# Terminal Attachment of Perfluorinated Polymers to Solid Surfaces

J. RÜHE,[1,*,†] G. BLACKMAN,[1] V. J. NOVOTNY,[1] T. CLARKE,[1] G. B. STREET,[1] and S. KUAN[2]

[1]IBM, Research Division, Almaden Research Center, 650 Harry Rd., San Jose, California 95120, and [2]Adstar, An IBM Company, 5600 Cottle Rd., San Jose, California 95124

## SYNOPSIS

Physisorption and chemisorption of perfluoropolyethers on solid surfaces is investigated using infrared spectroscopy, microcalorimetry, ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy. Physisorbed polymers show shifts of vibrational modes to lower frequencies in a few nanometers thick films, indicating interactions with the solid surfaces. Hydroxyl-terminated polymers are thermally attached to solid surfaces, and their thicknesses increase to saturated values with increasing heating time. The thermally attached thin polymer film consists of strongly physisorbed material as well as chemisorbed material. Strongly physisorbed polymer is slowly displaced from the surface by polar, low-molecular-weight compounds such as water or alcohols. This is to be expected on the basis of microcalorimetric results, which yield higher heats of immersion with water than with reactive perfluoropolyethers. Atomic force microscopy experiments show that the mobility of the polymer remaining on the surface decreases substantially as the amount of the physisorbed material decreases. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

In recent years the tribological properties of ultrathin polymer films attached to solid surfaces have attracted considerable attention. Very thin films with thicknesses of the order of monolayers can dramatically influence the tribological properties of a surface to which they are attached.[1-5] Such is the case for the lubricants used to enhance the tribological behavior of thin-film magnetic media. Monolayer films of long-chain alkyl compounds[2,3] such as stearic acid, alkylsilanes,[4] or perfluoropolyethers (PFPE)[5] are examples of materials that have been used for such a purpose. In order to ensure an adequate lifetime, these films must be sufficiently strongly attached to the surface so that they can avoid a depletion caused by head–disk interactions, spin-off from the rapidly rotating disks, or simple displacement by adsorbed water or airborne organic species.

Polymer films with thicknesses on the order of monolayers can be deposited by the Langmuir–Blodgett (LB) technique,[6] adsorption of polymers from dilute solution,[7,8] or deposition of low-molecular-weight polymers from the vapor phase. A subsequent covalent bonding of the polymers to the surface can occur via a chemical reaction with appropriate surface groups.[9,10] Such an attachment can be achieved by first applying a comparably thick polymer film (5–20 nm) by dip coating from solution and then performing the surface reaction and subsequent removal of the nonreacted polymer by extraction.

Polymers such as perfluoropolyethers can be attached to surfaces[5] provided they have end groups capable of reacting with the carbon surface of the disk. However, the microscopic behavior of the attached polymer chains and especially the attachment mechanism(s) are not well understood. In fact, it is difficult to distinguish polymer chains that are chemically attached to the surface and those that are strongly physisorbed but can be removed from the surface only with great difficulty, i.e., if good solvents for the polymer cannot be found.

In this study the process of adsorption of some

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perfluoropolyethers on carbon and oxidized silicon surfaces and their displacement is examined using microcalorimetry, ellipsometry, and Fourier transform infrared spectroscopy (FTIR). In addition, the attached layers themselves are studied using X-ray photoelectron spectroscopy (XPS), ellipsometry, and atomic force microscopy (AFM). Using the resulting data, we show that the strength of attachment of the polymer to the carbon can vary from weak physisorption to strong physisorption and to actual chemical bonding.

## EXPERIMENTAL

All the perfluoropolyethers (PFPEs) used in this study had similar polymer structure and molecular weights, but different end groups [difluoro hydroxyethyl- (DFHE) vs. trifluoromethyl (TFM) end groups] were employed. The polymers were commercially available and were used as received. They were random copolymers consisting of difluoromethylene oxide ($-OCF_2-$) and tetrafluoroethylene oxide ($-OC_2F_4-$) repeat units. Table I shows the structure of the compounds used in this study, their average-number molecular weights, and abbreviations we will use in the following text. The abbreviations consist of the end group and the approximate molecular weight.

The solvents used for dissolution of the polymers 1,1,2-trichloro-trifluoroethane (TTFE), perfluorooctane, trifluoro-ethanol, and various mixtures of polyfluorinated hydrocarbons, as well as those used for displacement experiments (water, ethanol, chloroform, toluene, and acetone) were of analytical grade with residues after evaporation < 0.2 ppm. Depending on the desired film thickness, films of the polymers were coated on the surface of a substrate by wiping (for thick polymer films > 1 $\mu$m) or dip coating (typical film thickness 10 nm). Dip coating experiments were performed employing TTFE as a solvent. Concentration (0.5–5 g/L) and

withdrawal speed (1–3 mm/s) were adjusted in order to obtain the desired thickness. To perform the surface reaction, the samples were typically heated to 150°C in air for 1 h, the nonattached polymer was subsequently extracted by washing with fluorinated solvent and dried in a stream of filtered, dry nitrogen.

Organic contaminants, which adsorb rapidly on the as-deposited carbon surfaces from the ambient, were removed by rinsing thoroughly with chloroform and TTFE and UV irradiation (wavelength 185 nm) under nitrogen (to avoid generation of ozone). The carbon films discussed in the following were about 25.0 nm thick and were obtained by sputtering onto Si wafers (for ellipsometry measurements) or aluminum discs (for FTIR measurements).

Grazing incidence infrared absorption spectra were recorded with a Nicolet model 510 FTIR spectrometer using $p$-polarized IR light with an angle of incidence of 76°. A carbon film sputtered onto a highly reflecting aluminum surface under exactly the same conditions was used as reference. Only small differences in background spectra were observed as long as the substrates came from the same deposition. For polymer thickness measurements by FTIR a calibration curve referenced to ellipsometrically measured samples was established. The polymer thickness values obtained by FTIR measurements were found to be in good agreement with XPS for which escape depth was also calibrated using ellipsometry.

Heat of immersion of the PFPEs and the heat of dissolution of the polymers in solvent were measured with an isothermal heat flow microcalorimeter (LKB Bioactivity monitor). The microcalorimeter had a temperature stability of better than $10^{-4}$°C per day and the noise was typically smaller than 2 $\mu$W. Samples were equilibrated for 4–12 h before and 12–72 h after the experiments. In all experiments the PFPE was flowed into the cell containing adsorbate or solvent to avoid artifacts generated by solvent evaporation or breaking of an ampoule.

