Low Pressure Plasma-Based Approaches to Fluorocarbon Polymer Surface Modification

M. Nitschke,[1,2] U. König,[2,3] U. Lappan,[1] S. Minko,[4] F. Simon,[1] S. Zschoche,[1,2] C. Werner[1,2]

[1]Leibniz Institute of Polymer Research Dresden, 01069 Dresden, Germany
[2]Max Bergmann Center of Biomaterials Dresden, 01069 Dresden, Germany
[3]Institute of Materials Science, Dresden University of Technology, 01069 Dresden, Germany
[4]Chemistry Department, Clarkson University, Potsdam, New York 13699-5810

ABSTRACT: A survey and comparison of several low pressure plasma-based approaches to fluorocarbon polymer surface modification is reported including ''simple'' plasma treatment, ''grafting to'' and ''grafting from'' plasma activated surfaces, plasma immobilization of predeposited molecules and the adsorption of charged macromolecules on plasma activated surfaces. Examples of each method are discussed in detail based on results from surface analytical experiments using X-ray photoelectron spectroscopy, ellipsometry, contact angle goniometry, and electrokinetic measurements. All reported examples refer to one and the same experimental setup. This makes the different approaches comparable and helps to exploit a wide range of plasma-based techniques for a particular goal and a given apparatus. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 100–109, 2007

Key words: surfaces; fluoropolymers; plasma treatment; grafting; adsorption

INTRODUCTION

Low pressure plasma techniques provide a versatile tool meeting a wide range of requirements for the surface modification of polymeric materials.[1] The application of plasma treatments is particularly useful for fluoropolymer materials.[2] Accordingly, a multitude of studies suggested low pressure plasma treatments to be applied with fluorocarbon polymers. However, an overall comparison is complicated when considering treatments reported by different groups using rather different setups.

In front of this background, this study surveys and scrutinizes different strategies of low pressure plasma based fluoropolymer surface modifications realized in a number of previous own studies[3–7] by means of one and the same experimental setup. Water vapor, oxygen, ammonia, and argon were used as process gases. Fluoropolymers considered in this work comprise mainly poly(tetrafluoroethylene) (PTFE) and poly(tetrafluoroethylene-*co*-hexafluoropropylene). These materials are commonly applied in demanding products and technologies—such as medical implants and membranes—where control over surface characteristics is a key to performance, and effective surface modification procedures are urgently needed.

Basic goals of polymer surface modification include durable changes of wettability, selective introduction of functional groups for subsequent chemical reactions as well as the creation of charged surfaces. For many purposes, a simple plasma treatment, i.e., a short exposure of the polymer to a low pressure discharge,[8–11] is adequate. A crucial point of this kind of processes affecting only the topmost nanometers of the material is the lack of long term stability. On the time scale of days or weeks, reorientation and migration of surface moieties to the polymer bulk and/or postplasma reactions with the ambient air lead to a gradual decay of modification effects (hydrophobic recovery).[12–15] However, in some cases, promising results were obtained by selecting appropriate plasmas and operating parameters.[3,16] Another disadvantage of simple plasma treatments is the variety of functional groups simultaneously formed on the treated polymer surface.[17,18] Also this problem can be solved by the optimization of process parameters.[19,20]

To avoid the problems mentioned earlier, grafting techniques on plasma activated surfaces can be applied.[21–27] As a result, layers with a thickness from a few nanometers up to a few micron are formed. Contrary to simple plasma treatments, grafting processes can provide swellable and soft surfaces. Among the grafting techniques there are two strategies, ''grafting from'' and ''grafting to,'' both with distinct advantages.
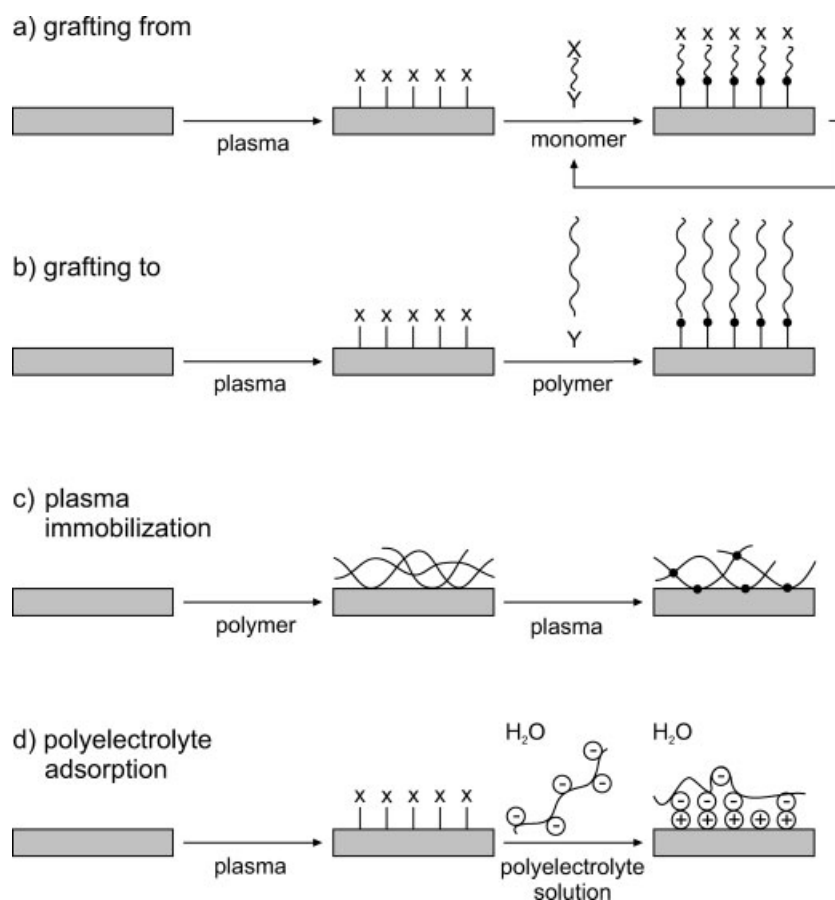
Figure 1 Schematic representation of the multistep surface modification strategies discussed in this work.

The "grafting from" strategy [Fig. 1(a)] comprises a polymerization initiated from plasma treated surfaces. When an exceptionally high grafting density is needed, "grafting from" is the preferred method. This technique can be used for the preparation of thick grafted layers.

