

Smart Surfaces of Biobased Materials. II.
Micelle-Formation in cellulose esters with F-functional endgroups.

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Abstract:

The solution and film-forming behavior of fluorinated (F)-terminated CP segments was investigated. The solutions of all segments examined exhibited typical critical micelle concentration (CMC) behavior with the CMC depending on the molecular weight of the CP segment and on the type of F-group. Solvent cast (from THF) blended films containing CP and the F-terminated segments showed a linear decrease in wetting force with increased F-component content. The adherence to the rule of mixing indicated the absence of surface segregation. This was explained with the retention of the micellar structure in the solid state which produced regular protrusions on the surface seen by atomic force microscopy. The dimension of the protrusions varied between 35 and 100 nm and depended on the CP-segment size and concentration in the blends.

Introduction:

The self-assembly behavior of polymers is of interest for various practical and theoretical implications¹. Self-assembly is a purposeful response to environmental conditions and as such constitutes smartness in materials².

In the case of block copolymers, self-assembly behavior includes the formation of aggregates in solution as well as surface segregation. Aggregation occurs in solvents with preferential solubilization of only one block³ and a variety of structures are possible, including micelles, worm-like structures, lamellae, bi-layers, sheets, crew-cut micelles and vesicles^{4,5}. For AB di-block copolymers, the aggregation is usually limited to the formation of micelles similar to the ones observed in small molecule surfactants⁶. The micelles are formed by hiding the insoluble block in the core, thus preventing precipitation.

Surface segregation in solids (often films from either melt or solution) is the preferential absorption of the more hydrophobic block at the surface (air-solid interface)⁷ and it is driven by a repulsion of that block from solution and by free energy differences between the components^{8,9}. Fluorine-containing molecules are especially prone to surface segregate due to the high hydrophobicity of fluorocarbons¹⁰. Although surface segregation can be detrimental to a performance of the material (for example in the migration of plasticizers), it is also a convenient tool for tailoring surface properties to specific applications¹¹.

Surface segregation is usually examined in films cast from non-micellar solutions and not much research has been conducted on the surface segregation from micellar solutions. Since the non-soluble part is hidden in the core of the micelle, the driving force for segregation is greatly reduced since no repulsion from the solvent occurs. It might therefore be possible to repress surface segregation when films are cast from micellar solutions under retention of their micellar structure in the solid state. Possible application of solid state micelles can include encapsulation, among others.

We have synthesized and characterized fluorine containing cellulose derivatives in our laboratory^{12,13}. The introduction of fluorine (F)-atoms into cellulose has originally been attempted with the aim of promoting compatibility between cellulose and synthetic polymers. Introduction was achieved by incorporation of either single F-atoms into the cellulose backbone or F-containing substituents onto cellulose¹⁴.

These materials are inherently amphiphilic molecules having a hydrophobic moiety (the fluorine-containing substituent) covalently attached to a hydrophilic moiety (the cellulose backbone). As amphiphiles, these molecules are thought to self-assemble and this has lead us to the investigation of the self-assembly behavior of these materials. In a previous paper¹⁵ the ability of F-containing cellulose derivatives to surface segregate was indicated when statistical polymers were blended with cellulose propionate in solvent cast films. However, when a single F-containing endgroup was introduced onto segmentic cellulose propionate segments (instead of uniform substitution along the backbone), the solution behavior indicated micelle formation.

This paper is to explore in greater detail the micelle forming characteristics of a number of F-terminated cellulose propionate segments in solution. Furthermore, films cast from micellar solutions will be examined with respect to their self-assembly behavior.

Experimental:

I. Materials:

Cellulose propionate was obtained from Eastman Chemical Co. The F-terminated segments were synthesized in our laboratory as described elsewhere¹⁵. Briefly, low

molecular weight cellulose propionate segments were synthesized by degradation using HBr. The resulting 1-monohydroxy terminated segments were coupled with toluene diisocyanate and subsequently reacted with the appropriate F-containing reactant.

II. Methods:

Critical micelle concentration determination: The critical micelle concentration (CMC) was determined by measuring the wetting force of solutions of low molecular weight, fluorine (F)-terminated segment in THF on glass slides. For every segment, a 1% (w/v) solution in THF was made (stock solution). Subsequently, solutions with lower concentrations were made by taking an aliquot from the stock solution and diluting it with the appropriate amount of THF. The wetting force of the solutions were measured using a CAHN balance. A clean, round glass slide was connected to the balance beam of the CAHN instrument and the force was measured when the glass slide was lowered into the segment solution. Every measurement was done in triplicate and the average was used for the CMC determination. The value for the CMC was determined as % (w/v) of segment in THF, and the value was then converted into a value of mole/l.

Blend Preparation: Cellulose propionate (CP)/ terminated segment (CP-F) blends were prepared by mixing the appropriate volumes of stock solutions (5% w/v) to the desired content of F-containing species, keeping the total solids content of all solutions at 5% w/v. The concentration of F-species in a blend is given as the mass % value of F-species with respect to the total amount of solids.

Wetting Force Measurements: Static contact angle measurements were based on a modified Wilhelmy Plate method. Microscope cover slides (18 mm diameter) were

cleaned thoroughly with hexane, dried and subsequently dip-coated (one coat) with the respective solutions. The glass slide served as a sinker to ensure that the films would submerge in the wetting liquid. 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 wetting force depending on the immersion depth¹⁶. Three to six measurements were performed per sample. The film was initially placed above the fluid and lowered into the water. The force that was registered when the film touched the water was measured as the wetting force. The raw data was not converted into contact angles using the perimeter of the sample and the surface free energy of the wetting liquid because a round specimen demands correction factors for the variable meniscus height (caused by the circular shape of the sample)¹⁷ and not all factors were available. Thus the reported wetting forces depend on the sample geometry, which was the same for all samples.

AFM measurements: AFM measurements were conducted on films cast on glass slides. The films were coated with the respective solutions at room temperature and stored at 4°C until the measurements. The measurements were conducted on a Dimension 3000 Scope, controlled by a Nanoscope IIIa controller, both by Digital Instruments. Several samples using at least two different silicon nitride tips were used per film in order to exclude artifacts.

Results and Discussion:

1. Critical micelle concentration:

The critical micelle concentration (CMC) is the characteristic solution concentration at which solubilized single molecules aggregate into micellar structures. A number of parameters, including osmotic pressure, conductivity, turbidity and surface tension experience dramatic changes at CMC. One method of measuring the CMC involves surface tension measurements using a modified Wilhelmy plate method. The CMC of various F-terminated cellulose ester segments was determined in THF solution by solution free energy measurements according to the modified Wilhelmy plate method. The F-terminated cellulose esters varied with the size of the cellulose ester (cellulose propionate, CP) segment, which ranged between the degree of polymerization (DP) of 15 and 70, and it varied with the type of F-containing end group, which was either trifluoroethoxy, octafluoropentoxy, or perfluorooctanoxy acetate end group (Table I, Figure 1).

