4532 *Macromolecules* **2000,** *33,* 4532−4537

Toward High Resolution Mapping of Functional Group Distributions at Surface-Treated Polymers by AFM Using Modified Tips

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Received August 11, 1999; Revised Manuscript Received February 14, 2000

ABSTRACT: The lateral distribution of functional groups at polymer surfaces was studied with high resolution using atomic force microscopy with chemically modified tips (“chemical force microscopy”). Pull-off force measurements carried out on oxyfluorinated films of isotactic polypropylene as a function of pH using OH-functionalized tips revealed a “force pK_a” of 5.5−6.0. At pH values close to or slightly higher than the “force pK_a”, position-resolved maps of pull-off forces showed laterally inhomogeneous adhesive forces on a *sub-50 nm* scale. These variations, which can be related to variations of local pK_a values, are attributed to locally different hydrophobicity and thus to inhomogeneous distribution of the functional groups introduced by the surface treatment.

Introduction

In numerous applications the surface properties of polymeric materials are crucial for the final product application. To enhance for instance biocompatibility or adhesion, apolar polymers, such as polyolefins, are usually surface-modified by introducing polar functional groups.[1] While different surface analytical techniques which provide “*in-depth*” resolution are available for studies of functional group distributions, the lateral resolution which can at present be achieved on polymers is of the order of several hundred nanometers.[2,3] Hence, little is known about the functional group distributions in surface-treated polymers.

The capability of atomic force microscopy to achieve high-resolution real space imaging of polymer surfaces is well documented in the literature.[4] By functionalizing gold-coated AFM tips with self-assembled monolayers (SAMs) of ω-functionalized alkanethiols,[5] the interaction between tip and sample surface in force−distance[6] and lateral force (friction) measurements can be controlled (Figure 1). The imaging and discrimination of areas composed of SAMs which expose different functional groups by using this approach were first reported by Lieber et al.[7−10]

Previously we have reported that the average pull-off forces measured on flat, surface-treated polyolefins using for example −COOH-terminated tips in ethanol can be correlated with the surface energy of the polymer films.[10a−e] These results correspond to average values obtained over the entire surface of the specimens. Because of the limited dynamic range of the pull-off forces measured in ethanol and the width of the force distributions, laterally resolved pull-off force measurements were inconclusive in the aforementioned studies. In addition, the absence of coupling of topography into the force images was difficult to prove.[11] Therefore, pH-dependent experiments were carried out in aqueous solutions on oxyfluorinated iPP specimens.

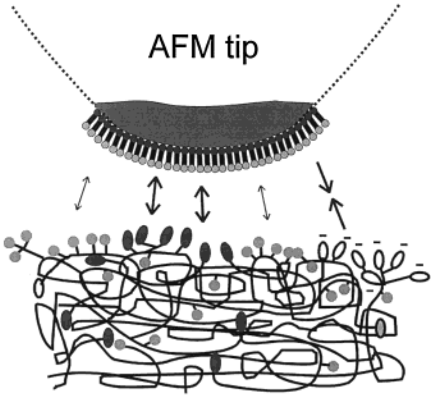

Figure 1. Schematic diagram of force measurements with chemically modified AFM probe on polymers containing functional groups at the surface. By performing pH-dependent force measurements, the ionizable functional groups can be studied with high resolution.

As we report in this paper for the first time, laterally resolved force spectroscopy in aqueous environment with variable pH allows one to study *the spatial distribution of ionizable functional groups* in surface-treated polymers on a *sub*-50 nm scale. The results constitute a significant step toward the ultimate aim of detecting functional group distributions in surface-treated or functionalized polymers with nanometer resolution.

Experimental Section

Materials. Isotactic polypropylene films (SOLVAY ELTEX P KL 177) were oxyfluorinated at 60 °C in a $F_2/N_2/O_2$ gas mixture. By varying the treatment time and the gas composition, different surface compositions were achieved. The characterization of the iPP films by means of contact angle measurements and XPS analysis is described in ref 10a.