In the "grafting to" strategy [Fig. 1(b)], end-functionalized polymers react under appropriate conditions with a plasma treated surface to form a tethered polymer brush. This method is very effective even if the concentration of reactive functional groups on the surface is not very high. The polymers are grafted onto the substrate via chemical reaction of the end-groups and complementary functional groups on the surface. The advantage of this method is that polymers (homopolymers, random copolymers, or block-copolymers) with a narrow molecular weight distribution can be used for grafting, and as a result, well-defined grafted layers can be synthesized. On the other hand, the technique has constraints in terms of the maximum grafting that can be obtained, namely that the grafting is self-limiting by the diffusion of polymer chains into the grafted layer.

Toward soft and swellable surface layers, plasma immobilization[28–31] [Fig. 1(c)] is an alternative approach to the grafting techniques mentioned earlier. Predeposited polymer films with a thickness up to a few 10 nm can be crosslinked with a polymeric substrate by low pressure plasma treatment. Argon discharges can be used for this purpose.[32] Important properties of the immobilized polymer like the presence of functional groups, the mobility of polymer chains in the swollen state, or the phase transition behavior of a thermoresponsive material can be preserved.

Except for covalent fixation, electrostatic interactions can be used to attach functional molecules to a surface [Fig. 1(d)], which leads to a durable and chemically well-defined modification of polymer materials.[33–35] A multiple anchorage of the functional molecule to the solid surface by its charged groups is necessary to prevent the detachment of the molecule during the contact with liquids. In this approach, low pressure plasma is applied to obtain, e.g., positively charged moieties after contact with an aqueous medium that allow adsorbing oppositely charged polyelectrolytes. Following this strategy, multilayer structures of alternating charged polyelectrolytes can be built up in simple dip coating processes.[36,37] Surface properties can be controlled by the chemical structure of the polyelectrolytes used.
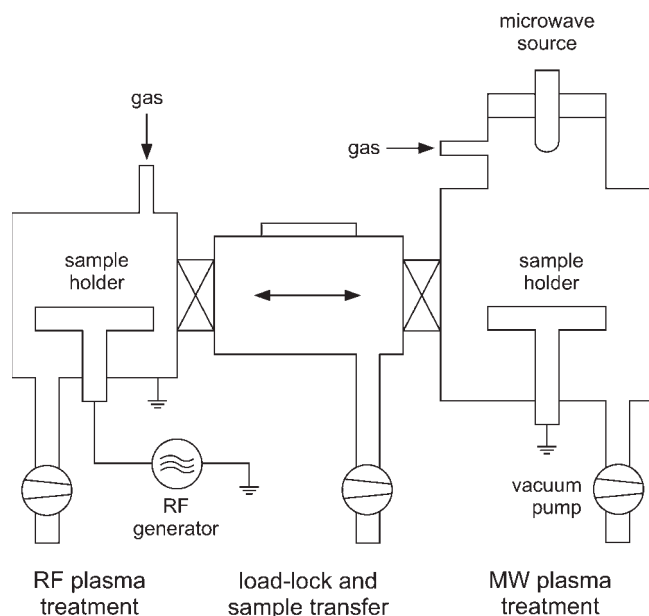
Figure 2 Setup for low pressure plasma treatment.

EXPERIMENTAL

Materials

PTFE foils of 0.1 mm thickness were purchased from Nünchritz, Germany. Poly(tetrafluoroethylene-co-hexafluoropropylene) foils, 0.1 mm thick (Hostaflon FEP 6107), were purchased from Dyneon (Gendorf, Germany). Foils were cleaned before use in an ultrasonic bath in ethanol and subsequently rinsed with distilled water.

Nonbranched fluorocarbon films (model surfaces) with a structure close to PTFE were kindly provided by the Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences (Chernogolovka, Russia). The films were deposited by plasma polymerization. Tetrafluoroethylene (C_2F_4) was introduced downstream into a low pressure argon discharge. Silicon substrates were placed further downstream of the discharge.[38,39]

Acrylic acid, anhydrous, (99.0%, Fluka) was used for "grafting from" experiments. Poly(sodium 4-styrenesulfonate) (PSS, molecular weight 70,000 g/mol, Aldrich) was used for adsorption experiments. Poly

(ethylene imine) (Polymin P, molecular weight 500,000 g/mol, number of primary, secondary, and tertiary amino groups 1 : 2 : 1, BASF AG), poly(N-vinyl pyrrolidone) (molecular weight 1270,000 g/mol, Fluka) and poly(acrylic acid) (molecular weight 450,000 g/mol, Aldrich) were used for plasma immobilization.

For "grafting to" experiments, carboxyl-terminated poly(styrene-co-2,3,4,5,6-pentafluorostyrene) (PSF-COOH) (styrene units : pentafluorostyrene units = 0.75 : 0.25) (M_n = 16,000 g/mol, M_w = 29,500 g/mol) was synthesized by free-radical polymerization in tetrahydrofuran solution using 4,4'-azobis(4-cyanopentanoic acid) as initiator. Anionically polymerized carboxyl-terminated poly(2-vinyl pyridine) (PVP-COOH; M_n = 39,200 g/mol and M_w = 41,500 g/mol) was purchased from Polymer Source.

The plasma apparatus was operated with the following process gases: oxygen (99.95%), ammonia (99.999%), and argon (99.999%), all provided by Messer Griesheim.

Plasma treatment

Plasma treatments and "grafting from" reactions were carried out in a computer-controlled MicroSys apparatus (Fig. 2) by Roth and Rau (Wüstenbrand, Germany). The parameters of all plasma processes as obtained by different optimization procedures are summarized in Table I. The plasma apparatus consists of three vacuum chambers (1–3) connected to a central sample-handling unit. Samples can be transferred within 1 min from one chamber to another on aluminum sample holders with 130 mm diameter without breaking the vacuum. The base pressure of the whole vacuum system obtained with turbomolecular pumps was 10^{-7} mbar.