XPS measurements were carried out using an exit

**Table I  Structures, Abbreviations, and Molecular Weights of Polymers**

| Structure | Abbreviations | Molecular Weight ($M_n$) |
|---|---|---|
| $HO-CH_2-CF_2-O(CF_2-O)_n$ ⎤ | DFHE2 | 2200 |
| $HO-CH_2-CF_2(O-CF_2-CF_2)_m$ ⎦ | DFHE4 | 4000 |
| $F_3C-O(CF_2-O)_n(CF_2-CF_2-O)_mCF_3$ | TFM4 | 3700 |
| | TFM9 | 9300 |

angle of photoelectrons of 38° and a spot size of 600 $\mu$m. Flux densities were kept below $10^{12}$ photons/ $cm^2$ in order to avoid decomposition, because it was observed that PFPE molecules are strongly susceptible to radiation damage by X-rays.

The AFM used in these experiments has been described previously.[11] The cantilevers were constructed by bending a 50-$\mu$m diameter tungsten wire at a right angle, then etching the end to a sharp point (typically 50–100 nm radius). The force on the tip was determined by measuring the deflection of the wire by optical interference, where the interference occurred between the laser light reflected off the back of the wire and laser light reflected internally off the end of the optical fiber. The deflection could be determined to within ±0.03 nm; therefore, with a typical lever force constant of 50 N/m, the force sensitivity was $1.5 \times 10^{-9}$ N. For each type of film the force vs. distance measurements were performed at several hundred different locations on the sample and the curves shown in the figures are typical for each type of film.

## CHARACTERIZATION OF THE POLYMERS

It should be noted that all polymers employed have a relatively broad molecular weight distribution with a polydispersity larger than 1.3. They are liquids at room temperature and have glass transition temperatures between 200 and 250 K. $^{19}$F-NMR (nuclear magnetic resonance) analysis showed that the only significant impurity present was a small amount (approx. 3%) of perfluoropropyl and perfluorobutyl oxide groups incorporated in the polymer backbone. Furthermore it was found that DFHE contained about 5% of a material with $-OCF_3$ end groups instead of $-CF_2CH_2OH$ end groups.

During the thermal treatment procedure used to attach the DFHE polymer, the molecular weight of the polymer increases significantly through evaporation of lower molecular weight fractions. End-group analysis of extracted polymer with $^{19}$F-NMR showed that upon heating a sample coated with 10 nm of DFHE2 for 1 h at 150°C the number-average molecular weight increased from 2200 to about 6000 g/mol. $^{19}$F-NMR spectra of the polymer before heating and a sample extracted from a carbon surface after 1 h heating to 150°C are shown in Figure 1. The spectral shifts are reported in parts per million relative to the position of the fluorine signal of fluorotrichloromethane ($CCl_3\underline{F}$), which was used as an internal standard. Note the pronounced differ-
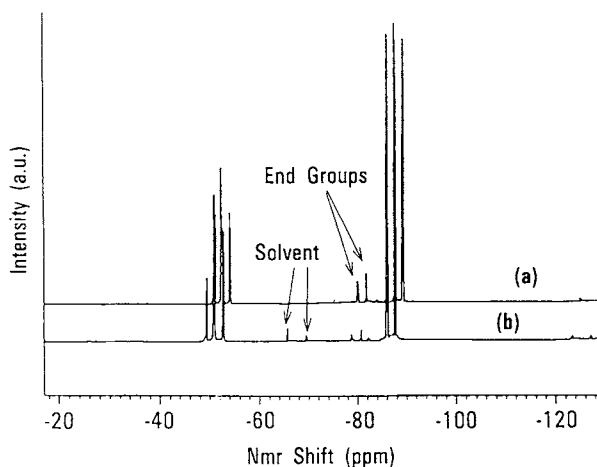


**Figure 1**    NMR spectra of DFHE (a) before thermal treatment and (b) extracted from disk after 1 h heating to 150°C; curve (b) is displaced by 2 ppm for clarity.

ences of the intensities of the NMR signals due to the end groups at $-81$ and $-83$ ppm, which are marked with arrows (Fig. 1). The two signals can be attributed to the $-OCF_2-OC\underline{F}_2-CH_2OH$ and the $-OCF_2CF_2-OC\underline{F}_2-CH_2OH$ end groups of the copolymer.

This increase in average molecular weight is not the result of a condensation reaction of the hydroxyl end groups but rather due to evaporation of low-molecular-weight oligomers; indeed a sample heated in a sealed container at 150°C for 1 h showed no changes in the number-average molecular weight according to NMR end-group analysis. It could be argued that surface catalysis might facilitate the condensation reaction. However, treatment of PFPE with strong Brönstedt acids ($H_2SO_4$) or Lewis acids ($TiCl_4$) leads to considerable degradation of the perfluoroether rather than an increase in the molecular weight. $^{19}$F-NMR end-group analyses after treatment of the perfluoroethers with such strong Brönsted or Lewis acids show the formation of materials with acid, unsaturated and various other end-group chemistries accompanied by a significant decrease in the average molecular weight. In contrast to this, NMR spectra of samples before and after heating the perfluoroether in a sealed tube with a weak acid, i.e., stearic acid, showed no changes. Although the acidity of the surface might play an important role in the attachment of the polymer layer, a surface-catalyzed self-condensation of the polymers to form insoluble, high molecular weight polymers can be excluded. A detailed analysis of the thermal behavior of the polymers, especially under acidic conditions, will be published elsewhere.[12]

## CHARACTERIZATION OF THE CARBON SURFACES

The chemical composition of the surface of the different carbon-coated substrates was analyzed using XPS. A direct quantitative analysis of the groups attached to the surface carbon atoms, e.g., hydroxyl, carbonyl, and carboxylic acid groups, is relatively difficult even with high-energy resolution XPS analysis because adsorbates contribute to these signals and the penetration depth is much larger than the actual surface layer thickness. Consequently, the signal due to the surface groups contributes only a small fraction of the C–O and oxygen signals in the XPS spectra even at grazing exit angles. Most of the signal is due to oxygen containing species below the surface, which are inaccessible to a chemical reaction. To measure the actual surface groups, a surface derivatization technique using fluorinated tag molecules was therefore employed prior to XPS analysis, as indicated in Figure 2. Hydroxyl groups on the carbon surface were reacted with tridecafluorooctyldimethyl chlorosilane; surface carbonyl groups were reacted with pentafluorophenyl hydrazine; and carboxylic acid groups were derivatized with pentafluorobenzylbromide according to literature procedures.[13]

