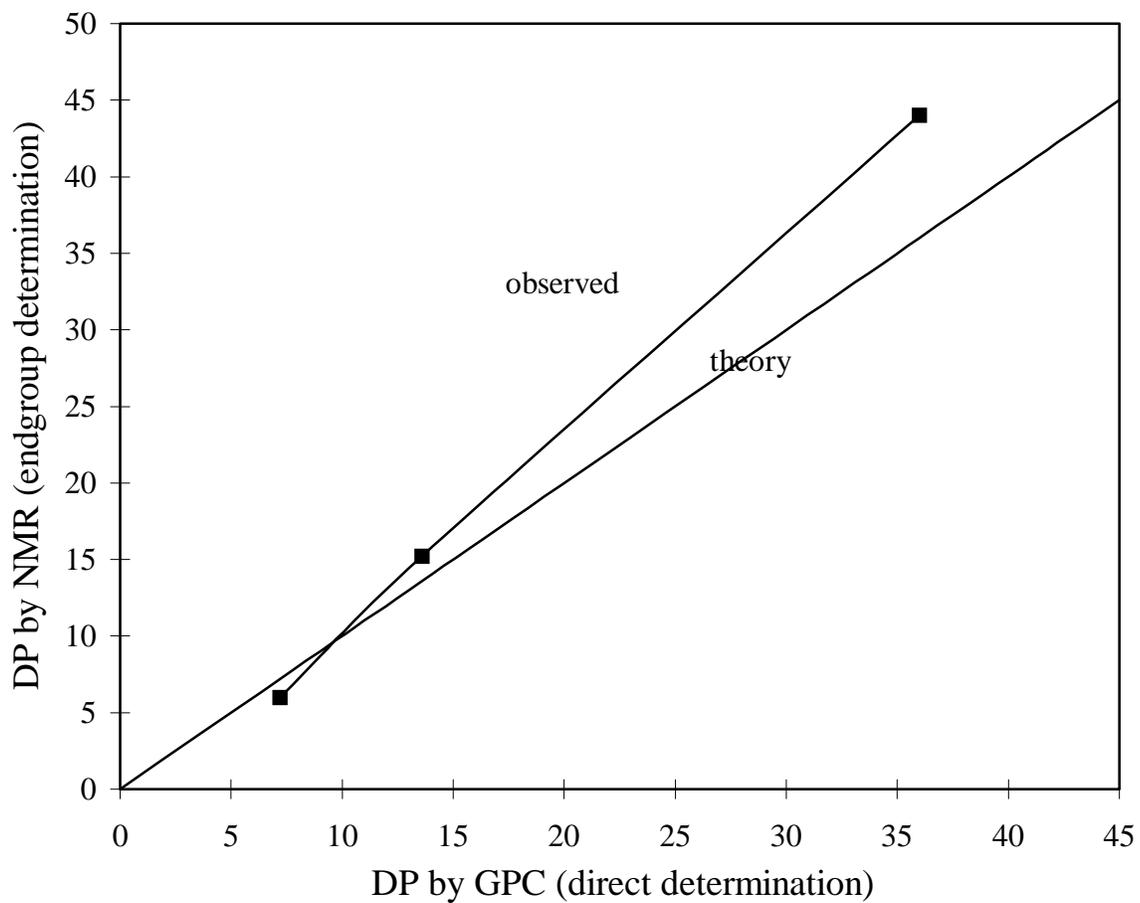


Figure 3.
Comparison of DP determination by GPC and by NMR; GPC determination represents direct determination, while NMR is an indirect determination by means of determining the endgroup concentration.