1. A load-lock-chamber allowed the introduction of samples into the system while keeping the vacuum in the other chambers.
2. A cylindrical vacuum chamber, made of stainless steel, with a diameter of 350 mm and a height of 350 mm, was used for plasma surface modification. On the top of the chamber, a 2.46 GHz microwave electron cyclotron resonance (MW-ECR) plasma source RR160 by Roth

TABLE I
Parameters of the Plasma Treatments Discussed in the Present Work

	Process gas	Plasma excitation	Effective power (W)	Pressure (mbar)	Treatment time (s)
Simple plasma treatment	Water vapor	MW	400	2.0×10^{-3}	60
Activation for "grafting from"	Water vapor	MW	400	2.0×10^{-3}	60
Plasma etching	Oxygen	RF	200	2.0×10^{-2}	600
Activation for "grafting to"	Ammonia	MW	220	7.0×10^{-3}	60
Plasma immobilization	Argon	MW	120	8.0×10^{-3}	10
Activation for adsorption	Ammonia	MW	300	3.6×10^{-3}	30

and Rau with a diameter of 160 mm and a maximum power of 800 W was mounted. The sample holder was placed by the sample-handling unit near the center of the chamber (electrically grounded). The distance between the sample position and the excitation volume of the MW-ECR plasma source was about 200 mm. Process gases were introduced into the active volume of the plasma source via a gas flow control system. During plasma operation, the pressure was measured by a capacitive vacuum gauge.

3. A cylindrical vacuum chamber made of stainless steel with a diameter of 250 mm and a height of 250 mm was used for plasma etching. Oxygen was introduced into the chamber via a gas flow control system. During plasma operation, the pressure was measured by a capacitive vacuum gauge. The sample holder was placed by the sample-handling unit near the center of the chamber. The holder was capacitively coupled to a 13.56 MHz radio frequency (RF) generator (Dressler Cesar 136) via an automatic matching network. The metallic wall of the whole chamber worked as a grounded electrode, i.e., the electrode configuration was highly asymmetric causing significant self-bias voltages and ion energies at the sample position.[40] This leads to higher etching rates compared to the MW-ECR plasma which was exploited for specific purposes (Table I). The same vacuum chamber was used for ''grafting from'' reactions without operating a discharge. Acrylic acid was evaporated at room temperature from an evacuated glass vessel and introduced into the chamber via a manual valve. The pressure was measured by a capacitive vacuum gauge.

X-ray photoelectron spectroscopy

XPS studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with an Al Kα X-ray source of 300 W at 15 kV. The radiation of the source was monochromated by a quartz crystal monochromator. The information depth of the XPS method corresponds with the mean free path of the electrons in the material under investigation. In the case of polymer samples, the information depth of XPS is not more than 8 nm. The kinetic energy of photoelectrons was determined using a hemispherical analyzer with constant pass energy of 160 eV for survey spectra and 20 eV for high-resolution spectra. During measurements, electrostatic charging of the sample was avoided by means of a low-energy electron source working in combination with a magnetic immersion lens. Quantitative elemental compositions (atomic ratios) were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function.[41]

Ellipsometry

Ellipsometric data were collected by means of a VASE M44 ellipsometer by Woolam, USA, at 44 wavelengths between 428 and 763 nm and three angles of incidence: 65°, 70°, and 75°. The obtained data sets were analyzed in a fit procedure based on an optical multilayer model. The swelling behavior of layers was investigated in quartz cuvette with a fixed incident angle of 68°.

Contact angle goniometry

Advancing and receding water contact angles were measured by means of the sessile drop or the captive bubble technique respectively, using a G40 goniometer by Krüss (Hamburg, Germany). The advancing and receding contact angles were determined by increasing and decreasing the water droplet volume (decreasing and increasing the bubble volume) with a micrometer syringe until a steady value was obtained.

Electrokinetic measurements

Steaming potential measurements were applied to obtain the ζ potential in dependence on pH.[42] Two samples adjusted in parallel formed a rectangular streaming channel in the Electrokinetic Analyzer EKA (Anton Paar, Austria). All measurements were carried out in a 3×10^{-4} mol L^{-1} aqueous KCl solutions as background electrolyte. The pH values were varied by adding of 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. Since the apparatus does not consider the surface conductivity, the obtained values are too high in case of swelling samples. Consequently, results are indicated as apparent zeta potential ζ_a.[43]

RESULTS AND DISCUSSION

Simple plasma treatment

For many applications, a short exposure of the polymer surface to a low pressure plasma is sufficient to obtain, e.g., a better wettability or an improved adhesion. However, for practical reasons, hydrophobic recovery and surface restructuring should be as slow as possible. Toward this goal, different plasma treatments of PTFE were compared including carbon dioxide, hydrogen, and water vapor discharges.[3]
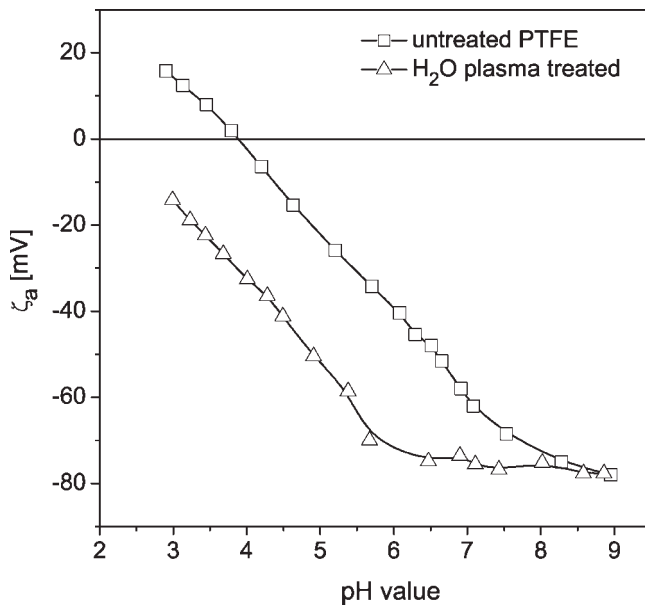
Figure 3 Zeta potential values (ζ_a) in dependence on pH of PTFE samples before and after a water vapor plasma treatment. (Reproduced from Ref. 3, with permission from © Elsevier (2002)).

Here, the results for the water vapor plasma are discussed, which was identified as the most favorable treatment (effective MW power 400 W, water vapor flow 38 sccm, pressure 2×10^{-3} mbar, treatment time 60 s). Figure 3 shows the ζ potential values versus pH for untreated and water vapor plasma treated PTFE. The low isoelectric point of pH = 4 obtained for PTFE is typical for polymers without dissociating surface groups. In this case, the charge formation can be attributed to the effect of asymmetric ion adsorption.[42] After plasma treatment, a pronounced shift of the isoelectric point indicates an additional contribution of acidic functional groups to the interfacial charge. This corresponds with an introduction of oxygen into the PTFE surface, where an O : C ratio of 0.16 was determined by XPS. The advancing and receding water contact angles were lowered from $124 \pm 2°$ and $111 \pm 2°$ for the untreated PTFE to $84 \pm 2°$ and $34 \pm 2°$ for the water vapor plasma treated PTFE. Contrary to other plasmas like CO_2, no hydrophobic recovery was observed after storage in air or water for several weeks.