Atomic Force Microscopy and Tip Modification. Triangular-shaped silicon nitride cantilevers with silicon nitride tips (Digital Instruments (DI), Santa Barbara, CA), which were coated with 2 nm Ti and 75 nm Au in high vacuum (Balzers), were functionalized with 11-hydroxyundecanol following the procedures described in ref 10a. The AFM measurements were carried out with a NanoScope III multimode AFM (DI) with

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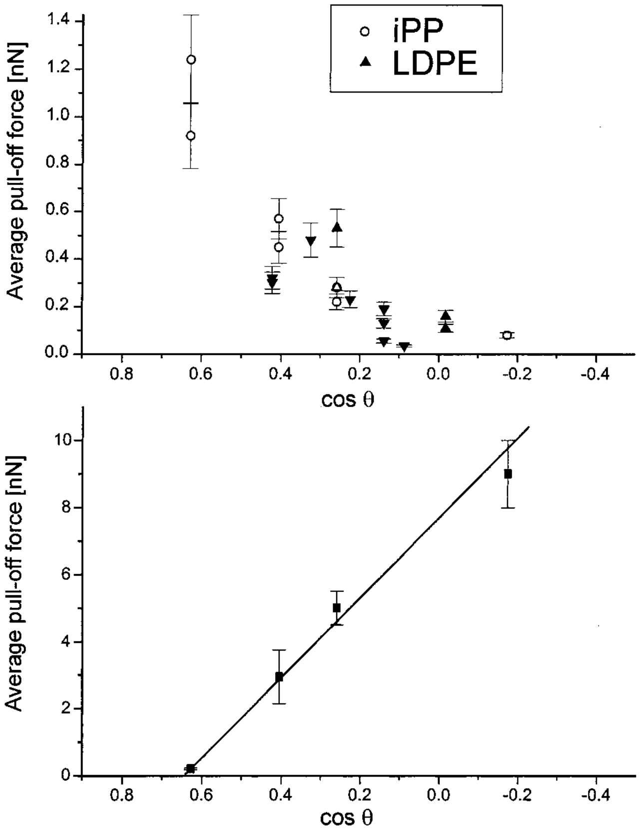

Figure 2. Average pull-off forces measured with −COOH-terminated tips on modified polyolefin surfaces (oxyfluorinated iPP[10a] and chromic acid-treated LDPE[10b]) in ethanol (top) and with −OH-terminated tips in water (pH 3.8, bottom) as a function of cos θ (θ = contact angle measured with water).

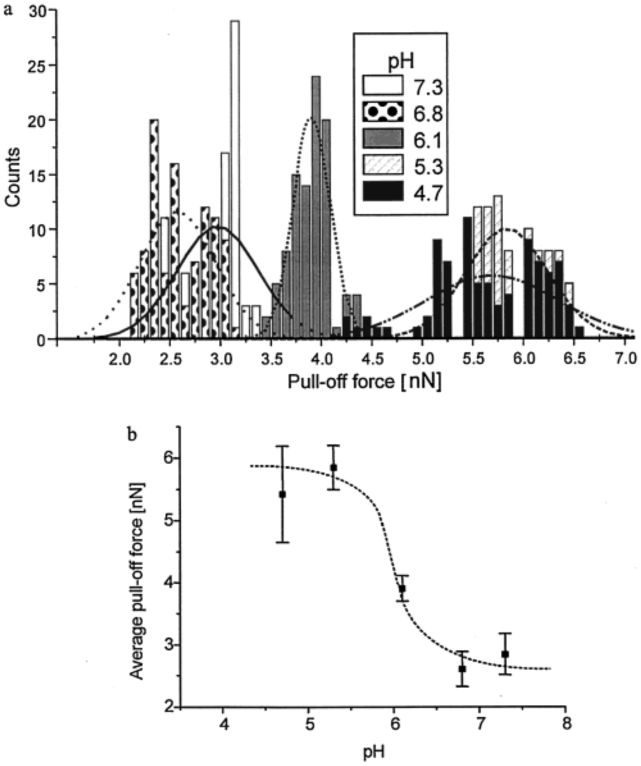

Figure 3. (a) Histograms of pull-off force distributions measured with a OH-terminated tip in buffered solutions on oxyfluorinated iPP (γ = 33.9 mN/m; curves: Gaussian fits). (b) Force titration curve of oxyfluorinated iPP constructed from data in (a) (the line has been added to guide the eye).