When the copolymer solutions in THF were examined by free energy measurements in relation to solution concentration, a steep decrease in wetting force with increase in solution concentration was observed at low concentrations (Figure 2). This steep decline in wetting force was followed by an almost invariable wetting force with further increases in solution concentration (Figure 2). The CMC was determined as the intercept of the two lines representing the wetting force versus solution concentration relationship. All CMCs were found to be in the range between 10^{-5} to 10^{-4} moles L^{-1} (Figure 3). Both CP DP and type of F-containing end group were found to influence CMC. The CMC decreased with increasing size of CP segment (Figure 4); and it was

found to decline with F-group type from octafluoropentoxy to trifluoroethoxy to perfluorooctanoxy end group (Figure 3). A CMC in the range of 10^{-5} to 10^{-4} moles L^{-1} is consistent with other micelle-forming block copolymers such as PEOX/PDMS¹⁸, which was reported to have a CMC of 3.8×10^{-5} moles L^{-1} . The CMC was expected to decline with increasing F-content in the end group since a higher F-content strengthens the amphiphilic character. It amounts to an enrichment of the hydrophobic portion and an increase in the hydrophobic/hydrophilic balance. It was thus surprising that the octafluoropentoxy end group had a higher CMC than the trifluoroethoxy-terminated functional groups, which had significantly lower number of F-atoms in the end-group. This behavior is explained with a difference in the nature of the terminus. The octafluoropentoxy end group has a CF_2H -terminus, whereas both the trifluoroethoxy and the perfluorooctanoxy-end group have CF_3 -termini. The lone proton on the CF_2H -terminus is able to engage in secondary interactions, like hydrogen bonding, with neighboring molecules. The proton is covalently linked to a carbon atom, which in turn is connected to two F-atoms. The small negative inductive effect of the carbon onto the hydrogen atom is enlarged by the electronegativity of the F-atoms. Therefore the proton carries a strong partial positive charge, and this enables it to interact with solvent molecules.

The influence of the end groups on CMC was compounded by the size of the CP-segment (Figure 4). This is explained with a change in the hydrophobic/hydrophilic balance with molecular weight varying. At small CP segment sizes, the hydrophobic/hydrophilic balance is greater, i.e., the end group constitutes a larger part of the molecule and it predominates the solution behavior; conversely, at large CP segment

sizes, the end group is only a small part of the molecule and does not have a large influence on the solution behavior.

2. Static wetting force measurements:

Neat films of the F-terminated segments as well as films consisting of blends with CP were solvent cast from THF and subjected to wetting force measurements using a Wilhelmy plate method. The measurements were to assess the hydrophobicity of the films, which is expected to give an indication of surface segregation. The wetting force which is acting on the film when it is dipped into the interrogating liquid, in this case water, is measured. The wetting force of neat and blended films containing segments with a CP block size of DP 30 and 70 were evaluated. Blends containing segments with a CP segment of DP 15 could not be examined because the films peeled off the supportive glass slide as soon as they contacted the water surface and no accurate wetting force could be measured. The wetting force for all six samples examined decreased in a linear fashion with increasing blend content of the segment (Figure 5). The rate of the decrease varied in relation to the wetting force registered for the neat film.

The strikingly linear decline in the wetting force with increasing blend content of the F-containing segment species corresponds to behavior characterized by the absence of surface segregation¹⁹, and this is contrary to the frequent observation that end groups arrange at the surface²⁰. Exploratory XPS measurements on two films confirmed this. The measurements showed good agreement between the calculated F-content in the film and the F-content determined by XPS, indicating no F-enrichment at the surface (Table II).

The effect of the molecular weight and type of end group of the F-containing segment on blend properties can be evaluated from the results obtained for the neat films containing the segments. At constant type of end group, the CP film of DP 70 shows higher wetting forces than their corresponding copolymers with shorter CP segments (Figure 6). This can be explained with the fact that the higher molecular weight samples have a lower fluorine concentration (see Table I). The wetting force is also influenced by the end group (Figure 6). At constant molecular weight, the segment with the perfluorooctanoxy end group displayed a lower wetting force than the corresponding species containing the trifluoroethoxy end group. This was expected since the perfluorooctanoxy group has a higher F-content, which leads to a higher F-content in the sample. However, the samples terminated by the octafluoropentoxy group have the highest wetting force despite the fact that they have a higher F-content than the trifluoroethoxy-containing segments. This is again explained with the nature of the terminus of the F-group. The lone proton at the CF_2H -terminus of the octafluoropentoxy group is able to engage in hydrogen bonding with water molecules, and this enhances its higher wetting force with water despite the higher F-content.

3. Atomic force microscopy (AFM):

AFM micrographs obtained in the tapping mode (representing height images) were obtained from neat and blended films containing two CP block sizes, DP 30 and 70. (The DP 15 films were unstable and could not be examined.) The height image of a film of high molecular weight CP (i.e. the CP used as blending material) revealed a slightly wavy but overall featureless surface (Figure 7). All films containing segments (not terminated)

showed rough surfaces with irregular crevices (Figure 7). This behavior is thought to be caused by the low molecular weight of the samples which is likely to be below the entanglement molecular weight of CP. In contrast, the film of a neat F-terminated segment showed less rough surface with distinct and regular features resembling half-dome protrusion of an average height of 3 nm (Figure 7). Measuring the peak to peak distance of neat segment films (Figure 8), dimensions in the 35 ± 4.5 and 100 ± 4.3 nm range were found for the copolymers having CP segments of DP 30 and 70, respectively. The type of end group did not seem to have a significant influence on the peak to peak distance. These regular spherical protrusions are attributed to the presence of solid state micelles, which are the remnants of the spherical micelles originally formed in solution, similar to a system recently described for a rod-coil copolymer system²¹. The micelle is hypothesized to have a core of the non-polar end groups surrounded by a corona of polar CP-segments (Figure 9). At the surface, the micelles are thought to form pancake-shaped half-micelles giving rise to the surface texture as detected by AFM and the experienced decrease in wetting force. The arrangement creates a maximum exposure of the F-containing groups at the surface while, at the same time, maintaining the micellar structure (Figure 9). Similar structures have recently been described elsewhere²².