"Grafting from" plasma activated surfaces

A more homogeneous surface functionalization compared to simple plasma treatments can be obtained by grafting processes either from the monomer solution or the monomer vapor phase. Vapor phase processes are often preferred due to a lower tendency to homopolymer formation. The efficiency of the grafting process is governed by the reactivity of the surface and by parameters such as temperature, monomer concentration, and reaction time.

In the following example, the grafting of acrylic acid from plasma treated PTFE is discussed.[4] The surface was activated in a water vapor plasma (effective MW power 400 W, water vapor flow 38 sccm, pressure 2×10^{-3} mbar, treatment time 60 s), which leads to the formation of radicals.[3] Subsequently, the activated surface was exposed to acrylic acid vapor without breaking the vacuum (pressure 0.5 to 4 mbar, grafting time 30 min at room temperature). An almost linear increase of the obtained poly(acrylic acid) layer thickness as a function of the vapor pressure was found by ellipsometry (Fig. 4).

For the following investigations, a vapor pressure of 4 mbar corresponding to a layer thickness of about 70 nm was used. Figure 5 shows the ζ potential versus pH before and after acrylic acid grafting. As in the example earlier, an isoelectric point of about 4 was measured for untreated PTFE. After grafting acrylic acid, a typical ζ potential behavior for a surface containing dissociable acidic groups was obtained. The isoelectric point was considerably shifted to a value below pH 3. However, instead of a plateau expected for high pH values due to the complete dissociation of carboxylic groups, an increase of the apparent ζ potential was observed. This effect is a consequence of the progressive swelling of the poly(acrylic acid) layer, which affects the surface conductivity (swelling ratio 7.3 at pH 8, determined by ellipsometry).
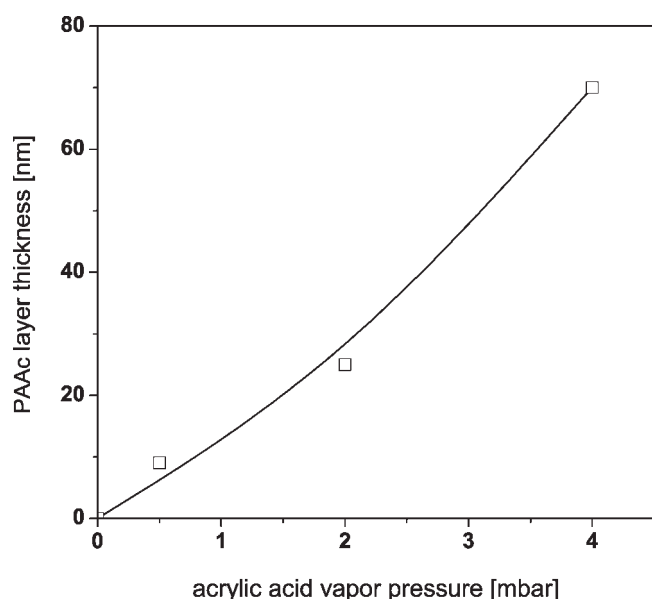
Figure 4 Poly(acrylic acid) layer thickness on PTFE model surfaces as a function of the vapor pressure for a grafting time of 30 min at room temperature. (Reproduced from Refs. 4 and 5, with permission from © Elsevier (2002)).
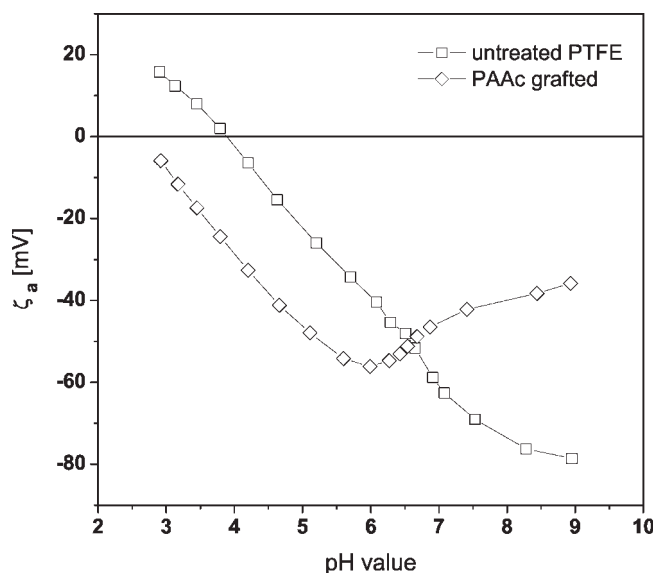
Figure 5 Zeta potential values (ζ_a) in dependence on pH of PTFE samples before and after grafting acrylic acid. (Reproduced from Refs. 4 and 5 with permission from © Elsevier (2002)).

The poly(acrylic acid) layers grafted onto the PTFE surfaces were subjected to different rinsing procedures at elevated temperature to prove its mechanical stability. No degradation of the grafted layer was detected by ellipsometry, ζ potential, and XPS analysis.

"Grafting to" plasma activated surfaces

The procedure described later aims at surfaces with a switchable wettability. The strategy takes advantage of phase segregation effects in responsive binary polymer brushes prepared by "grafting to" processes on plasma activated surfaces.[5] A rough substrate morphology was employed toward an exceptionally high switching amplitude of the water contact angle. This concept, that essentially combines switchable wettability and ultrahydrophobicity, is described in detail in Ref. 44.

A needle-like micron-scale morphology (Fig. 6) was obtained on the PTFE surface by plasma etching (effective RF power 200 W, oxygen gas flow 10 sccm, pressure 2×10^{-2} mbar, self bias voltage approximately 1000 V, treatment time 600 s) followed by an intense rinsing procedure in an ultrasonic bath. Oxygen plasma etching of polymers leads to a simultaneous functionalization of the actual surface. XPS investigations (Fig. 7) have shown that a certain concentration of oxygen containing functional groups was formed within the first seconds of plasma etching and remained unchanged for longer treatment times (Al appears as an impurity at 73 and 119 eV due to sputtering of the sample holder). However, a grafting of functionalized polymers was not effective on this surface. To overcome this problem, the plasma-etched PTFE surface was treated by ammonia plasma (effective MW power 220 W, ammonia gas flow 15 sccm, pressure 7×10^{-3} mbar, treatment time 60 s). Contrary to the RF oxygen discharge used for etching, MW ammonia plasma possesses rather low ion energies and etching rates at the sample position. Consequently, this kind of treatment allows a subsequent functionalization of the rough surface while its morphology is maintained (Fig. 6).