The number of surface groups was obtained from the ratio of the fluorine and carbon or silicon signals in the XPS spectrum of the derivatized surface, taking an escape depth for electrons of 3.4 nm and the same effective cross section as the bulk material.[14b] All calculations were based on a model assuming an incomplete monolayer film (one-layer model). The
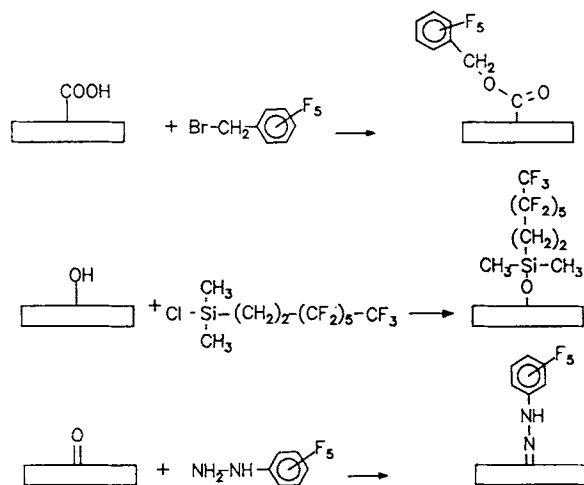
### Table II  Functional Groups on Carbon Surfaces as Obtained by XPS Analysis with Surface Derivatization[a]

| Sample[b] | Percentage of Functional Groups (%) | | |
|---|---|---|---|
|  | —COOH | $\diagdown$C—O$\diagup$ | —C—OH |
| Carbon I | 10–17 | 8 | 15–20 |
| Carbon II | 7–13 | 9 | 4–15 |
| Graphite | < 5 | — | < 5 |

[a] Relative concentrations of functional groups are expressed with respect to the estimate of surface areal density of carbon.

[b] Carbon I and II were deposited using the same sputtering conditions in different chambers.

samples had to be carefully extracted after the derivatization reaction in order to remove all unreacted tag molecules. Control samples with a small number of reactive surface groups proved that only traces of nonreacted tag molecule remained on the surface after extraction.

The results of the surface analyses are shown in Table II. It was found that although sputtering of the carbon layer was performed under reducing conditions, the total number of reactive surface groups is very high. In some samples almost every other surface carbon atom carried a hydroxyl or carboxylic acid group. When samples from the same deposition were compared, it was found that the number of surface groups measured was satisfactorily reproducible according to this analysis. However, the surface chemistry did depend very strongly on the sputtering conditions. Even in materials sputtered under nearly identical conditions ("same" parameters for the sputtering, but different geometry and handling) significant fluctuations in the number of surface hydroxyl versus surface carboxyl groups were observed as can be seen comparing carbon I and carbon II in Table II.

## REACTION OF THE PERFLUORINATED POLYMERS WITH A CARBON SURFACE

Regardless of the surface chemistry of the carbon, it was possible to attach 1.5–2.0 nm thick films of PFPEs 1a and 1b to the surface by heat treatment; however, the stability of the films against displacement with low-molecular-weight compounds changed significantly with surface chemistry as discussed further below. Polymers TFM, which contain only —OCF$_3$ end groups, cannot react with appro-



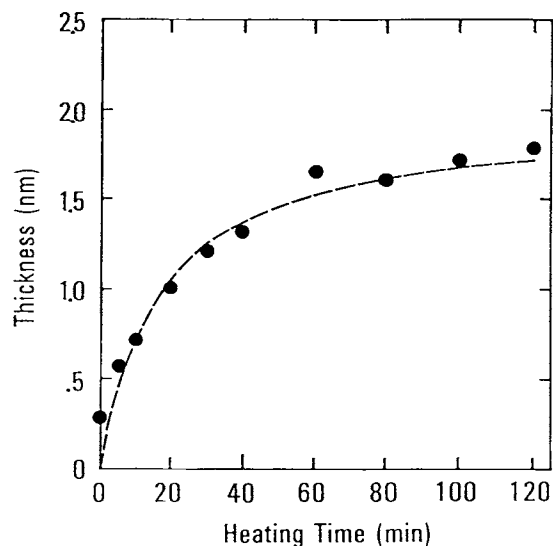Figure 2   Surface derivatization reactions by fluorinated tag molecules.

**Figure 3**  Film thickness by ellipsometry of DFHE attached to a carbon surface; initial film thickness 10.0 nm; heat treatment 150°C; extracted with TTFE.

priate reactive sites at the surface. The polymers are completely removed from the surface, when carefully cleaned with solvent after thermal treatment even though the samples were prepared and handled under identical conditions as those of DFHEs.

The thicknesses of the attached films were strongly dependent on the conditions of the thermal treatment, especially the temperature and duration of heating. As an example for this influence, the thickness of the attached polymer layer as a function of the heating time is shown in Figure 3. Each data point is obtained by heating a new sample for the desired time followed by TTFE extraction. The measurements shown in the figure represent an average over five samples (with five ellipsometry measurements each) prepared under identical conditions. A more detailed discussion of the kinetics of

the attachment process on various surfaces will be published elsewhere.[12]

The chemical nature of the surface strongly affects the attachment mechanisms available to the polymer film. Generally it was only possible to attach PFPE film onto surfaces that contained reactive groups. For example, no PFPE could be attached to polystyrene or $SiO_2$ surfaces made hydrophobic by treatment with hexamethyldisilazane as confirmed by XPS (cf. Table III).

## IR Spectroscopy

The IR spectra of the PFPEs employed consist of one strong band at about 1290 $cm^{-1}$ due to the C–F stretching vibration of the $CF_2$ groups and weaker bands due to C–O vibrations and the end groups (2980 and 3300–3500 $cm^{-1}$). The transmission spectrum of bulk DHFE2 is shown in Figure 4(a). It can be seen that the intensity of the IR bands due to the end groups is rather weak. Therefore these groups could not be detected in the grazing incidence reflection spectra of the ultrathin films.

It is observed that the peak maxima of the reflection spectra are slightly shifted compared to those of the transmission spectrum of the bulk material. This is due to the influence of the underlying thin film of a dielectric (sputtered carbon film) (15). It should be noted that, in the following, only spectra measured under exactly the same reflection conditions are discussed.