The size of the solid state micelles, 35 and 100 nm for DP 30 and 70-based copolymers, respectively, varied much more with CP segment size than with F-containing end group. Theoretical dimensions of the micelles can be estimated by calculating the dimensions of a round micelle. If the micelle is round, the peak-to-peak distance is equal to the diameter of the micelle (Figure 10). The theoretical diameter of a spherical micelle is calculated with its CP segment length and the size of the F-containing

end group. The size of the hydrophobic cavity is neglected at this point. Segment sizes of DP 30 and 70, have dimensions of 15 and 35 nm, respectively, if extended chain configuration is assumed (one repeat unit of CP has a dimension of 0.5 nm). The end group sizes are in the order of 2 nm (see Figure 10). The dimensions of the CP block and the end-groups result in theoretical spherical micelles of a size in the order of measured peak-to-peak distances, 34 nm and 74 nm for segments with a CP DP of 30 and 70, respectively. The pancake-shape of the surface micelles, as illustrated in Figure 9, results in a peak to peak distance which is smaller than the theoretical size of the micelle. The difference between the calculation and the observation can be explained with a cavity of the micelle, i.e. space between the head-groups.

4. Blends with CP

Similar round, regular features were observed when blends of CP with F-containing segments were examined by AFM. These features, however, varied in peak to peak distance in relation to segment concentration. The distances were found to follow a power law, and they were more pronounced in blends containing the DP 70-based copolymer than those based on CP having a DP of 30 (Figure 11). This change in dimension can be explained with a dilution process that is illustrated in Figure 12. The peak to peak distance increases faster with increasing dilution in blends with DP 70-segments than those having segments of DP 30.

The behavior can be approximated using the nearest neighbor model of the distribution of spherical objects in three dimensions. The average surface distance for

first neighbors (h), i.e. the separation between the perimeters of the spheres, in terms of particle diameter (D) and volume fraction (ϕ) can be calculated from²³

$$\frac{h}{d} = \left[\left(\frac{1}{3\pi\phi} + \frac{5}{6} \right)^{1/2} - 1 \right] \quad \text{Equation (1)}$$

The diameter of a micelle can be estimated by the peak-to-peak distance measured in neat films. Using equation 1, the distance between two micelles, h , can be calculated. The peak-to-peak distance equals the sum of the separation and the diameter of the micelle. The model calculation (Figure 11) accurately predicts the distance between the micelles in the blends of CP and the low molecular weight segments. The blends containing the high molecular weight segments did not produce a similar agreement. It at large CP block sizes (i.e. DP 70) the fully extended configuration does not accurately measure the diameter of a micelle. Events like folding and association may cause a breakdown of predictability using a simple geometrical model.

Conclusions:

Monofunctional, F-terminated cellulose ester segments with DP_ns of 15, 30 and 70 were found to self assemble into micellar structures.

Micelle formation was indicated in solutions having concentrations of between 10⁻⁴ to 10⁻⁵ moles L⁻¹, and critical micelle concentration depended on the nature of the segment. Both type of end group and size of CP segment influenced CMC.

The micelles apparently retained their shape during solvent removal (film formation); and solid state micelle formation is thought to prohibit surface segregation.

Solid state micelles were visualized by atomic force microscopy. The micelles are thought to be spherical in the interior of the films and pancake shaped at the surface.

Dilution of the films with CP resulted in films with increasing peak to peak distance and these distances followed the first neighbor model of Woodcock.

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Table I: Overview of terminated segments (see Figure 1 for structure)

Sample designation	DP of CP Block ¹	End-group Type ²	Number of F-atoms in substituent	F-content (%) ³	CP mass per endgroup (g/mole) ⁴	T _m ⁵ , °C
T ₁₅ ⁶ -TF ⁷	15	Trifluoro	3	0.87	4950	231
T ₁₅ -PF	15	Perfluoro	13	3.63	4950	231
T ₁₅ -OF	15	Octafluoro	8	2.29	4950	231
T ₃₀ -TF	30	Trifluoro	3	0.45	9900	238
T ₃₀ -PF	30	Perfluoro	13	1.91	9900	238
T ₃₀ -OF	30	Octafluoro	8	1.19	9900	238
T ₇₀ -TF	70	Trifluoro	3	0.18	23000	242
T ₇₀ -PF	70	Perfluoro	13	0.78	23000	242
T ₇₀ -OF	70	Octafluoro	8	0.48	23000	242

¹ calculated from molecular weight data

² see structure in Figure 1

³ calculated as atomic % of F-atoms on all atoms of the sample, excluding protons

⁴ calculated from GPC data

⁵ determined by DSC

⁶ indicates DP of CP block

⁷ indicates type of end-group

Table II: Results from XPS measurements of T₃₀-PF

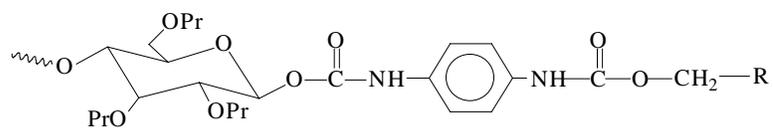
Content of segment in blend, % ¹	Theoretical F-content, % ²	Experimental F-content, % ³
50 ⁴	0.95	0.83
100	1.91	1.67

¹ based on weight fraction

² calculated as % of F-atoms on all atoms, excluding protons

³ based on XPS-measurements at 45° angle

⁴ blend of 50% T₃₀-PF and 50% CP



where R = - CF₃ (trifluoro)
 - CF₂CF₂CF₂CF₂H (octafluoro)
 - CH₂CF₂CF₂CF₂CF₂CF₂CF₃ (perfluoro)

Figure 1:
 Generic structure of an F-terminated cellulose propionate segment. Segment of DP 15, 30 and 70 are terminated with each of the three listed F-containing endgroups