Polymer chains of two carbonic acid terminated incompatible polymers of different polarities, PSF-COOH and PVP-COOH, were attached to the surface. Hydroxyl and amino functionalities, introduced by plasma treatments were used to graft mixed polymer brushes using a two-step procedure.[45] In a first step, a thin film of PSF-COOH was applied onto the PTFE surface and heated for 6 h at 150°C to graft the polymer from the melt. Nongrafted polymer was removed by Soxhlet extraction. In a second step, PVP-COOH was grafted using the same procedure. The
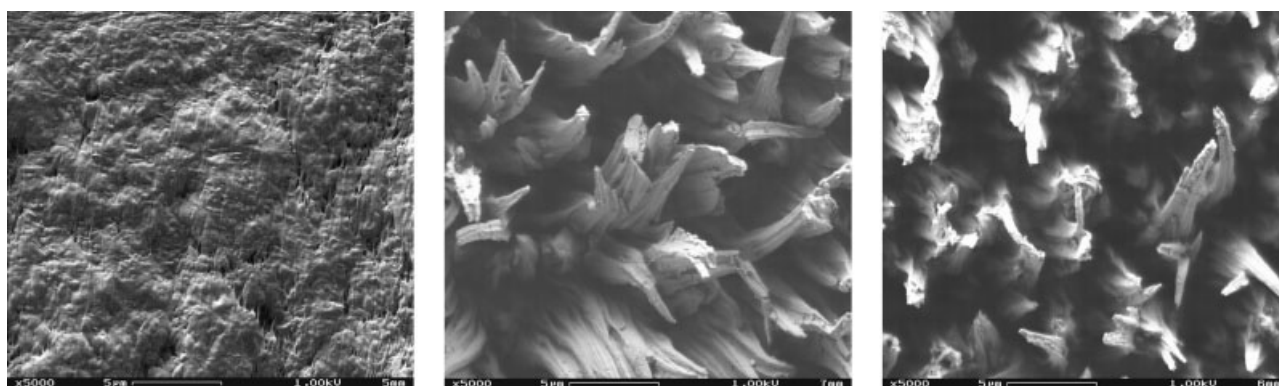
Figure 6 Morphology of the PTFE surface: untreated (left), after oxygen plasma etching (middle), and subsequent ammonia plasma treatment (right). (Reproduced from Ref. 5, with permission from © Am Chem Soc (2003)).
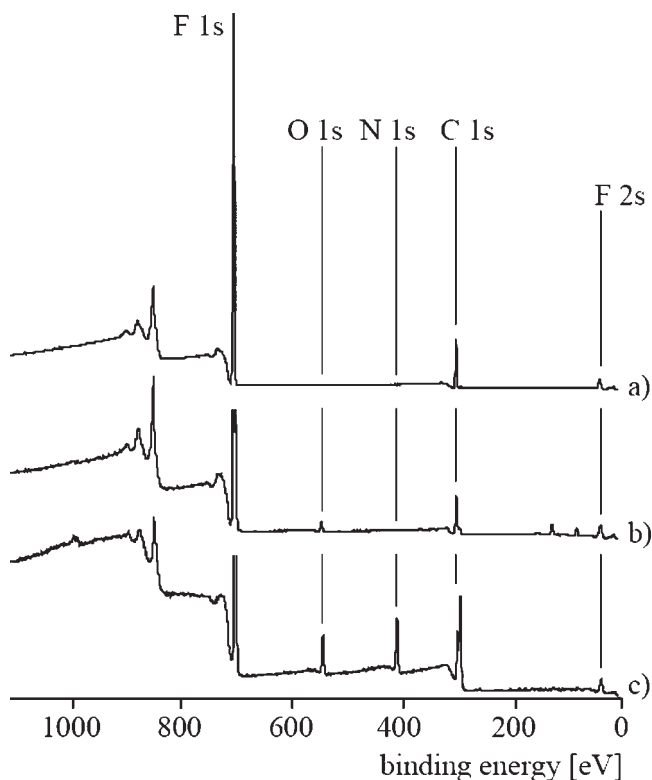
Figure 7 XPS survey spectra of the PTFE surface: untreated (a), after oxygen plasma etching (b), and subsequent ammonia plasma treatment (c). (Reproduced from Ref. 5, with permission from © Am Chem Soc (2003)).
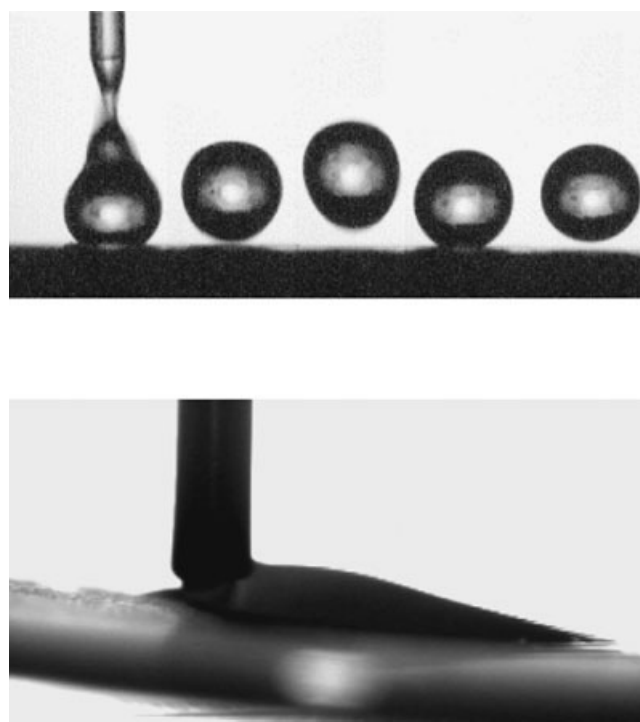

Figure 8 Switchable wettability of a rough PTFE surface grafted with a responsive binary brush: ultrahydrophobic behavior after exposure to toluene (top, stroboscopic image) versus hydrophilic behavior after exposure to acidic water (bottom). (Reproduced from Ref. 5, with permission from © Am Chem Soc (2003)).

formation of mixed polymer brushes was proved by infrared spectroscopy using characteristic bands of PSF-COOH (1601, 2923, and 3027 cm^{-1}) and PVP-COOH (1586 and 1590 cm^{-1}) respectively,[46,47] (diagrams not shown). The procedure was adjusted to fabricate 50 : 50 mixed grafted layers.[5]

Owing to the phase segregation mechanism between PSF-COOH and PVP-COOH,[48,49] the obtained coating exhibits responsive properties. Upon treatment with selective solvents (toluene for PSF and acidic water for PVP), the surface wetting behavior can be reversibly switched from ultrahydrophobic to hydrophilic (Fig. 8).