Not only the thickness of the attached polymer film but also the strength of interaction of polymers with a surface can be analyzed using IR spectroscopy.[16] In order to investigate this interaction, aluminum substrates with about 25.0 nm of sputtered carbon were coated with films of the PFPE of varying thickness (2.0–20.0 nm) by dip coating, and the spectra were measured as a function of the thickness of the PFPE layer. The results of these measure-

**Table III  Thickness of Films of DFHE2 Attached to Different Surfaces[a]**

| Material | Thickness (nm) | Method |
|---|---|---|
| Carbon (sputtered) | 1.5–1.8 | FTIR, XPS, ellipsometry |
| Graphite | 1.5 | XPS |
| $SiO_2/Si$ | 2.0–2.5 | XPS, ellipsometry |
| Poly(styrene) | < 0.5 | XPS |
| Methylated[b] $SiO_2$ | < 0.2 | ellipsometry, XPS |

[a] After 60 min heating of a 10-nm-thick film to 150°C and subsequent TTFE extraction.
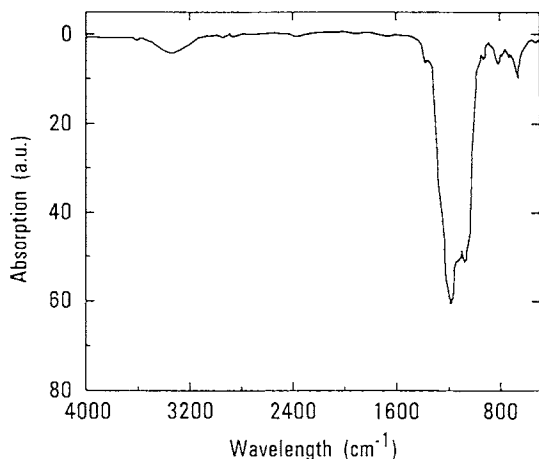[b] After treatment with hexamethylenedisilazane.

**Figure 4a** IR spectrum of DFHE2.

ments are shown in Figure 4(b). As the thickness of the polymer film decreases, the peak position of the band due to the C–F stretching vibration shifts to lower frequencies. Similar shifts have been observed in another PFPE[17] and other polymer–adsorbate systems.[16]

One possible explanation for the shift in the peak position is based on the relative amounts of strongly adsorbed and weakly adsorbed polymer. In this system there is a broad distribution of C–F stretching frequencies for the $CF_2$ groups as a result of their different chemical surroundings. The observed IR absorption band is then a weighted average of contributions from these different environments. When the polymer is adsorbed directly at the surface of the carbon, the interaction with the surface weakens the C–F bond. The resulting decrease in force con-
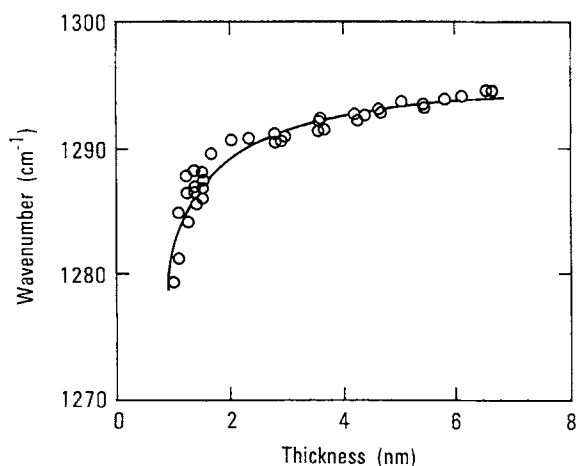


**Figure 4b** Peak position of C–F stretching vibration as a function of the film thickness.

stant is accompanied by a shift in the frequency of the C–F vibration to lower wave numbers. In thick polymer layers most of the polymer is not in direct contact with the surface but is surrounded by other polymer, and therefore the peak maximum is close to the bulk value. In thinner films, however, the relative amount of the polymer that is physisorbed directly onto the surface is larger and the weighted average shifts to lower wave numbers.

This interpretation of the observed peak shifts is further substantiated by the fact that heat treatment or vacuum exposure of thin PFPE films on a carbon surface also leads to comparable peak shifts. These procedures cause evaporation of adsorbed water (or other adsorbed low-molecular-weight contaminants), which provides additional sites at the substrate surface for strong polymer adsorption. This subsequently leads to a spreading of the polymer and enhancement of the adsorption of repeat units that can now contact the surface. In both cases a stronger interaction of the adsorbed polymer with the surface is achieved resulting in the observed peak shift to lower frequencies. However, this spreading of polymer molecules with an enhanced orientation of the repeat units parallel to the surface is not perfect, as the films obtained (1.5–2.5 nm) are too thick for one completely flat monolayer. The thickness of such a flat monolayer would be approximately equal to the cross-sectional diameter of the chain, which is estimated to be 0.5–0.7 nm using molecular models.

The increase in the density of attached polymer leads to a smaller number of available hydrophilic sites at the surface, which can also be seen in the changes of the water contact angle as a function of heating time. To study this effect, 10-nm-thick films of DFHE were coated onto a carbon surface, heated for the desired time at 150°C, and extracted with fluorinated solvent. As shown in Figure 5 the contact angle of water against the carbon surface increases rapidly from an initially relatively low value (48°) to a very high angle (110°) after 1 h of heating. The surface becomes more and more hydrophobic until the wetting angle is the same as for a very thick film of the PFPE.

## DISPLACEMENT OF THE POLYMERS BY LOW-MOLECULAR-WEIGHT COMPOUNDS

The influence of the end groups of the polymer on the attachment and the requirement for reactive sites on the surface to which the polymer can become attached are both strong indications of a chemi-

sorption process. This is further substantiated by the fact that the activation energy for attachment of DFHE (which has —$CF_2CH_2OH$ end groups) on a silica surface[12] is 60 kJ/mol, which is essentially the same as for surface esterification of a silica surface with low-molecular-weight, straight-chain alcohols.[18]

However, it should be noted that not all the polymer, which cannot be washed off after thermal treatment, is chemisorbed to the surface. Some strongly physisorbed material remains in the film. Some of it can be slowly removed by solvent extraction for a prolonged time. Although initial measurements seem to indicate that the final thickness of the polymer film is already reached after a short solvent extraction (30–40 min), some additional 25–30% of the polymer can be removed by long time extraction (Fig. 6). Within the experimental error no further changes in film thickness could be detected after several days of extraction and what appears to be an equilibrium value was reached.