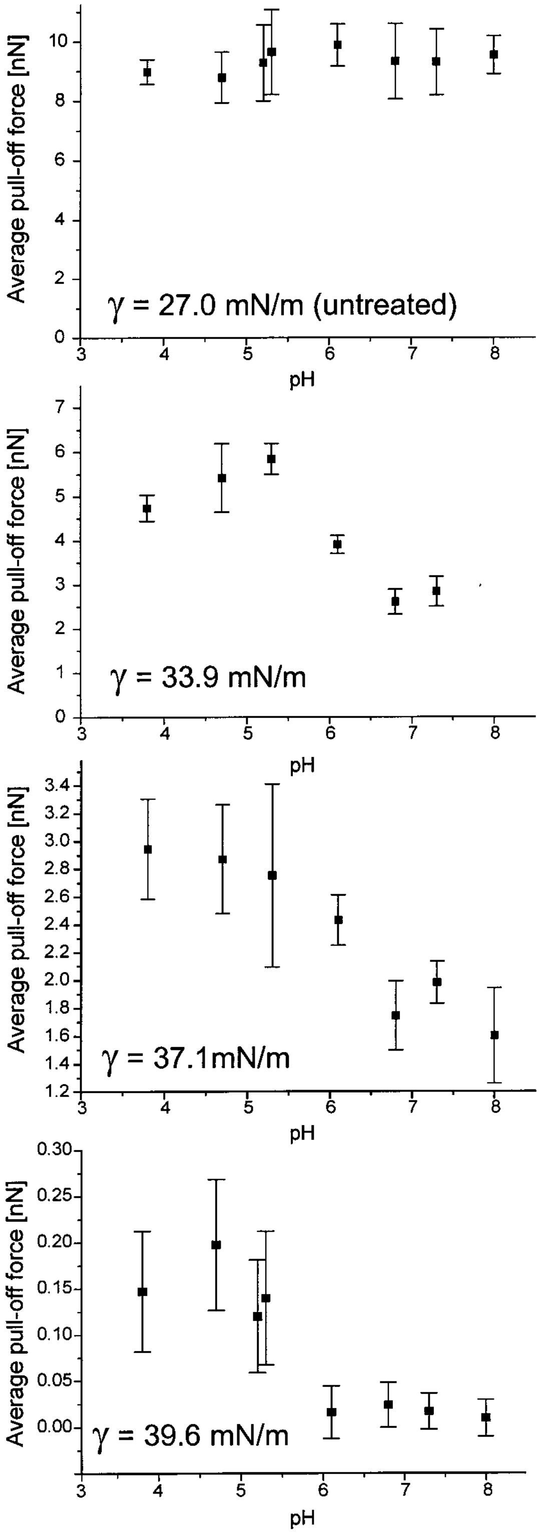

Figure 4. Force titration of an untreated iPP (top) and three oxyfluorinated iPP films using OH-terminated AFM tips. The total surface tension as determined in ref 10a is indicated. The error bars are the standard deviation of the average value calculated from the corresponding histograms.

modified tips in buffered aqueous solutions of constant ionic strength utilizing a liquid cell (DI).[12] The force−distance curves used for construction of force titration curves were obtained at 10 different positions (at least) for each sample. For laterally resolved pull-off force measurements the AFM was operated in the force volume (FV, DI) mode. Only subsequent up and down scans that showed the same force characteristics were considered.