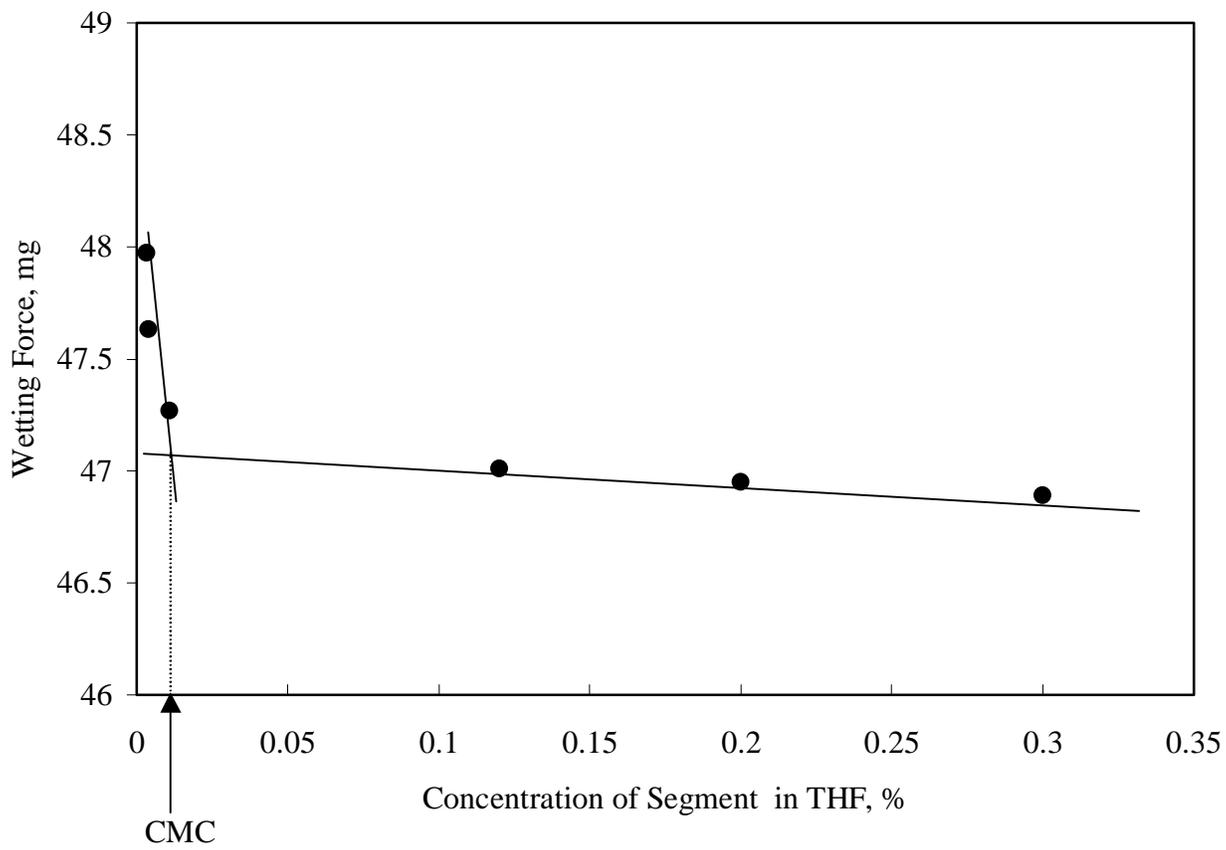


Figure 2:
 Surface tension data of T₇₀-CF3 as an illustration of typically obtained data for the CMC measurement. The CMC value is determined as the intercept of the two lines. The data points are average points of three measurements with a variation of ± 0.25 mg.

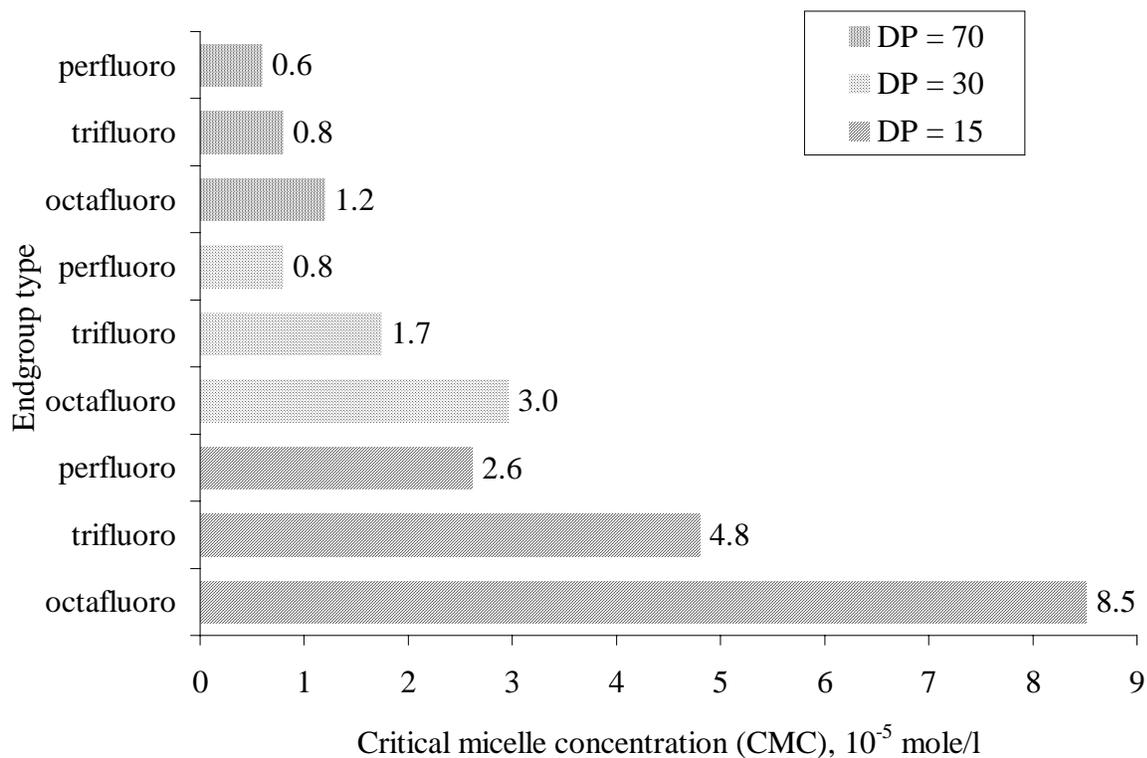


Figure 3:
 Critical micelle concentration for F-terminated CP-segments depending on the type of F-endgroup for three different CP-segment sizes. The CMC data was obtained as outlined in Figure 2.