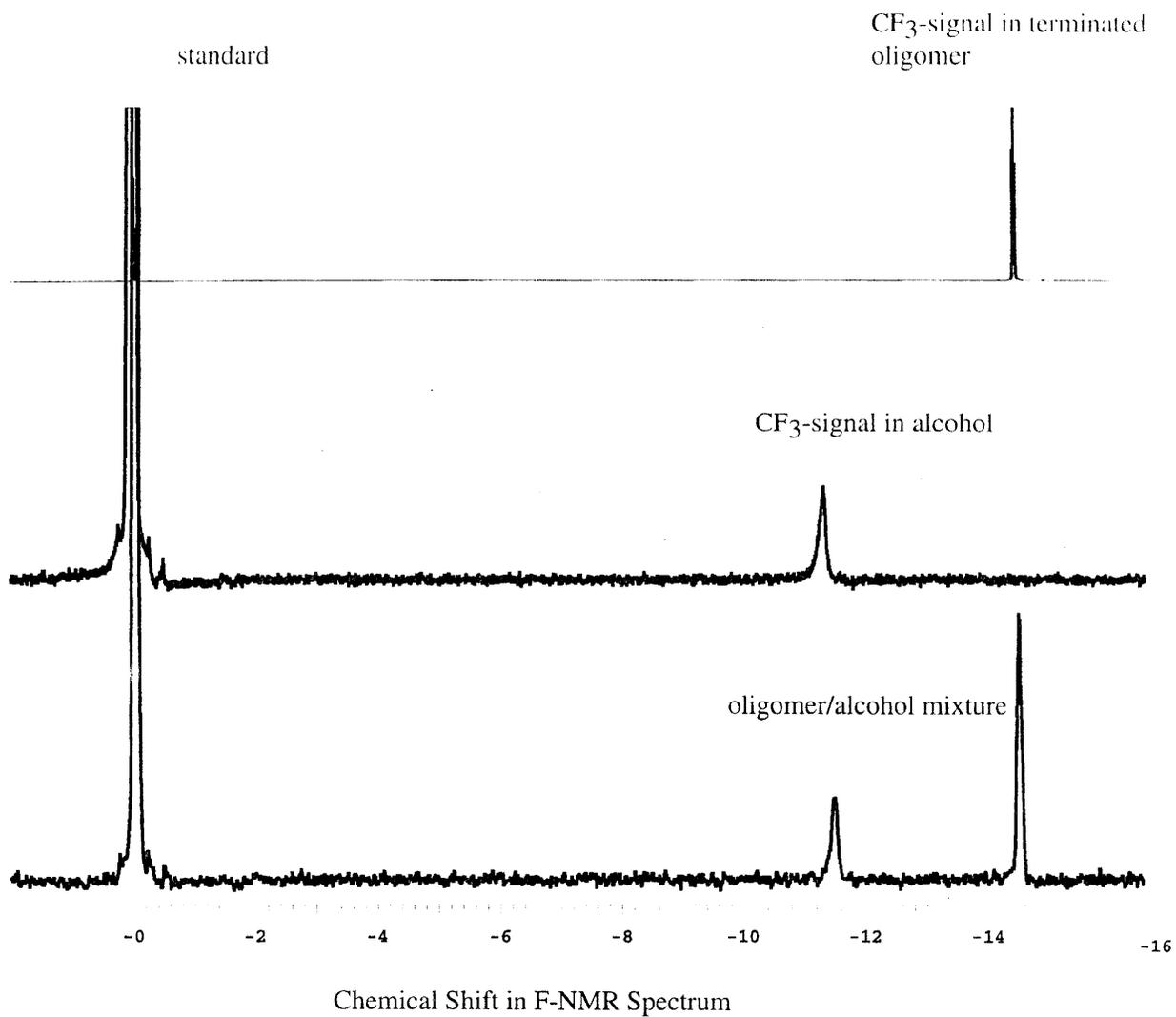


Figure 4.
 ^{19}F -NMR spectra of T30-CF₃ (top); trifluoro ethanol (middle); and T30-CF₃ spiked with trifluoro ethanol. The standard (3-(trifluoro)methyl benzophenone) is arbitrarily set to 0 ppm.

