Tailoring of Poly(ether ether ketone) Surface Properties via Surface-Initiated Atom Transfer Radical Polymerization

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The interfacial properties of commercial poly(ether ether ketone) (PEEK) have been tailored by tethering polymeric brushes to the PEEK surface via surface-initiated atom transfer radical polymerization (SI-ATRP). The immobilization of an ATRP initiator on the PEEK surface was achieved by an unprecedented simple two-step wet chemical method. The keto groups at the PEEK surface were first wet chemically reduced to hydroxyl groups, and then 2-bromoisobutyryl groups were covalently anchored at the PEEK surface as ATRP initiator. SI-ATRP was performed at these functionalized PEEK surfaces with the three different monomers: potassium 3-(methacryloyloxy)propane-1-sulfonate (MPS), monomethoxy-terminated oligo(ethylene glycol)methacrylate (MeOEGMA), and *N*-isopropylacrylamide (NIPAAm). Atomic force microscopy, scanning electron microscopy, attenuated total reflection infrared spectroscopy, water contact angle measurements, and X-ray photoelectron spectroscopy ascertained the successful grafting of these polymer brushes at the PEEK surface. These brush-modified PEEK surfaces exhibited fully the physiochemical properties of the respective polymer brush: the surface with polyMPS brush showed selective staining by electrostatic interaction, while the polyMeOEGMA-modified surface was biorepellent. The surface modified with polyNIPAAm brush demonstrated a thermally responsive polarity change.

Introduction

Poly(ether ether ketone) (PEEK) is a high temperature resistant, semicrystalline thermoplastic polymer. Excellent thermomechanical properties, chemical stability, low flammability with low toxic gas emission, no toxicity, and biological inertness have made PEEK an attractive material for applications in a wide variety of fields such as automotive, electrical engineering, home appliances, aerospace, microfiltration membranes, and medical industries.[1−7] Like many other polymeric materials, for example poly(dimethylsioxane) (PDMS),[8] polyimide (PI),[9] and poly(ethylene terephthalate) (PET),[10] PEEK exhibits a hydrophobic, chemically inert surface nature, which is problematic in adhesion, coating, painting, coloring, biocompatibility, etc. The success of any polymeric material for a certain application relies largely upon the properties of its surface, which acts as the phase boundary residing between the bulk polymer and the outer environment. Therefore, for a particular target application the regulation of the polymer surface interaction with other media in contact is of prime importance.[11] To date, mainly two different strategies have been explored for specifically tuning the surface properties of PEEK, which include exposure to high-energy species (plasmas, ozone, UV light, electrons, and γ-rays)[12−17] and wet chemical methods.[18−21] High-energy species have been applied mainly to improve adhesion whereas wet chemical methods have been utilized to effect rational control over surface chemical properties through selective organic surface transformations.

Recently, modification of a large variety of surfaces with thin polymer films has emerged as a powerful tool for tailoring the surface properties of many materials.[22] Such thin polymer

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films can be applied by either depositing or spraying a polymeric coating from solution,[23] or polymer chains can be covalently grafted to the surfaces by "grafting-to" and "grafting-from" approaches. In the "grafting-to" approach presynthesized polymers with reactive end groups are attached to surfaces while in the "grafting-from" approach a polymer chain is grown from the surface previously functionalized with a suitable initiator moiety. Both approaches result in so-called polymer brushes, which are assemblies of long-chain polymers attached by one end to a support and extended from the surface.[24] Such polymer brushes are attractive for controlling a variety of surface properties such as adhesion, wettability, biocompatibility, etc.[25] The advantage of polymer brushes over other surface modification methods is their mechanical and chemical robustness, coupled with a high degree of synthetic flexibility enabling the introduction of a variety of functional groups. Among the many methods used for the synthesis of polymer brushes (e.g., plasma polymerization, heat- or UV-assisted graft polymerization, nitroxide-mediated polymerization, and reversible addition−fragmentation chain-transfer polymerization), the "grafting-from" approach involving surface-initiated atom-transfer radical polymerization (SI-ATRP) is more versatile. SI-ATRP allows the preparation of well-defined polymer brushes on various types of substrates, in many solvents while minimizing polymerization in solution, which provides polymer brushes under controlled growth conditions with low polydispersities.[26−36] Despite the high potential of SI-ATRP to modulate material surface properties, only limited research has been conducted on subjecting macroscale polymeric substrates to SI-ATRP or similar surface-initiated polymerization techniques.[37−41]