## Plasma immobilization of predeposited polymer films

The technique allows to immobilize functional polymer films with a thickness up to a few 10 nm on polymer surfaces. At appropriate plasma parameters, a covalent fixation is achieved while important properties of the immobilized polymer are preserved.

This is demonstrated for PEI and PAAc on PTFE model surfaces. Figure 9 illustrates that a part of the material deposited by spin coating remains on the surface after argon plasma treatment (effective MW power 120 W, argon gas flow 38 sccm, pressure

8×10^{-3} mbar, treatment time 10 s) and rinsing (methanol, 1 h at room temperature). While in the case of PEI, about 50% of the initial film thickness is lost; the film thickness is almost preserved for PAAc.
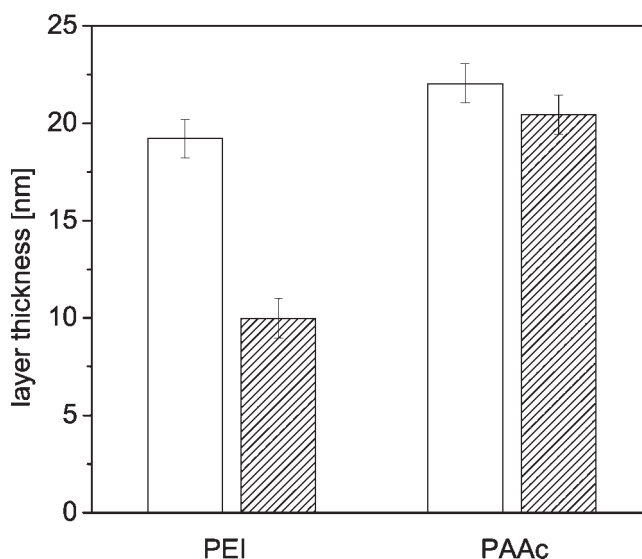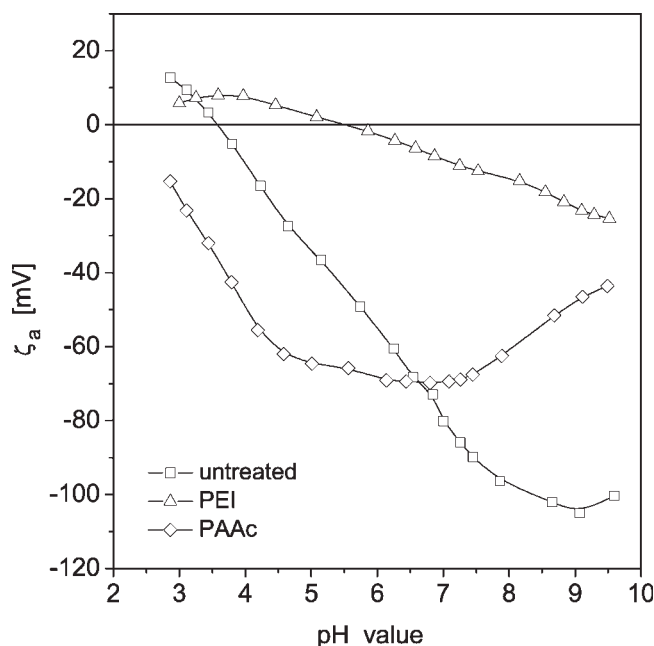

Figure 9 PEI and PAAc film thickness on PTFE model surfaces after spin coating (left bar) and after immobilization and rinsing (right bar). (Reproduced from Ref. 6 with permission from © Elsevier (2004)).
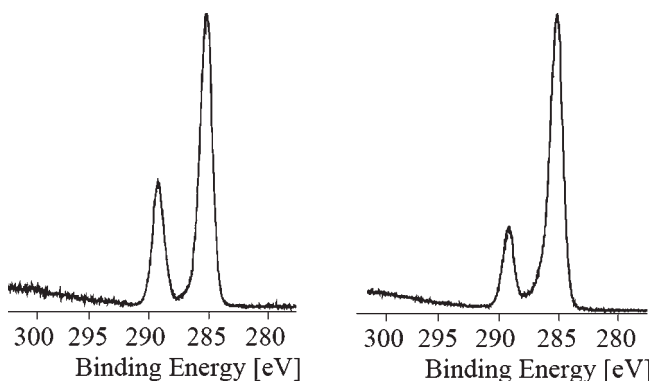
Figure 10 High-resolution C1s spectra of PAAc before (left) and after plasma immobilization (right). (Reproduced from Ref. 6 with permission from © Elsevier (2004)).

However, it is expected, that the immobilized polymers are also degraded during plasma treatment. This side-effect was investigated in detail in Ref. 6. As an example, Figure 10 shows XPS spectra of the PAAc layer before and after the immobilization procedure. Only minor structural changes are caused by the applied plasma treatment. In particular, the major part of the carboxylic groups is still present.

Figure 11 shows the ζ potentials versus solution pH of the two modified surfaces. The PAAc surface has an isoelectric point considerably below pH 3 as expected for the presence of carboxylic groups. As in the case of grafted PAAc coatings, an increase of the apparent ζ potential is observed for pH >7 (swelling
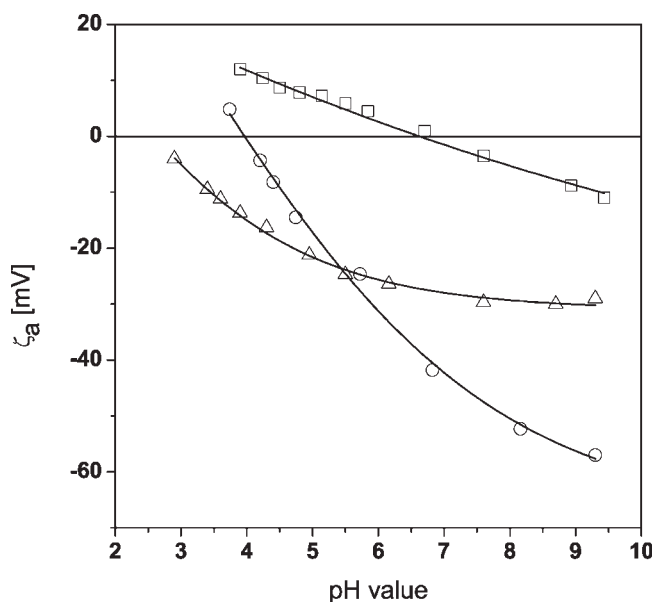
ratio 13 at pH 11, determined by ellipsometry[6]). For immobilized PEI, the isoelectric point is shifted to higher pH values compared to the untreated fluorocarbon surface, indicating the presence of basic sites.