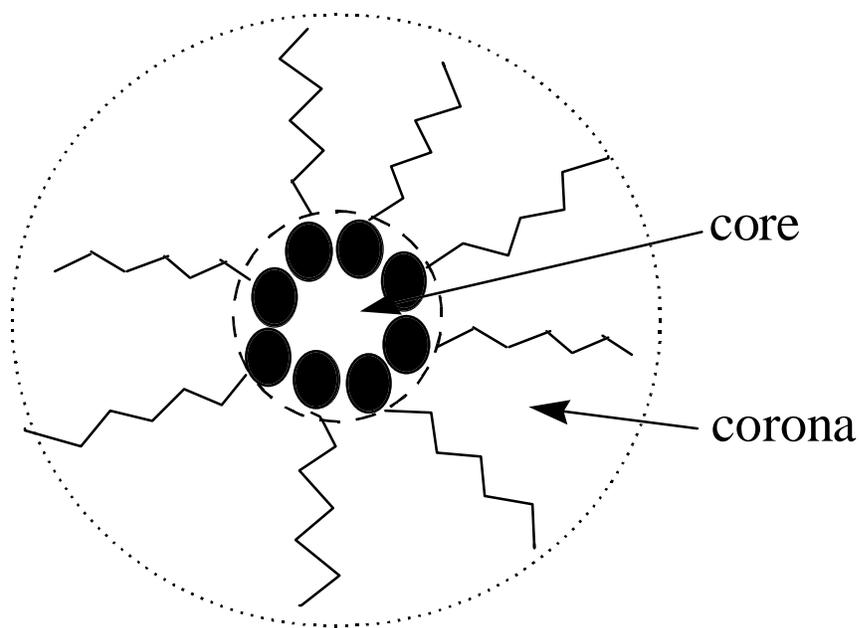


Figure 5:
Schematic representation of micelles believed to be formed by F-terminated cellulose propionate segments. The circles represent the endgroups which form the core of the micelles and the lines represent the cellulose propionate chains in the corona.

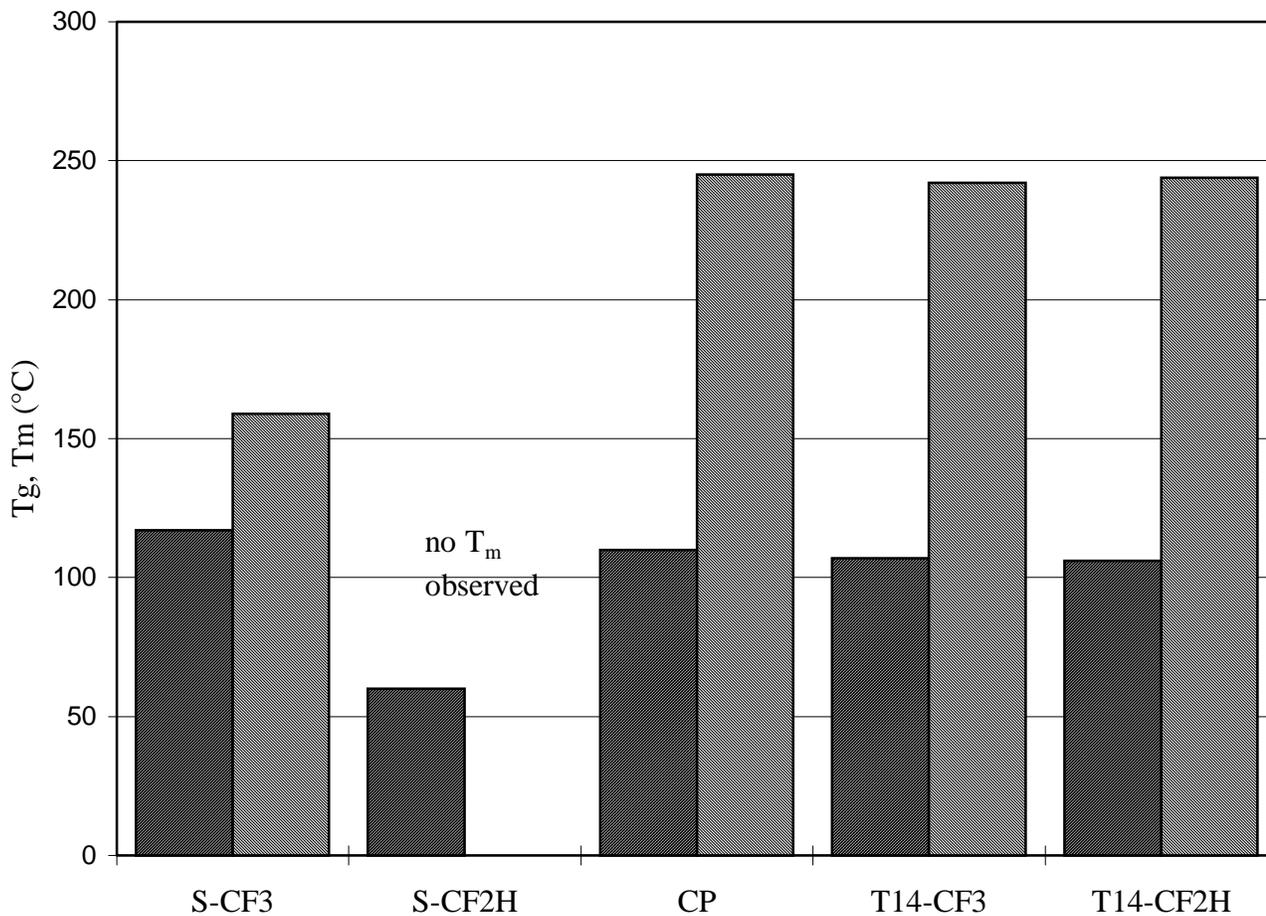


Figure 6.