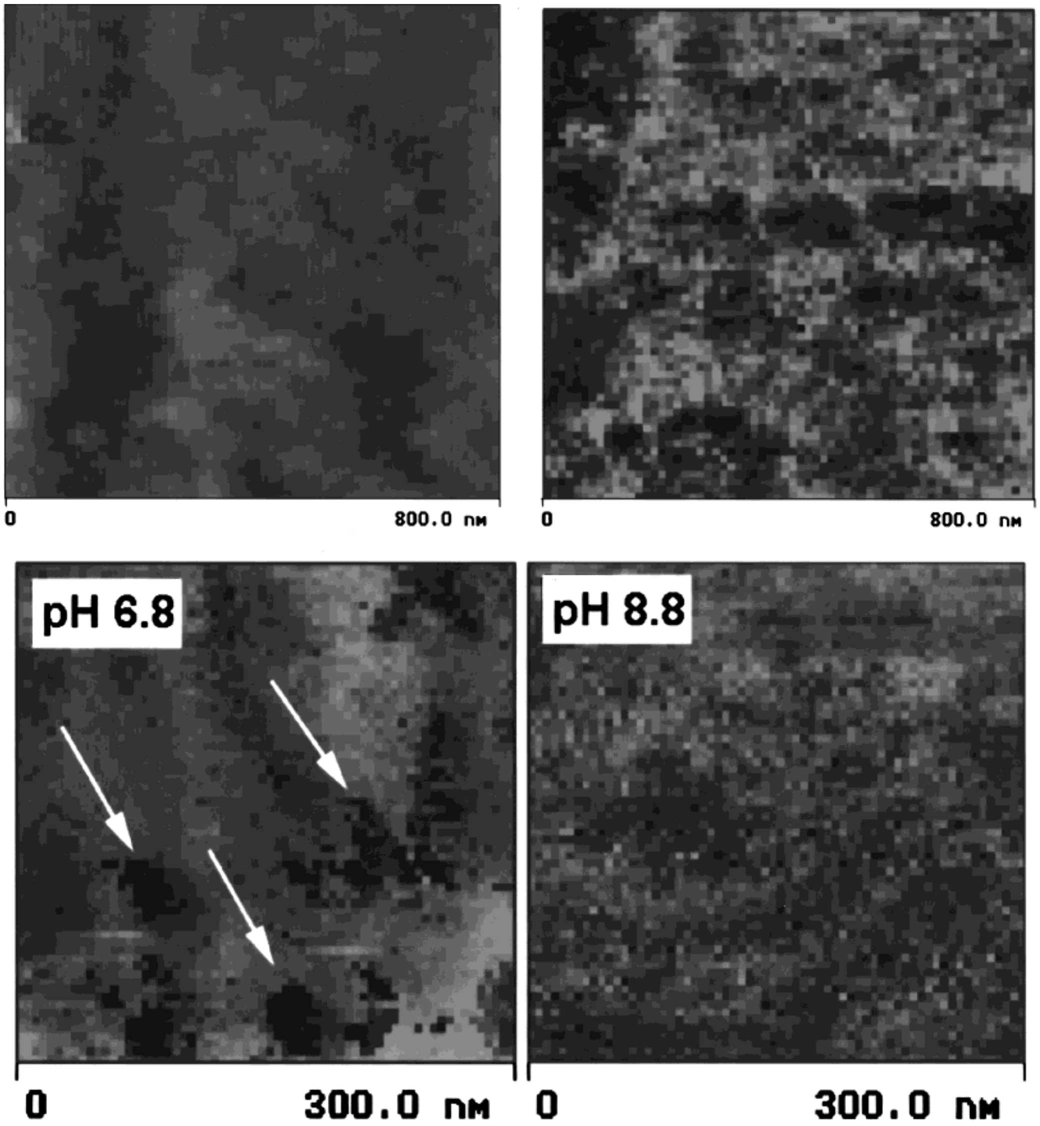

Figure 5. (a, top) Height (left) and pull-off force (right) images of oxyfluorinated iPP ($\gamma = 39.6$ mN/m) at pH 6.1. In the height image, the color scales go from dark (0 nm) to bright (100 nm). In the force image dark color indicates high adhesion (-0.5 nN) and bright color indicates low adhesion (0 nN).[24] (b, bottom) Pull-off force images of oxyfluorinated iPP ($\gamma = 39.6$ mN/m) at pH 6.8 (left) and pH 8.8 (right). Dark color indicates high adhesion (-0.3 nN for pH 6.8, ≈ 0 nN for pH 8.8), and bright color indicates low adhesion (0 nN for pH 6.8, 0 nN for pH 8.8). The arrows indicate small areas of high pull-off forces.

Results and Discussion

Average Force Measurements. Force–distance curves were measured in order to determine the pull-off forces.[6] The differences in surface energy as measured previously with −COOH-terminated tips in ethanol[10a] can be also recognized for pull-off force measurements in aqueous solution (Figure 2).

Carboxylic acid groups are the only ionizable functional groups expected at the surface of oxyfluorinated iPP.[13] At low pH these groups are completely protonated (vide infra).[14] By performing pH-dependent pull-off force measurements, the contribution of the ionizable functional groups to the pull-off forces can be separated from the rest. In aqueous solution, the sum of the different attractive forces is counteracted by the electrostatic repulsion of deprotonized carboxylic acid groups if the pH is close to or higher than the pK_a of these groups.[15] The balance of attractive forces and repulsive electrostatic forces is measured as "pull-off force".