The coatings are mechanically stable and withstand significant shear forces during streaming potential measurements. Moreover, this kind of surface modification is especially suited for micron-scale lateral structuring using simple masking techniques.[50]

Adsorption of charged macromolecules on plasma activated surfaces

Another route to durable surface modifications is the use of electrostatic interactions for the attachment of functional molecules. In the example below, a cationic surface was created on poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) by a low pressure ammonia plasma treatment (effective MW power 300 W, ammonia gas flow 15 sccm, pressure 3.6×10^{-3} mbar, treatment time 30 s). Subsequently, anionic poly (sodium 4-styrenesulfonate) (PSS) was adsorbed onto the positively charged surface (aqueous solution 0.02 mol/L based on repeat units, 5 min at room temperature).[7] This two step procedure is illustrated by the changes in the ζ potential versus pH (Fig. 12). After ammonia plasma treatment, the value of the isoelectric point is shifted toward higher pH indicating the presence of positively charged groups at the polymer surface. After applying the PSS solution, the isoelectric point is shifted into the opposite dir-

Figure 11 Zeta potential values (ζ_a) in dependence on pH of the PTFE model surface and the immobilized films of PEI and PAAc. (Reproduced from Ref. 6 with permission from © Elsevier (2004)).

Figure 12 Zeta potential values (ζ_a) in dependence on pH of NH3 plasma treated and PSS exposed FEP (triangles) compared to NH3 plasma treated FEP (squares) and untreated FEP (circles). (Reproduced from Ref. 7 with permission from © Plenum Publishing (2002)).
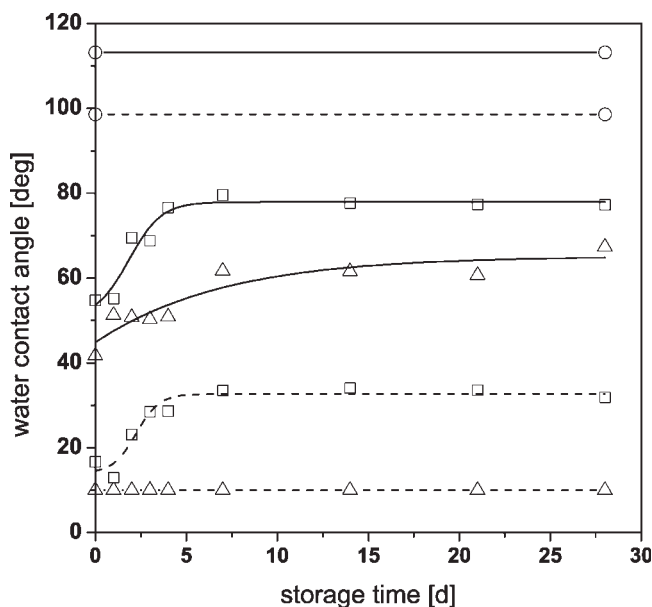
Figure 13 Advancing (solid lines) and receding water contact angles (dashed lines) of NH3 plasma treated and PSS exposed FEP (triangles) and plasma treated FEP (squares). The values for untreated FEP are plotted for reference (circles). (Reproduced from Ref. 7 with permission from © Plenum Publishing (2002)).

ection to a value of about 2.5, indicating that the negatively charged polyelectrolyte was attached to the surface.

As the aim of the procedure was to obtain a permanently hydrophilic surface, the long-term behavior of the water contact angle was investigated (Fig. 13). While FEP shows a pronounced hydrophobic recovery after simple plasma treatments,[7] the PSS coated FEP surface provides a more stable hydrophilization by comparison. Advancing and receding contact angles of $65 \pm 2°$ and $< 10°$ were measured. The multiple electrostatic anchorages of the PSS molecules to the ammonia plasma treated FEP surface withstands significant shear forces during the ζ potential measurements which is an excellent proof for the mechanical stability of the modified surface.

CONCLUSIONS

A wide range of low pressure plasma based surface modification techniques for fluorocarbon polymers was investigated using one and the same experimental setup to make the results more comparable. In case of a simple plasma treatment, the variation of parameters like process gas, plasma excitation, etc., allows to optimize the result with respect to the hydrophobic recovery. Beyond that, low pressure plasma was shown to be a key technique in various multistep strategies including the immobilization of predeposited molecules as well as the surface functionalization for subsequent grafting or adsorption procedures. Contrary to simple plasma treatments, this leads to a more defined surface chemistry. The choice among various multistep strategies allows exploiting the full potential of plasma based techniques for a particular application.