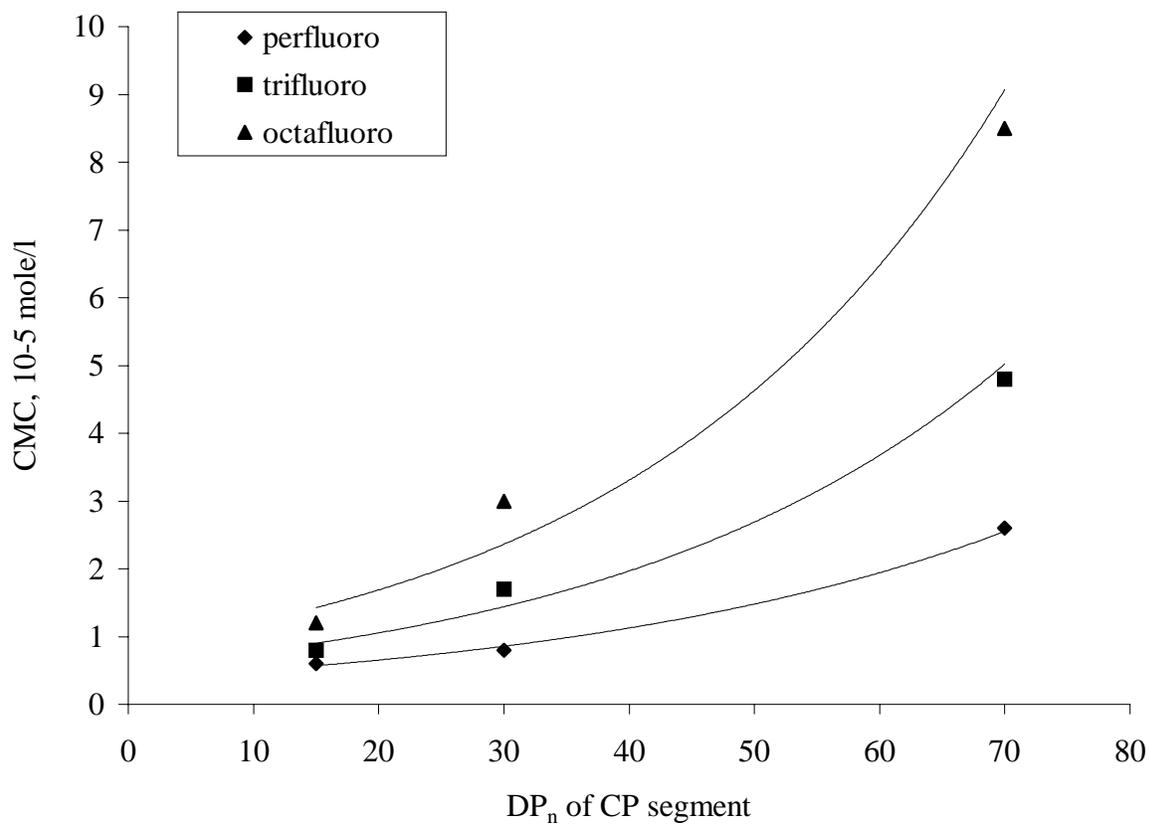


Figure 4:
Critical micelle concentration of F-terminated CP segments depending on the molecular weight of the CP segment for three different endgroups

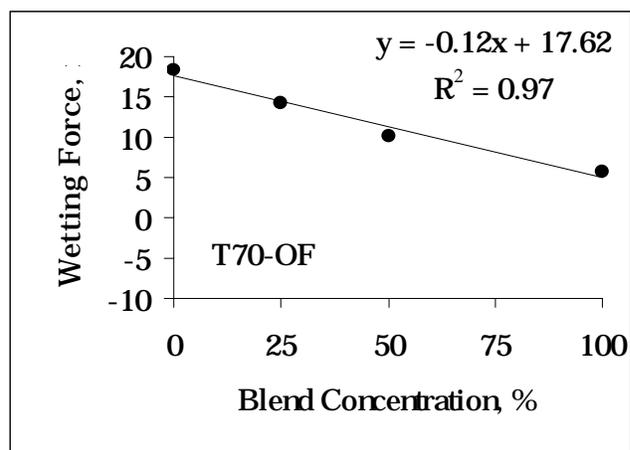
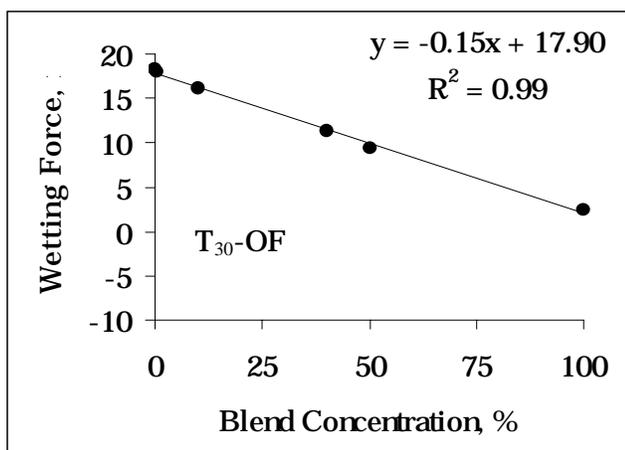
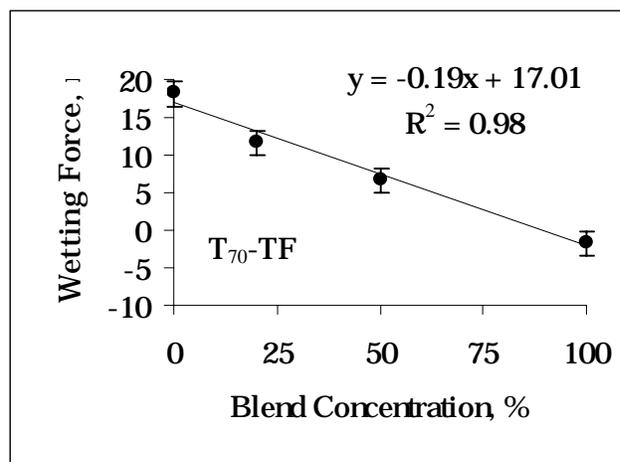
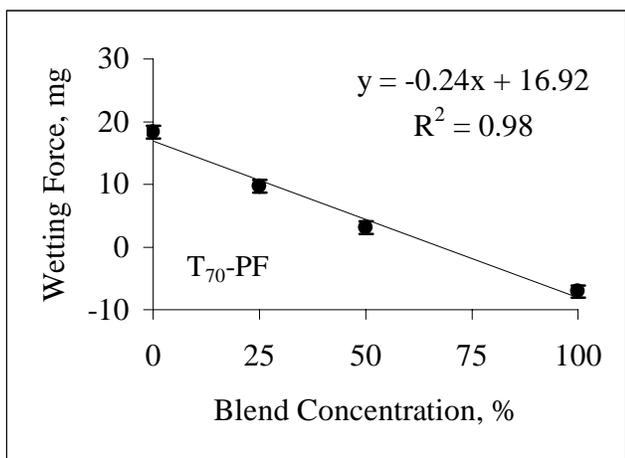
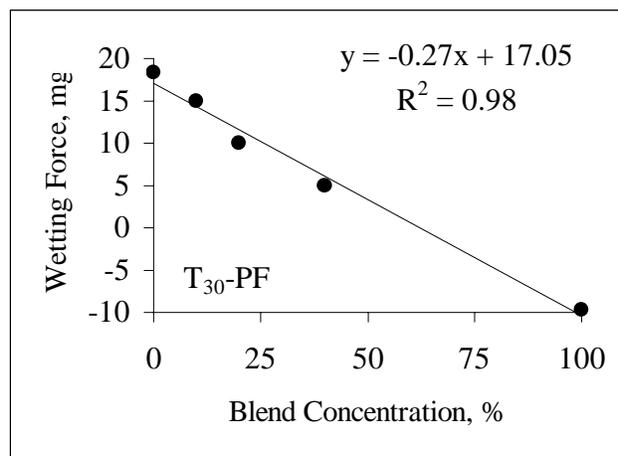
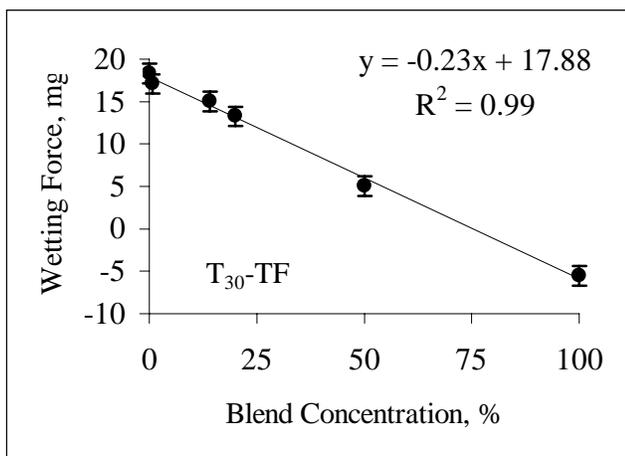