Even more polymer could be extracted when samples were exposed to various polar low-molecular-weight compounds. When the attached films were exposed to compounds such as water, alcohols, acetone, or chloroform and afterward washed in a solvent for the polymer, such as TTFE, trifluoroethanol, or polyfluorinated hydrocarbons, nearly half of the attached polymer could be removed from the surface, as depicted in Figure 6 and 7 (new samples for each data point; data represent an average of three different samples). Generally it was observed that more polar compounds such as acetone, alcohol, or water displace the polymer more effectively than nonpolar compounds such as toluene or chloroform.
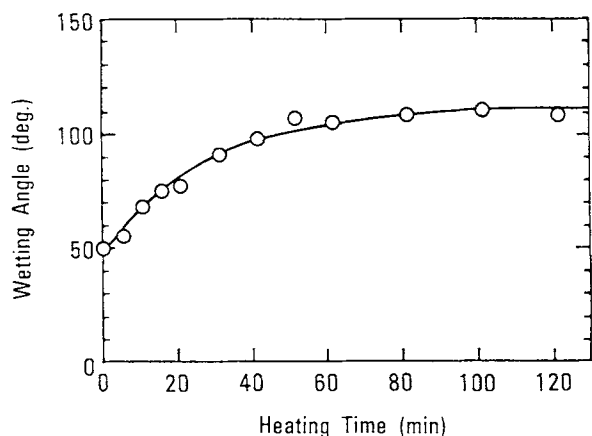
**Figure 6** Thickness of attached films of DFHE2 to a $SiO_2$/Si surfaces after (O) TTFE extraction; (∇) water exposure followed by TTFE extraction; initial thickness 10.0 nm; samples heated for 1 h to 150°C. Filled symbols represent measurements after 1 week of exposure. Error bars indicate variation in different samples.

However, it must be emphasized that although polar low-molecular-weight compounds displace some physisorbed polymer from the surface quite readily and enable a dissolution of the displaced material in a subsequent solvent extraction, it was not possible to remove the attached polymer completely. Even after boiling in water for 24–36 h with subsequent solvent extraction no significant additional polymer was displaced.

Consistent with these results water vapor from the ambient also slowly displaces physisorbed poly-

**Figure 5** Wetting angle of carbon surfaces with attached film of DFHE; samples coated, heated for the desired time and extracted with TTFE; each data point represents a separately prepared sample.
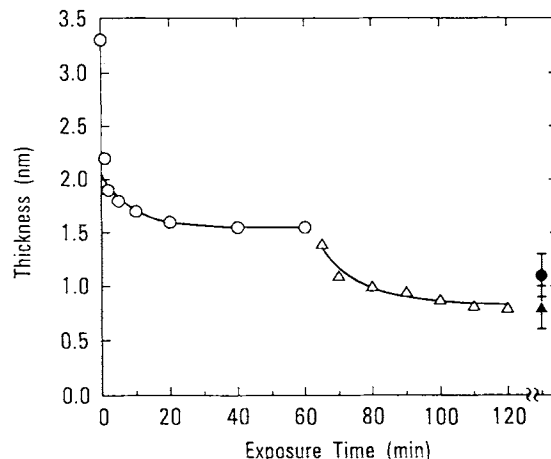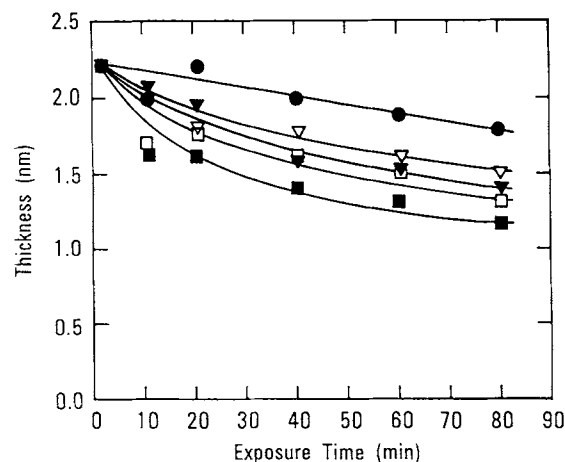
**Figure 7** Film thickness of films of DFHE as a function of exposure time to various displacers: (●) toluene, (∇) chloroform, (▼) acetone, (□) methanol, (■) water; sample preparation described in the text.

mer from the surface. When samples (after thermal treatment and 1 h solvent extraction) were kept under ambient conditions or in an environmental chamber (100% relative humidity, 55°C) for extended periods of time (several weeks) some 40–50% of the polymer could be removed in a subsequent solvent wash and a 0.8–1.2 nm thick film of the polymer remained.

Complete removal of the films of DFHE2 attached to a carbon surface by thermal treatment could only be achieved by boiling the sample in strong acids or bases. Under such conditions it can be expected that the covalent bond between the polymer and the reactive site of the surface would be cleaved. Quantitative measurements, however, are difficult to interpret because such conditions lead also to corrosion of the substrate below the carbon thin film.

In order to investigate how strongly the perfluoropolyethers DFHE and TFM are physisorbed and to estimate how much energy is required to remove such material from the surface, the integral heat of immersion and the heat of dissolution of the polymers in various fluorinated solvents were determined by microcalorimetry. The results of these investigations are shown in Table IV. Measurements of the heat of immersion were performed using dried silica powder (24–72 h at 200°C and 10 mbar) with a large surface area (200 m²/g by BET) in order to have a larger (and still well-defined) surface than that of the carbon thin films otherwise employed.

The measured integral heat of immersion of DFHE2 on silica (18.5 J/g) was much smaller than that of water adsorbing on the same surface (35–40 J/g).[19] Therefore it can be inferred that the effectiveness of water in displacing physisorbed PFPE from a carbon surface reflects its higher heat of adsorption to the surface relative to the polymer. Other polar low-molecular-weight compounds such as al-

cohols, which have comparably strong interactions with the surface, would also be expected to displace the PFPE. This agrees well with the results of the displacement experiments (comp. Fig. 7).