Hydroxyl (−OH)-terminated tips were used in this study as these do not show any pH dependence in force measurements,[16] while the interaction between these hydrophilic tips and various surfaces is relatively weak in aqueous environment.[16,17] By measuring pull-off forces as a function of pH, a corresponding "force titration" curve can be obtained. As displayed in Figure 3a, the pull-off forces show a clear dependence on the pH of the solution. Although the forces measured show a broad distribution, the mean values are clearly separated. From these distributions the average pull-off forces can be calculated and plotted as a force titration curve (Figure 3b).

The data shown allow one to roughly determine a surface "force pK_a". This "force pK_a" is higher than the thermodynamic pK_a for carboxylic acids in solution (pK_a $\approx 4.7-5.0$).[14,15] This deviation is indicative of a hydrophobic environment of the carboxylic acid groups in the iPP.[16] The experiments were performed in buffers with different ionic strength.[12] No shift of the pK_a was observed in the ionic strength regime utilized. In Figures 4 a complete set of experiments on four different iPP films is shown. While the untreated film does not

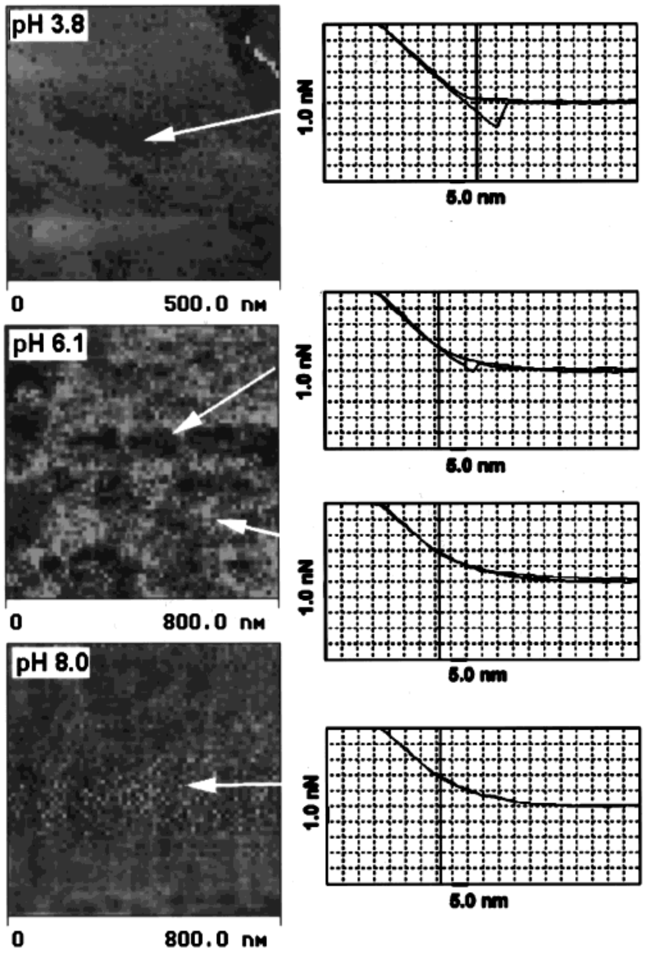

Figure 6. Pull-off force images of oxyfluorinated iPP ($\gamma = 39.6$ mN/m) at different pH. On the right, force−distance curves measured at the points indicated by arrows are depicted. In the force images dark color indicates high adhesion (−1.5, −0.5, and ≈0 nN for pH 3.8, pH 6.1, and pH 8.0, respectively), and bright color indicates low adhesion (−0.1, ≈0, and ≈0 nN for pH 3.8, pH 6.1, and pH 8.0, respectively).

show any pH-dependent behavior, the oxyfluorinated films do. The different oxyfluorinated iPP films did not show a pronounced difference in " force pK_a".