References

1. Chan, C. M.; Ko, T. M.; Hiraoka, H. Surf Sci Rep 1996, 24, 3.
2. Kang, E. T.; Zhang, Y. Adv Mater 2000, 12, 1481.
3. König, U.; Nitschke, M.; Pilz, M.; Simon, F.; Arnhold, C.; Werner, C. Colloids Surf B 2002, 25, 313.
4. König, U.; Nitschke, M.; Menning, A.; Eberth, G.; Pilz, M.; Arnhold, C.; Simon, F.; Adam, G.; Werner, C. Colloids Surf B 2002, 24, 63.
5. Minko, S.; Müller, M.; Motornov, M.; Nitschke, M.; Grundke, K.; Stamm, M. J Am Chem Soc 2003, 125, 3896.
6. Nitschke, M.; Zschoche, S.; Baier, A.; Simon, F.; Werner, C. Surface Coat Technol 2004, 185, 120.
7. Lappan, U.; Nitschke, M.; Pleul, D.; Simon, F.; Uhlmann, S. Plasmas Polym 2001, 6, 211.
8. Badey, J. P.; Urbaczewskiespuche, E.; Jugnet, Y.; Sage, D.; Duc, T. M.; Chabert, B. Polymer 1994, 35, 2472.
9. Caro, J. C.; Lappan, U.; Simon, F.; Pleul, D.; Lunkwitz, K. Eur Polym J 1999, 35, 1149.
10. Da, Y. X.; Griesser, H. J.; Mau, A. W. H.; Schmidt, R.; Liesegang, J. Polymer 1991, 32, 1126.
11. Wilson, D. J.; Eccles, A. J.; Steele, T. A.; Williams, R. L.; Pond, R. C. Surf Interface Anal 2000, 30, 36.
12. Chatelier, R. C.; Xie, X. M.; Gengenbach, T. R.; Griesser, H. J. Langmuir 1995, 11, 2585.
13. Nakamatsu, J.; Delgado-Aparicio, L. F.; Da Silva, R.; Soberon, F. J Adhes Sci Technol 1999, 13, 753.
14. Sabbatovskii, K. G.; Dutschk, V.; Nitschke, M.; Simon, F.; Grundke, K. Colloid J 2002, 66, 208.
15. Wilson, D. J.; Williams, R. L.; Pond, R. C. Surf Interface Anal 2001, 31, 397.
16. Xie, X. M.; Gengenbach, T. R.; Griesser, H. J. J Adhes Sci Technol 1992, 6, 1411.
17. Chevallier, P.; Castonguay, N.; Turgeon, S.; Dubrulle, N.; Mantovani, D.; McBreen, P. H.; Wittmann, J. C.; Laroche, G. J Phys Chem B 2001, 105, 12490.
18. Markkula, T. K.; Hunt, J. A.; Pu, F. R.; Williams, R. L. Surf Interface Anal 2002, 34, 583.
19. Inagaki, N. J Photopolym Sci Technol 2002, 15, 291.
20. Meyer-Plath, A. A.; Schröder, K.; Finke, B.; Ohl, A. Vacuum 2003, 71, 391.
21. Inagaki, N.; Tasaka, S.; Goto, Y. J Appl Polym Sci 1997, 66, 77.
22. Kang, E. T.; Neoh, K. G.; Chen, W.; Tan, K. L.; Liaw, D. J.; Huang, C. C. J Adhes Sci Technol 1996, 10, 725.
23. Matsuda, K.; Nakamura, T.; Yamada, K.; Hirata, M. J Photopolym Sci Technol 2002, 15, 335.
24. Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. Macromolecules 1993, 26, 2832.
25. Vasilets, V. N.; Hermel, G.; König, U.; Werner, C.; Müller, M.; Simon, F.; Grundke, K.; Ikada, Y.; Jacobasch, H. J. Biomaterials 1997, 18, 1139.

26. Yoshikawa, C.; Goto, A.; Tsujii, Y.; Fukuda, T.; Yamamoto, K.; Kishida, A. Macromolecules 2005, 38, 4604.
27. Yu, W. H.; Kang, E. T.; Neoh, K. G. Langmuir 2005, 21, 450.
28. Schmaljohann, D.; Beyerlein, D.; Nitschke, M.; Werner, C. Langmuir 2004, 20, 10107.
29. Sheu, M. S.; Hoffman, A. S.; Feijen, J. J Adhes Sci Technol 1992, 6, 995.
30. Terlingen, J. G. A.; Feijen, J.; Hoffman, A. S. J Biomater Sci Polym Ed 1992, 4, 31.
31. Zou, X. P.; Kang, E. T.; Neoh, K. G. Surf Coat Technol 2002, 149, 119.
32. Hansen, R. H.; Schonhorn, H. J Polym Sci Part B: Polym Lett 1966, 4, 203.
33. Hsieh, M. C.; Farris, R. J.; McCarthy, T. J. Macromolecules 1997, 30, 8453.
34. Vargo, T. G.; Calvert, J. M.; Wynne, K. J.; Avlyanov, J. K.; MacDiarmid, A. G.; Rubner, M. F. Supramol Sci 2005, 2, 169.
35. Lappan, U.; Buchhammer, H. M.; Lunkwitz, K. Polymer 1999, 40, 4087.
36. Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. Macromol Rapid Commun 2000, 21, 319.
37. Decher, G.; Hong, J. D.; Schmitt, J. Thin Solid Films 1992, 210, 831.
38. Vasilets, V. N.; Werner, C.; Hermel, G.; Pleul, D.; Nitschke, M.; Menning, A.; Janke, A.; Simon, F. J Adhes Sci Technol 2002, 16, 1855.
39. Nitschke, M.; Uhlmann, S.; Schulze, R.; Werner, C. e-polymers 2006, 6.
40. Köhler, K.; Coburn, J. W.; Horne, D. E.; Kay, E.; Keller, J. H. J Appl Phys 1985, 57, 59.
41. Beamson, G.; Briggs, D. High resolution XPS of organic polymers—The Sienta ESCA 300 Database; Wiley: Chichester, 1992.
42. Werner, C.; König, U.; Augsburg, A.; Arnhold, C.; Korber, H.; Zimmermann, R.; Jacobasch, H. J Colloids Surf A 1999, 159, 519.
43. Dukhin, S. S.; Zimmermann, R.; Werner, C. J Colloid Interface Sci 2005, 286, 761.
44. Grundke, K.; Nitschke, M.; Minko, S.; Stamm, M.; Froeck, C.; Simon, F.; Uhlmann, S.; Pöschel, K.; Motornov, M. In Contact Angle, Wettability and Adhesion, Vol. 3; Mittal, K. L., Ed.; VSP: Utrecht, 2003.
45. Minko, S.; Patil, S.; Datsyuk, V.; Simon, F.; Eichhorn, K. J.; Motornov, M.; Usov, D.; Tokarev, I.; Stamm, M. Langmuir 2002, 18, 289.
46. Hummel, D. O. Atlas of Polymer and Plastics Analysis; VCH: Weinheim, 1991.
47. Hummel, D. O.; Scholl, F. Atlas der Polymer-und Kunststoffanalyse; VCH: Weinheim, 1988.
48. Minko, S.; Müller, M.; Usov, D.; Scholl, A.; Froeck, C.; Stamm, M.; Phys Rev Lett 2002, 88, 035502.
49. Minko, S.; Luzinov, I.; Luchnikov, V.; Müller, M.; Patil, S.; Stamm, M. Macromolecules 2003, 36, 7268.
50. Schmaljohann, D.; Nitschke, M.; Schulze, R.; Eing, A.; Werner, C.; Eichhorn, K. J. Langmuir 2005, 21, 2317.