Figure 5:
Wetting force measurements of blends containing a varying amount of the F-terminated segments. Only samples containing segments with DP 30 and 70 of the CP block could be measured. The measurements were conducted in triplicate with an average variation of ± 0.8 mg.

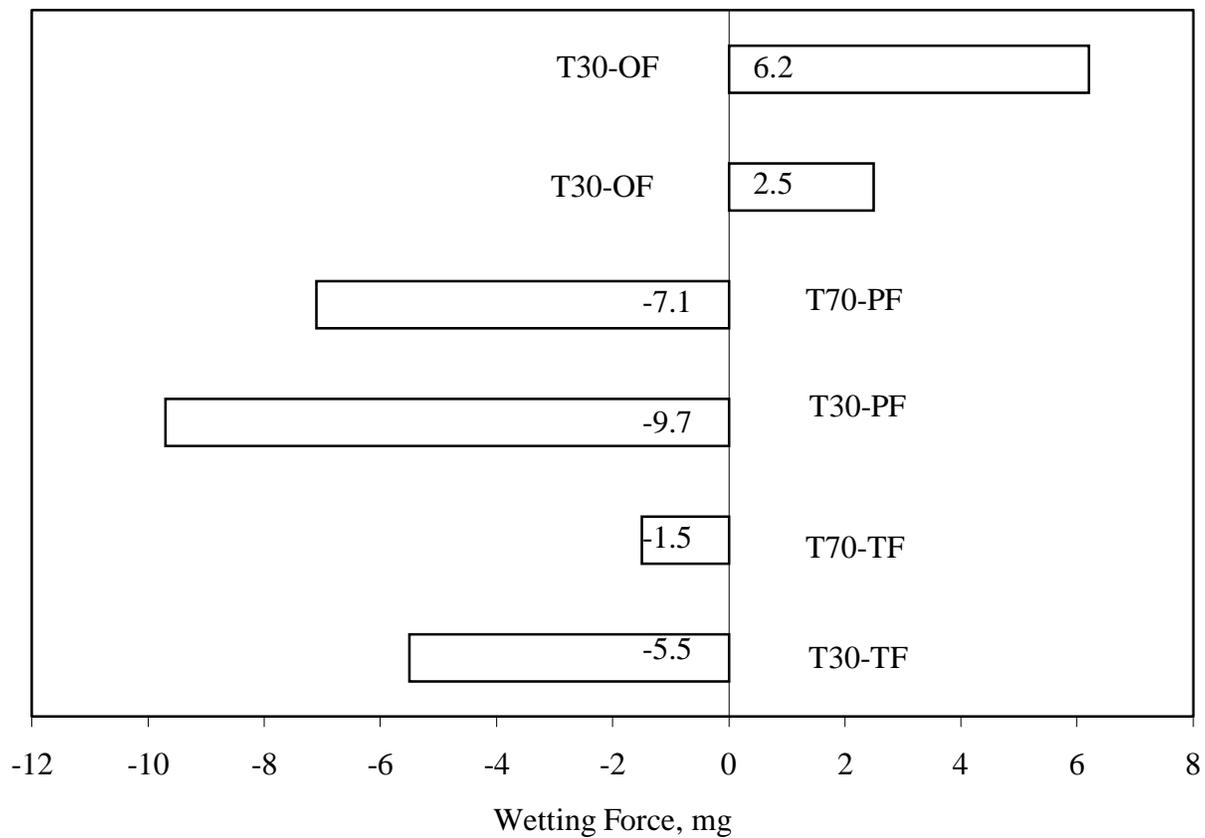


Figure 6:
 Wetting forces of neat films of F-terminated segments depending on the molecular weight of the CP block and the type of F-group