Laterally Resolved Force Measurements. The adhesion data on the samples discussed in the previous section were collected at many spots of the sample surface. The precise positioning of the sample and the very small contact area between tip and sample at pull-off in AFM allow one to acquire the pull-off forces as a function of the lateral position. Only in position-resolved force measurements one can take full advantage of the high-resolution microscopic nature of the AFM experiment and thus obtain novel insight into forces and adhesive properties on a nanometer scale. For this purpose, the adhesion data were collected as a function of lateral displacement. Pull-off forces were measured in so-called force volume images between pH 3.8 and 8.8. The measurements were performed after a long equilibration period of up to 8 h in order to minimize the instrumental drift. In all cases the drift could be minimized, and more importantly, the pull-off force data did not change in time. This indicates that the surface is in equilibrium with the buffer.[18] In Figure 5a a dual height[19] and force image of the most hydrophilic oxyfluorinated iPP ($\gamma = 39.6$ mN/m), acquired at pH 6.1, is shown. The film surface is fairly flat, and the patches of high pull-off force do not correspond to topological depressions or elevations. Pull-off force images acquired at pH < 8.0 often showed a laterally heterogeneous distribution of pull-off forces. This is illustrated in detail in Figure 5b. Arrows indicate small areas of high pull-off force measured at pH 6.8, which can be interpreted as areas where the carboxylic acid groups are protonated (vide infra). The diameter of these areas is ca. 30 nm. For higher pH values (pH > 8.0) only repulsion is detected.

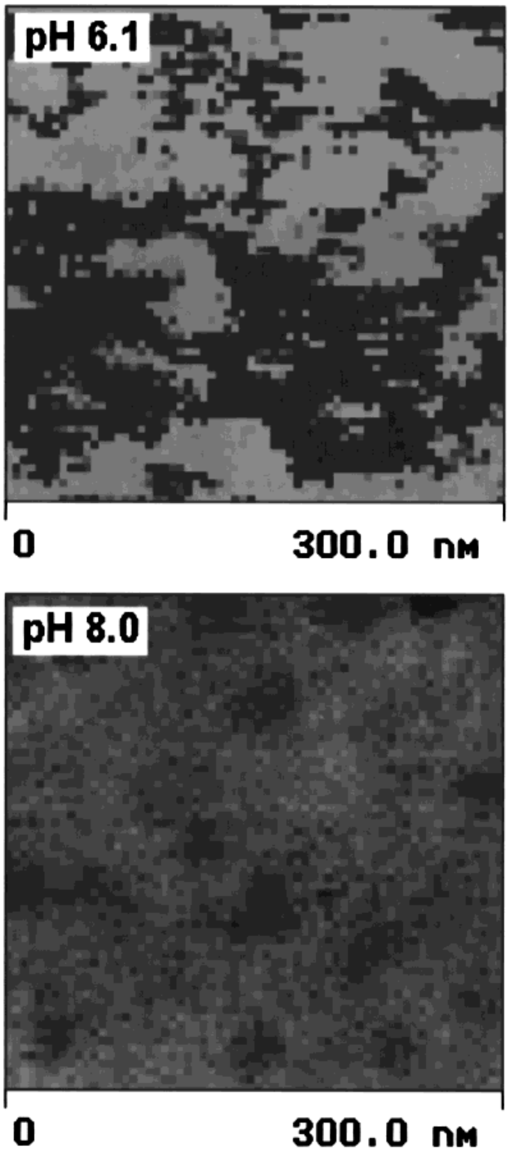

Figure 7. Pull-off force images of oxyfluorinated iPP ($\gamma = 37.1$ mN/m) at different pH. In the force images dark color indicates high adhesion (−1.3 and −0.4 nN for pH 6.1 and pH 8.0, respectively), and bright color indicates low adhesion (−0.2 and ≈0 nN for pH 6.1 and pH 8.0, respectively).

The force images at pH 3.8 showed a laterally heterogeneous distribution of pull-off forces as well. At pH 8.0 the interaction was exclusively repulsive for the most hydrophilic sample ($\gamma = 39.6$ mN/m). In Figure 6 representative pull-off force images and force−distance curves measured at different pH are depicted.