It is interesting to note that the polymers DFHE and TFM, which have a similar backbone structure and molecular weight but differ in the end groups, show significant differences in the heat of adsorption onto silica (cf. Table IV). That the heat of adsorption of polymer DFHE is much larger than that of TFM reflects the fact that the nonpolar (weakly Lewis basic) backbone adsorbs only weakly to the polar (weakly Lewis acidic) surface. The hydroxyl end groups of DFHE2, however, can form hydrogen bonds to the hydroxyl groups of the silica surface (at room temperature; at elevated temperature a chemical bond is established) and thus the polymer adsorbs more strongly.

This difference in adsorption enthalpy of the two polymers is also reflected in their adsorption/desorption behavior. When thin (= 3.0 nm) polymer films of DHFE and TFM physisorbed to the carbon surface are extracted with solvent polymer TFM can be almost completely desorbed from a carbon surface by exposure to a solvent (> 30 min) or washing with solvent during treatment with ultrasonics. Polymer DFHE, however, deposited under identical conditions cannot be removed completely using these procedures. Even after ultrasonic treatment (40 KHz, 5 min) in TTFE, a thin layer (0.4 nm) of the polymer remained on the surface as measured by FTIR analysis. This layer could only be removed after exposure of the film to water and subsequent rinsing with TTFE.

The dissolution of polymers DFHE and TFM in TTFE, perfluorooctane, and trifluoroethanol is a slightly endothermic process (about 10 J/g). It is quite common for polymers that the dissolution is endothermic or only weakly exothermic if the poly-

Table IV   Integral Heat of Immersion of Silica into DFHEs and TFMs and Heat of Dissolution in Various Solvents

| | | | Heat of Dissolution[a] | |
|---|---|---|---|---|
| Polymer | Heat of Immersion[a,b] | TTFE | CF₃OH | C₈F₁₈ |
| DFHE2 | −18.5 ± 0.5 | 10.1 | 4.5 | 6.7 |
| TFM4 | −9.2 ± 0.5 | 10.0 | 0.2 | 5.4 |
| TFM9 | −9.5 ± 0.5 | | | |
| Water[c] | −35–40 | | | |

[a] In J/g, negative values represent heat released; measured at 20°C.
[b] Aerosil, Degussa, 200 m²/g by BET.
[c] According to Ref. (16).

mer is above the glass transition temperature.[20] This reflects the fact that the solvent–solvent and polymer–polymer interactions are stronger than the solvent–polymer interactions. In order to determine whether there was an additional effect through heat released by dilution of the polymer solution, the heat of dissolution was measured in a wide range of final polymer concentrations (0.1–33%). It was observed that the heat of solution was independent of concentration in that range.

Not only does the exposure to solvent or displacer molecules affect the attachment of the polymers to the surface but also the chemical composition of the surface plays an important role. This was demonstrated by comparing films of DFHE2 attached to two different carbon surfaces.

One sample consisted of a carbon film sputtered onto a silicon substrate, the other pyrolytic graphite. While the first one was shown to contain a large number of functional groups at the surface (especially hydroxyl- and carboxylic acid groups), the last one can be cleaved along the basal plane of the crystals creating surfaces with a very small number of functional groups (cf. Table II). The graphite was cleaved and heated under a thick film of the liquid polymer, thereby minimizing air exposure and surface oxidation. As shown by XPS measurements a film of 1.5–1.8 nm of DFHE2, which could not be washed off with solvent, was attached to both surfaces during the heat treatment (cf. Table III). Samples prepared under identical conditions, but kept at room temperature for 1 h, could be almost completely extracted (remaining thickness of 0.2–0.3 nm according to XPS measurements).

The polymer films thermally attached to graphite and sputtered carbon, although of comparable thickness, are quite different when the two samples are exposed to water. Whereas the water contact angle of the graphite sample is initially very high (about 110°), it decreases very rapidly (Fig. 8). The spreading of the water droplet is so very fast that even within a few minutes the contact angle of pure graphite is reached. AFM mapping after drying off the water shows that a bare spot remains at the former position of the water droplet and the polymer is transferred to the edges of the droplet. The contact angle of the PFPE film attached to sputtered carbon in comparison changes only very slowly. A slight decrease of the wetting angle was observed within several hours.

One possible explanation for this striking difference in behavior is that the relative amounts of chemisorbed vs. physisorbed polymer vary, whereas the total amount of attached polymer is the same
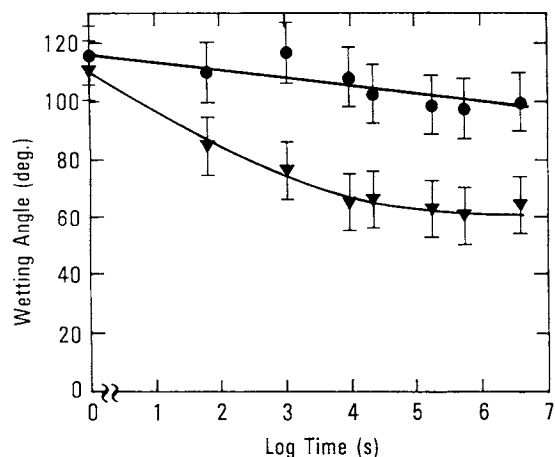


**Figure 8**    Wetting angle of films of DFHE on (●) sputtered carbon (1.8 nm) and (▼) pyrolytic graphite (1.5 nm) against water; droplet 10 μL; ambient conditions.

within experimental error. It can be expected that films attached to a surface with a large number of reactive groups (such as sputtered carbon) contain more chemisorbed polymer than films attached to a surface with a small number of reactive surface groups such as graphite. The physisorbed polymer, however, gets rapidly displaced from the surface by polar, low-molecular-weight compounds. Thus in films with a relatively large amount of physisorbed material (such as the film attached to the graphite) the film properties will change more rapidly upon displacer exposure than those of films with less physisorbed polymer. This is in close agreement with the experimental findings.

The weakly attached polymer may be attributed to physisorbed polymer or polymer molecules trapped in the film by entanglement. These physisorbed chains are expected to have a broad distribution of interactions with the polymer surface depending on the number and length of trains of adsorbed repeating units, and therefore a broad distribution of energies required for the removal of the individual polymer chains can be expected.

Although the critical molecular weight for entanglement of polymer chains is usually higher than the molecular weights of the PFPEs used here,[14,17] two additional facts must be considered. One is that although the average molecular weight of the solvent-extractable polymer is below the critical weight for entanglement (even after evaporation of low-molecular-weight polymer), the weight of some of the nonextractable polymer might be considerably higher. Additionally, the calculation of the critical molecular weight for entanglement is always per-

formed for polymer chains either in solution or in the bulk (melt). In very thin films, however, the polymer chains are much more constrained by the proximity of the surface, and many of the motions, which could lead to disentanglement, are no longer possible. Therefore, although we do not have direct evidence for entanglement in the physisorbed polymer, we cannot *a priori* exclude the possibility that it plays a significant role.