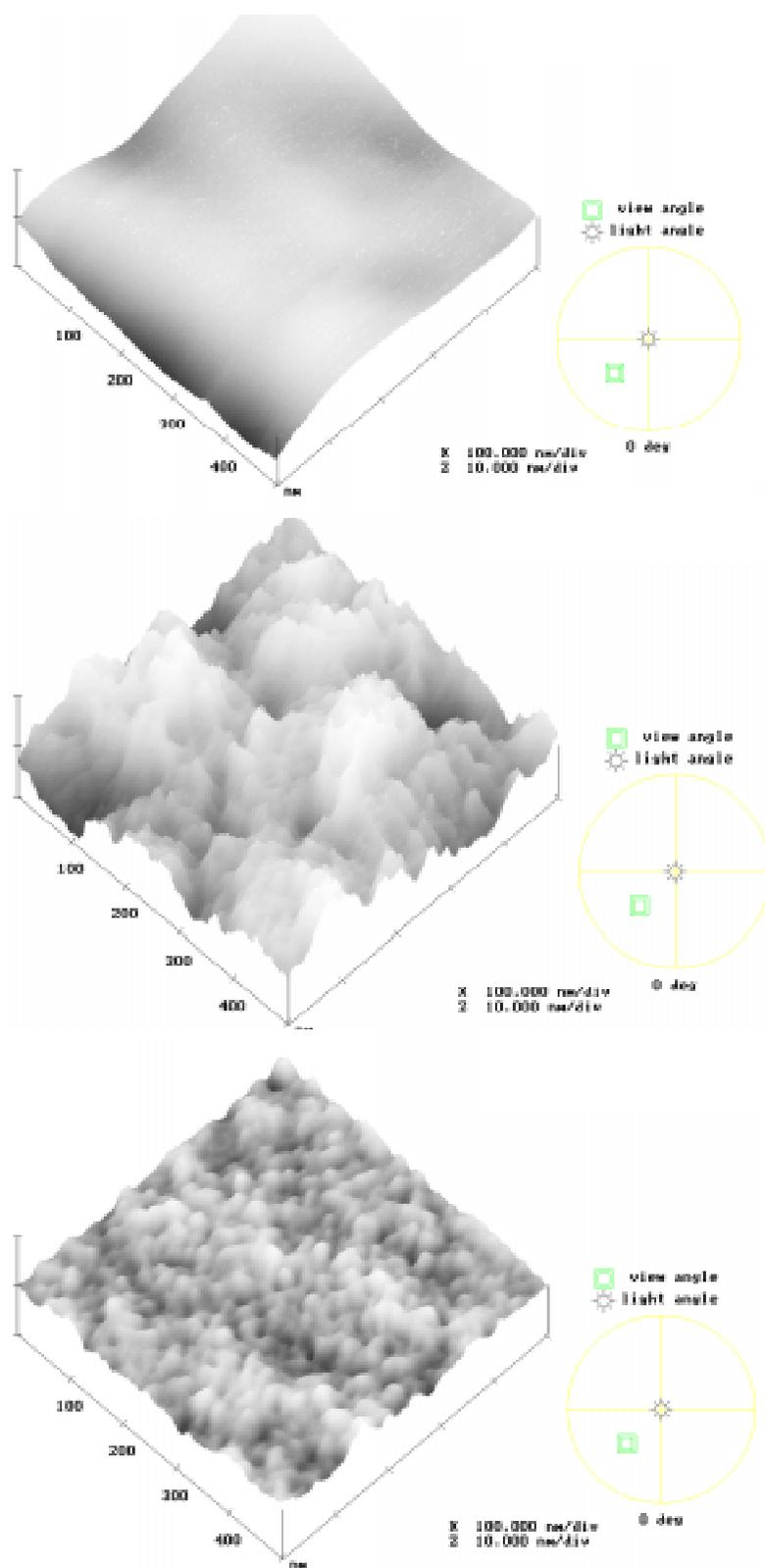


Figure 7:
 Atomic force height image micrographs of neat films of cellulose propionate, CP (top), a CP segment (middle) and an F-terminated CP segment. Both segments have a degree of polymerization of 30.

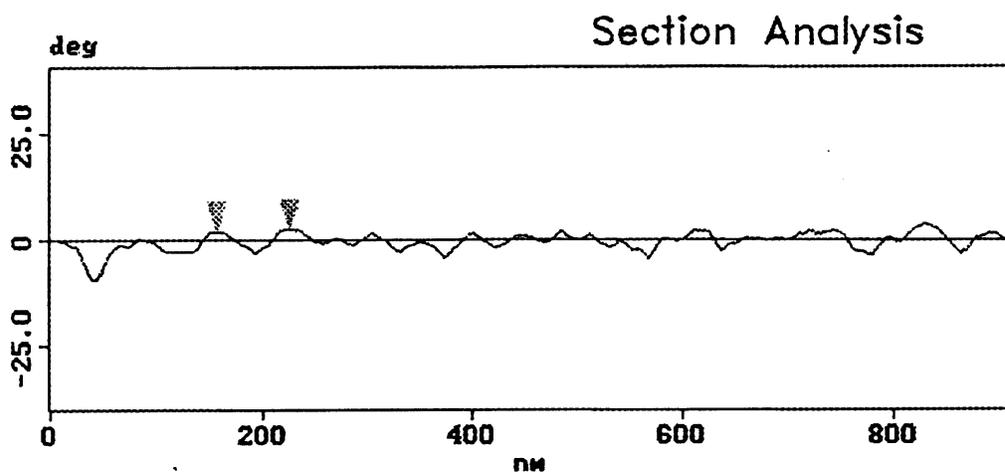


Figure 8:
Principle of peak-to-peak determination illustrated with T₃₀-TF. The AFM software allows for the creation of cross sections and the distances between any two points in a cross section can be measured.

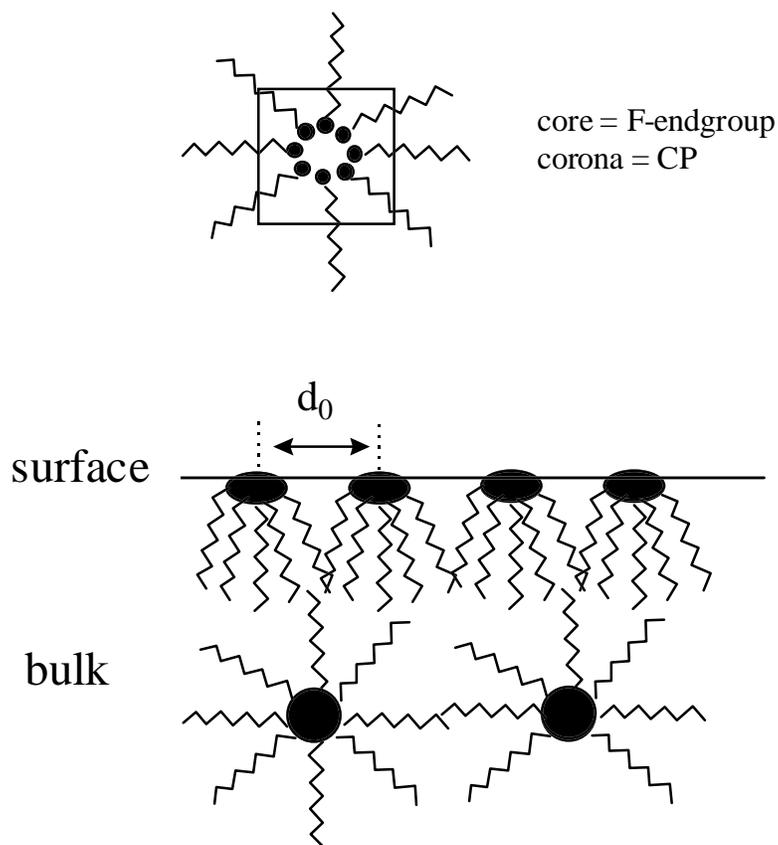


Figure 9:
Model of micelle of F-terminated oligomers (top) and pancake-shaped and full micelles at the surface and in the bulk phase (bottom). The micelle is thought to consist of a core of the F-endgroups and a CP corona. At the surface, the micelles are pancake-shaped in order to maximize the exposure of F-moieties at the surface while at the same time maintaining the micellar structure.