The observation of patches in which high forces are measured at pH close to the "pK_a" and the observation of homogeneous repulsion at pH > "pK_a" indicate that the local functional group distribution cannot be homogeneous. In addition, the coupling of topography into

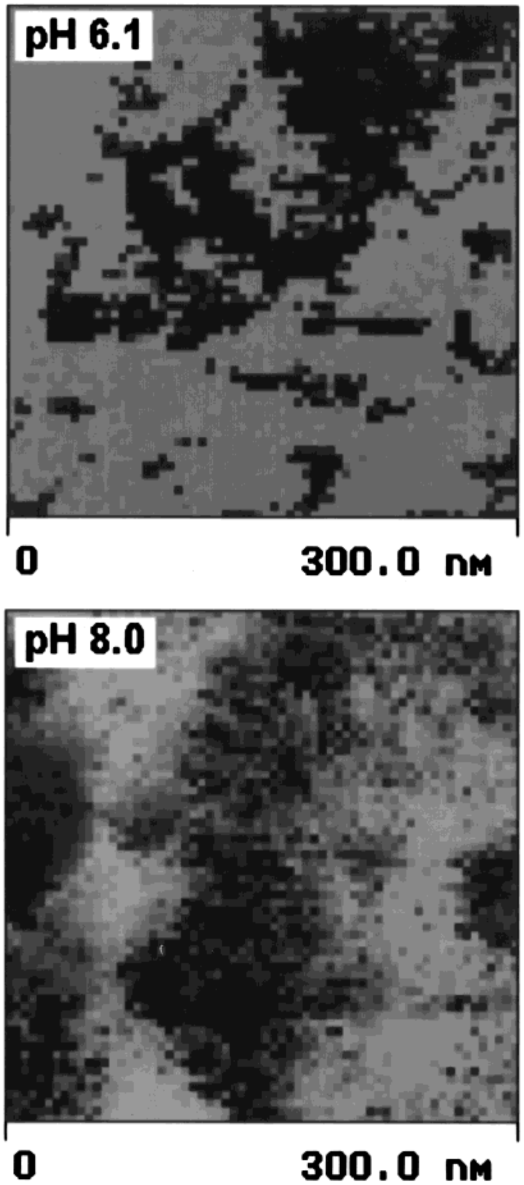

Figure 8. Pull-off force images of oxyfluorinated iPP ($\gamma = 33.9$ mN/m) at different pH. In the force images dark color indicates high adhesion (-3.5 and -1.5 nN for pH 6.1 and pH 8.0, respectively), and bright color indicates low adhesion (-0.3 and ≈ 0 nN for pH 6.1 and pH 8.0, respectively).

the force images (which may cause a heterogeneous appearance of the adhesion force map) can be excluded. This is evident by comparing height and FV images. The areas in which attractive interactions are measured at pH 6.1 contain carboxylic acid groups with a higher "pK_{a}" compared to the regions where repulsion is observed. This can be attributed to a difference in local hydrophobicity.[16,20] The most hydrophobic local environments will be the areas where the deprotonation of carboxylic acid groups is least favored. Similar results were obtained on samples with $\gamma = 37.1$ mN/m (Figure 7).

For the sample with a surface tension of 33.9 mN/m some areas showed attractive interactions even at pH of 8.0 and higher (vide infra). The results for the more hydrophobic sample are less conclusive as the coupling of topography cannot completely be excluded (Figure 8).[21] However, similar to the other oxyfluorinated iPP samples, the pull-off forces were inhomogeneous also for these specimens.

Additional force microscopy experiments on thin films of amino group-containing polymers support our conclusions regarding force titrations and heterogeneous distributions of functional groups in functional polymers.[22] For the amino groups the corresponding titration behavior is observed in these films. In addition, the shift of the measured "force pK_{a}" to lower values compared to the thermodynamic pK_{a} of amines in solution is in accordance with literature data.[16a,23]

Conclusions

AFM pull-off force measurements carried out on oxyfluorinated films of isotactic polypropylene as a function of pH using OH-functionalized tips revealed "force pK_{a}" values of 5.5−6.0. Laterally resolved force spectroscopy gave clear evidence for inhomogeneous adhesion on various oxyfluorinated iPP films which can be related to inhomogeneous *local* "force pK_{a}" and thus inhomogeneous distribution of hydrophobicity. Areas of high adhesion, which have a typical diameter of 30 nm, possess higher "force pK_{a}" compared to low adhesion areas. This information can be collected *locally* with a practical resolution of ca. ≤ 20 nm. These data constitute the first results on laterally resolved imaging of functional group distributions on a nanometer level using atomic force microscopy with chemically modified tips ("chemical force microscopy").

Acknowledgment. The oxyfluorinated iPP samples were kindly provided by SOLVAY S.A. and SOLVAY ALKOR-DRAKA Snc. This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) in the priority program materials (PPM).

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