## AFM MEASUREMENTS

These differences in the strength of interactions of the polymer with surfaces described above can be expected to influence the mobility of the polymer molecules on the surface substantially. This mobility can be studied indirectly by investigating meniscus formation of the polymer on a solid by atomic force microscopy (AFM). For these experiments samples were used in which the PFPE DFHE2 was attached to $SiO_2$ (natural oxide of a silicon wafer) by thermal treatment, and the attached polymer films were subjected to various cleaning procedures.

When the polymer is only physisorbed to the surface, then at a certain distance between the tip of the AFM cantilever and the sample an attractive force suddenly arises, which drags the tip closer to the surface. The onset of the force, at which the tip suddenly jumps in, is at a very well defined distance as it is depicted in the uppermost curve of Figure 9. This distance is larger than the initial film thickness (approx. 2.5 nm) because after the first contact between the AFM tip and the polymer some polymer is transferred to the tip, and in subsequent measurements the interaction between the polymer film and a polymer-coated tip is measured. In addition attractive force may redistribute the liquid on the surfaces at short separation.[21] The attractive force observed has been attributed to the formation of a meniscus of the liquid (or better "liquidlike") polymer around the AFM tip.[11] The attractive meniscus force increases gradually until the tip contacts the solid wall and the force becomes repulsive.

A sample of a comparable thickness (2.2 nm), where the weakly or nonattached polymer was removed after thermal treatment (1 h, 150°C) by dipping it in TTFE for 3 min, still shows some onset of an attractive force at about 5.0 nm separation due to full or partial formation of a meniscus. But the force due to this meniscus formation is much weaker than for a sample with physisorbed polymer only. Additionally the onset of this force is much less defined than in the sample with the physisorbed poly-

mer, and a more gradual increase over some distance [curve (b) in Fig. 9] is observed.

In a second set of samples the weakly adsorbed (or entangled) polymer was removed by cleaning with TTFE using ultrasound or by immersion of the solvent-cleaned sample in water for 18 h followed by additional TTFE cleaning. Samples prepared by using both cleaning procedures showed almost identical force distance curves; an example is depicted in curve (c) of Figure 9. The thicknesses of the polymer films were 1.2 and 1.7 nm, respectively, as measured by ellipsometry. Upon reducing the tip–sample distance under 5.5 nm these samples showed only a very slow increase of the attractive force. Contrary to the sample with physisorbed polymer only, and the sample in which weakly interacting polymer was removed by dipping in solvent, no abrupt increase in the attractive force due to a meniscus formation could be observed [curve (c) of Fig. 9]. It is expected that the extended solvent exposure of the samples removed most of the mobile polymer—at least mobile on the time scale of the experiment—either by dissolution or displacement and only immobile, firmly attached perfluoropolyether remains.

The shift of the AFM tip–sample separation at which the attractive force deviates from very low force [5.2 nm in sample (a), 5.5 in (b), and 6.5 nm in (c)] depends not only on the overall thickness of the polymer films on both surfaces but also on the molecular weight of the polymer. During the thermal treatment the molecular weight of polymer increased significantly due to evaporation of low-molecular-weight oligomers and subsequent solvent extractions are also likely to remove, preferentially, low molecular weights. This displaces the detectable meniscus force to greater separations despite the lower film thickness.

Careful analysis of curves (a)–(c) in Figure 9 shows that, despite the striking differences between the samples concerning the meniscus formation, the *total* attractive force (= force at infinite distance − force in the minimum of the force–distance curve) does not change significantly (approximately 2.5 $\times 10^{-8}$ N). If the tip is moved closer to the surface (< 3 nm) additional attractive forces occur. This can be explained if one takes into account that the surface covered by the polymer has also some water and possibly other adsorbates coadsorbed at the surface. The total attractive force between the tip and the sample is governed not only by the meniscus formation but also by interaction of water molecules coadsorbed on both surfaces. Upon very close contact between tip and sample this coadsorbed water gives rise to some hydrophilic/hydrophilic inter-
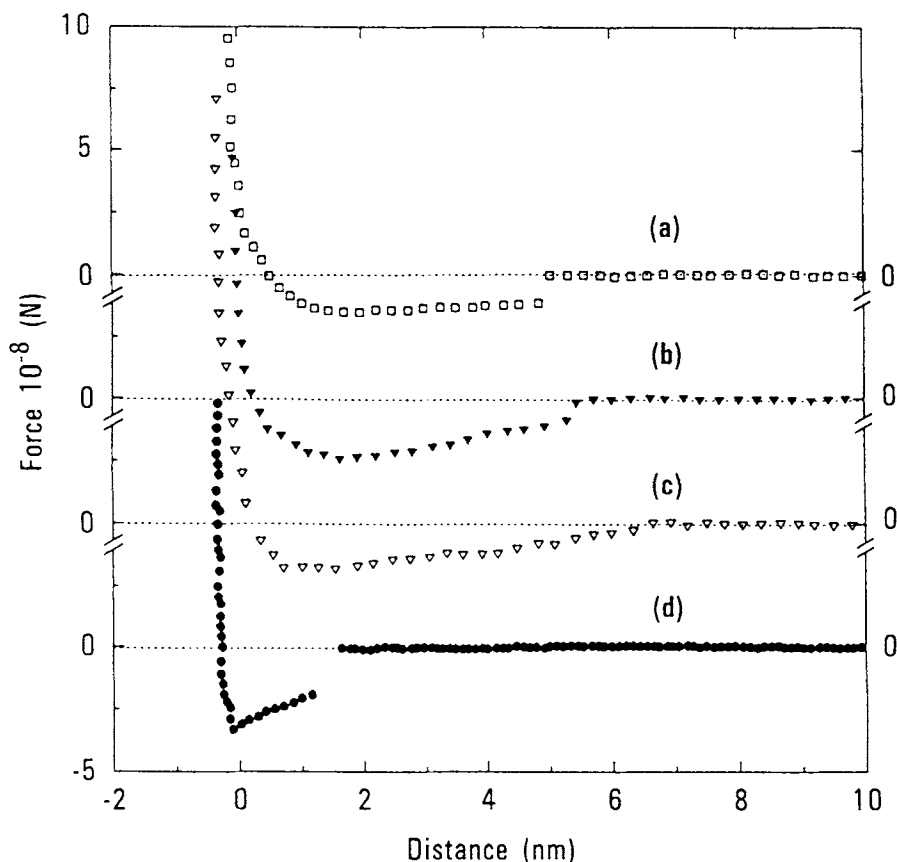
**Figure 9**  Force–distance curves measured with atomic force microscope: (a) physisorbed film of DFHE2; (b) thermally treated film (1 h, 150°C) after TTFE extraction (final thickness 2.0 nm); (c) film as in (b) after additional water exposure (12 h) and TTFE extraction; (d) cleaned silicon wafer. All measurements performed under ambient conditions.