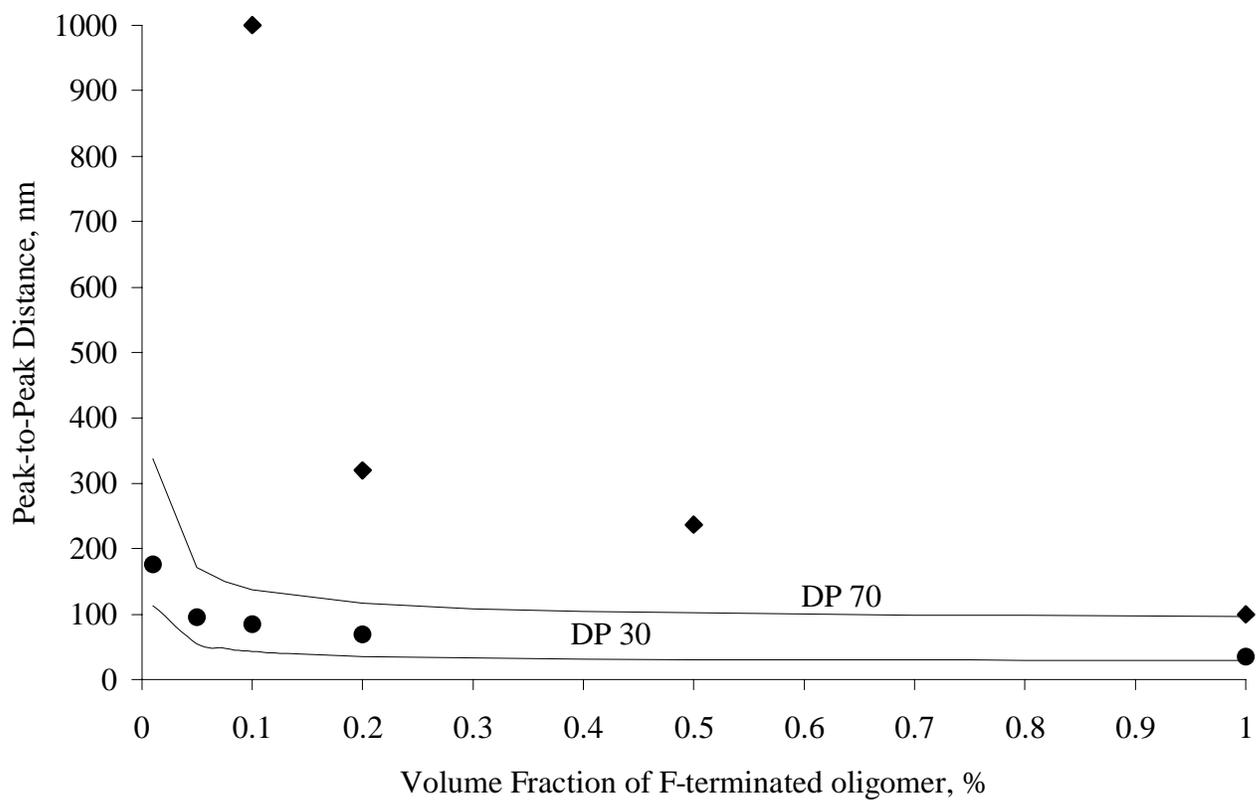


Figure 11:
 Comparison of measured peak-to-peak distances of films containing F-terminated oligomers to values calculated from equation 1. The measured peak-to-peak distance fits well in the case of segments of DP 30, but the observed peak-to-peak distances are larger than calculated in the case of segments of DP 70.

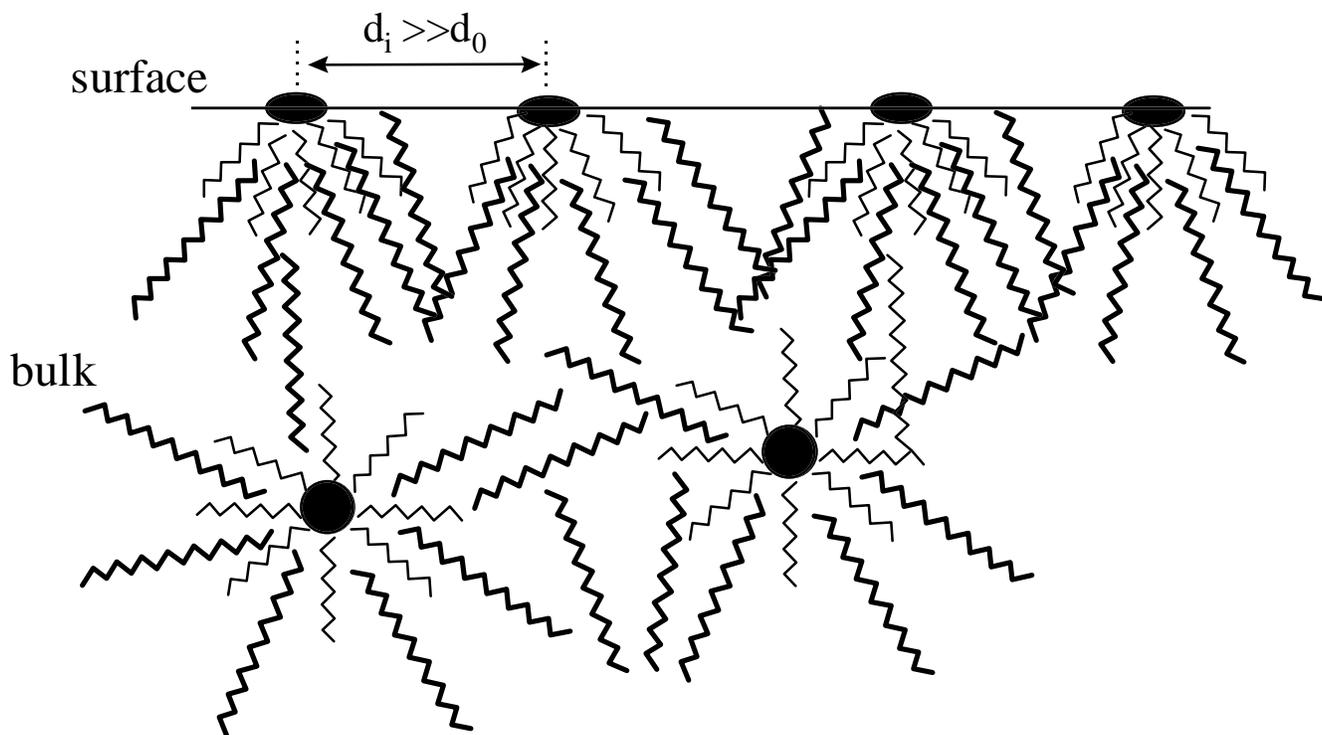


Figure 12:

Model of dilution of micelles by CP. The circles represent the micelle core and the thin lines CP of the micelle. When CP (thick line) is added to the blend, the micelles are pushed apart, thus increasing the peak-to-peak distance measured using AFM