Melting transitions of cellulose propionate (CP) compared to blocky and randomly fluorinated derivatives: thermal behavior of the blocky oligomers is similar to CP and independent of the chemistry of the F-containing endgroup but random copolymers show a clear dependence of thermal transitions on the chemistry of the F-containing substituent. No melting transition for R-100-CF₂H was observed. Sample abbreviation is as outlined in Table II.

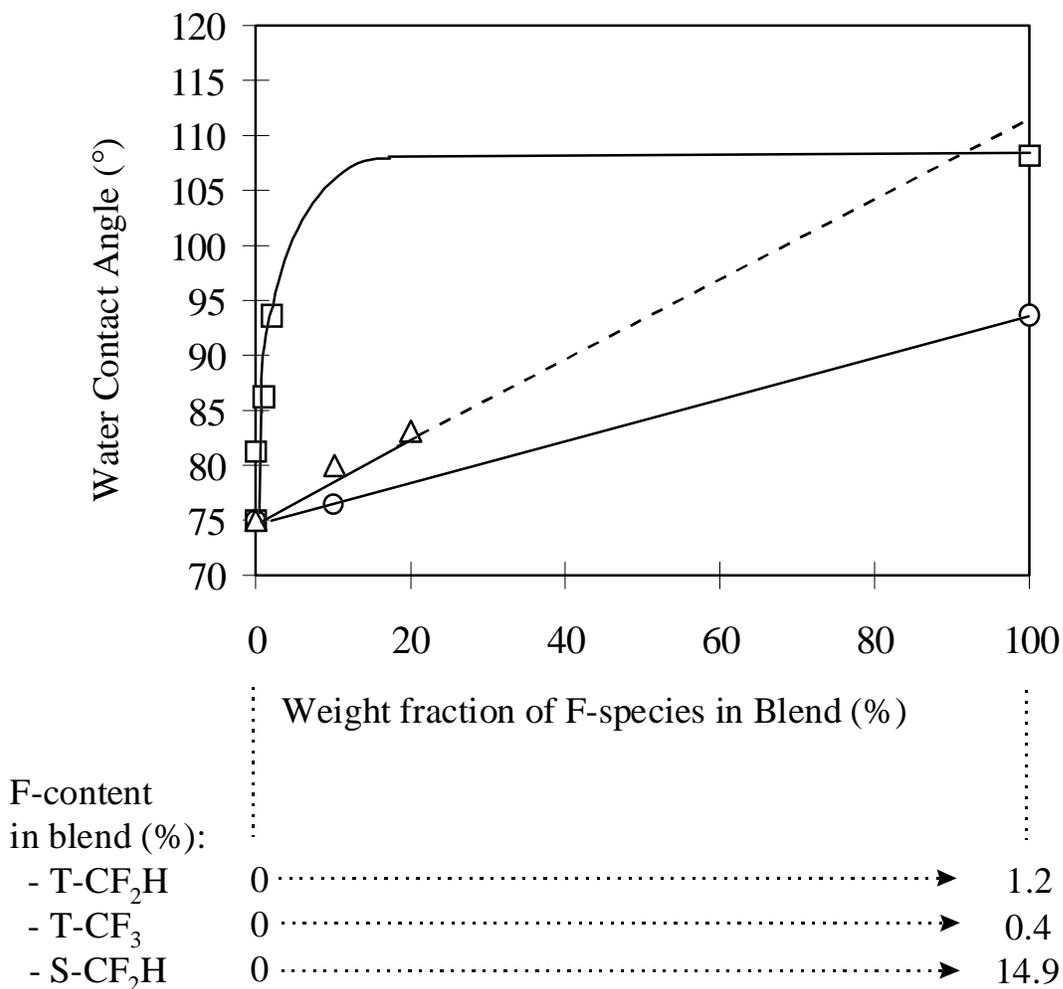


Figure 7. Experimental water contact angle for blends with statistical F-ester R-CF₂H (with octafluoropentyl substituent) (□); and for two blends with terminated segments: T-CF₃ (trifluoroethyl-terminated) (Δ) and T-CF₂H (octafluoropentyl-terminated) (○). The dashed line for the T-CF₃ indicates extrapolated values. Pure T-CF₃ could not be cast into a stable film. Note that the F-content (in %) is higher in the random copolymer than in the blocky oligomers