actions leading to a gradual increase of an attractive force, however, it cannot form a meniscus on samples (a), (b), and (c) because of the PFPE present. This can be seen when the force distance curve of PFPE films (Fig. 9) are compared with a cleaned silicon surface without any fluorocarbon polymer [curve (d) in Fig. 9].

## CONCLUSIONS

In this study we have shown how thin films of perfluoropolyethers with functional and nonfunctional end groups interact with surfaces of carbon, silicon dioxide, and others. Both physisorbed and chemisorbed thin films were characterized. Interaction of physisorbed polymers with solid surfaces is demonstrated by the shift of vibrational modes to lower frequencies in films a few nanometers thick when compared with thicker films. Microcalorimetry measurements show that heats of immersion in-

crease for nonreactive perfluoropolyethers, reactive perfluoropolyethers, and water, respectively, suggesting why these polymers are easily displaced by water and other polar low-molecular-weight compounds.

Polymers with hydroxyl-terminated end groups were attached thermally to solid surfaces. Thicknesses of these thermally attached polymers and wetting angles of the treated surfaces approach saturated values with increasing heating time. When these thin films are exposed to solvents or water, some polymer is displaced. A finite thickness around 1 nm remains, however, and is defined as the chemisorbed amount. The chemical attachment occurs only to surfaces with reactive surface groups such as hydroxyl and carboxylic groups and not on surfaces of polystyrene or methylated silicon dioxide. Dissolution and displacement experiments show that there are varying strengths of attachment in thermally treated samples. The relative amounts of chemisorbed and strongly physisorbed polymer are

dependent on the surface chemistry of the substrate, the attachment conditions, and the previous exposure to low-molecular-weight displacers. Atomic force microscope measurements show that the mobility of the polymer decreases as the amount of the physisorbed material is lowered. Any evaluation of the physical, especially tribological, properties has to take the varying amounts of physisorbed and chemisorbed polymer into account.

## REFERENCES

1. For review see: (a) A. Homola, M. Mate, and G. B. Street, *MRS Bull.*, **15**, 45 (1990); (b) B. Bhushan, *Wear*, **136**, 169 (1990).

2. V. Novotny, J. D. Swalen, and J. P. Rabe, *Langmuir*, **5**, 485 (1989).

3. J. Seto, T. Nagai, C. Ishimoto, and H. Watanabe, *Thin Solid Films*, **134**, 101 (1985).

4. E. Ando, Y. Goto, K. Morimoto, K. Ariya, and Y. Okahato, *Thin Solid Films*, **180**, 287 (1989).

5. (a) A. M. Scarati and G. Caporiccio, *IEEE Trans. Magn. Mag.*, **23**, 106 (1987); (b) M. Suzuki, Y. Saotome, and M. Yanagisawa, *Thin Solid Films*, **160**, 453 (1988); (c) T. Miyamoto, I. Sato, and Y. Ando, in *Tribology and Mechanics of Magnetic Storage Systems*, Vol. 5, B. Bushan and N. S. Eiss, Eds., 1988, p. 55; (d) D. Sianesi, V. Zamboni, R. Fontanelli, and M. Binaghi, *Wear*, **18**, 85 (1971).

6. See, for example, H. Möhwald, *Angew. Chem. Int. Ed. Adv. Mater.*, **27**, 728 (1988); B. Tieke, *Adv. Mater.*, **2**, 222 (1990).

7. (a) M. Cohen-Stuart, T. Cosgrove, and B. Vincent, *Adv. Coll. Interf. Sci.*, **24**, 143 (1986); (b) A. Takahashi and M. Kavaguchi, *Adv. Polym. Sci.*, **46**, 1 (1982).

8. C. D. Bain and G. M. Whitesides, *Angew. Chem. Adv. Mater.*, **110** (1989).

9. K. P. Krenkler, R. Laible, and K. Hamann, *Angew. Makromol. Chem.*, **53**, 101 (1976).

10. A. Vidal and J. B. Donnet, *Bull. Soc. Chim. Fr.*, **6**, 1088 (1985).

11. C. M. Mate, M. R. Lorenz, and V. J. Novotny, *J. Chem. Phys.*, **90**, 7550 (1989).

12. J. Rühe, V. Novotny, T. Clarke, and G. B. Street, to appear.

13. G. Barth, R. D. Cormia, and L. A. Teasley, *Sol. State Tech.*, **1**, 219 (1989).

14. (a) W. Graessley, *Polymer*, **21**, 258 (1980); (b) V. Novotny, *J. Chem. Phys.*, **92**, 3189 (1990).

15. D. Saperstein, *Appl. Spectrosc.*, **43**, 481 (1989).

16. C. van der Linden and R. van Leemput, *J. Colloid Interface Sci.*, **67**, 48 (1978).

17. V. J. Novotny, I. Hussla, J. M. Turlet, and M. R. Philpott, *J. Chem. Phys.*, **90**, 5861 (1989).

18. R. K. Ihler, *The Chemistry of Silica*, Wiley, New York, 1979, p. 692.

19. A. M. Khalil, *J. Colloid Interface Sci.*, **66**(3)509 (1978); S. Kondo et al., *J. Chem. Soc., Faraday Trans.*, **75**, 646 (1979); A. Kryszta f kiewicz, *Colloid Polymer Sci.*, **267**, 399 (1989).

20. R. Orwool, in *Polymer Handbook*, J. Brandup and E. H. Immergut, Eds., Wiley, New York, 1989, p. VII-517.

21. C. M. Mate and V. J. Novotny, *J. Chem. Phys.*, **94**, 8420 (1991).