The present work demonstrates the unexplored capacity of SI-ATRP as a versatile methodology for controlling the surface properties of PEEK. A simple two-step method is presented for the covalent immobilization of an ATRP initiator at the surface of PEEK (Scheme 1) followed by SI-ATRP of potassium 3-(methacryloyloxy)propane-1-sulfonate (MPS),[42] monomethoxy-terminated oligo(ethylene glycol)methacrylate (MeOEGMA),[43] and N-isopropylacrylamide (NIPAAm).[44] The polymer brush-modified PEEK surfaces were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), attenuated total reflection infrared (ATR-IR) spectroscopy, water contact angle (CA) measurements, and X-ray photoelectron spectroscopy (XPS). The modulation of the PEEK surface properties by polymer brush growth was demonstrated by (1) staining by electrostatic interaction of the negatively charged polyMPS brush with the positively charged Rhodamine 6G dye, (2) PEEK grafted with polyMeOEGMA was subjected to bacterial growth for the evaluation of its biorepellency, and (3) thermally responsive wettability of the PEEK surface grafted with a polyNIPAAm brush was demonstrated by measuring the water CA at temperatures below and above the critical transition temperature, T_c, of film collapse corresponding to the lower critical solution temperature (LCST) of polyNIPAAm solutions.

Experimental Section

Materials and Methods. PEEK membranes, grade 1000-050, with a thickness of 50 μm were obtained from Victrex (Lancashire, England). Prior to use, the PEEK membranes were immersed in refluxing acetone for 48 h, rinsed twice with acetone, and dried under vacuum (1 mmHg) at 60 °C for 3 h. Thus, the obtained PEEK membranes are designated "pristine" PEEK. 2-Bromoisobutyryl bromide (98%), 2,2′-bipyridine (BiPy, 99%), copper(II) chloride (CuCl$_2$, ≥98% (Fluka)), Rhodamine 6G (99%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), and potassium 3-(methacryloyloxy) propane-1-sulfonate (MPS, 98%) were used as received from Sigma-Aldrich, Schnelldorf, Germany. Monomethoxy oilgo(ethylene glycol) methacrylate (MeOEGMA, average M_n ∼300, Sigma-Aldrich) was passed through a short plug of basic alumina to remove the stabilizer. N-Isopropylacrylamide (NIPAAm, 97%, Aldrich) was purified by recrystallization from a mixture of toluene/hexane (1/4) and dried in vacuum. Dry dichloromethane and sodium borohydride (99%) were obtained from Acros Organics, Geel, Belgium. Copper(I) chloride (CuCl, ≥97% (Fluka)) and copper(I) bromide (CuBr, 98% (Aldrich)) were purified according to the procedure of Keller and Wycoff.[45] Dimethyl sulfoxide (DMSO) was distilled prior to use. Triethylamine was refluxed overnight with calcium hydride before distilling and stored under argon. E. coli−BL12 (DE3), Cat. No. 70235-4, and SOC medium, Cat. No. 69319, were obtained from Novagen, Merck Biosciences, Darmstadt, Germany. LB-Agar (Luria/Miller) medium, Cat. No. X969.2, was obtained from Carl Roth GmbH + Co. KG, Karlsruhe, Germany. The membrane samples used for antifouling experiments were sterilized by exposure to ethylene oxide gas at room temperature. Sterilization was conducted in an Anprolene gas sterilizer (Prod. No. AN74i, Andersen Products, Inc., Haw River, NC) for 24 h. This method of sterilization was chosen to avoid the high temperatures associated with autoclave sterilization, and it is a clinically relevant sterilization process.[46] Atomic force microscopic images of the samples were taken in air at room

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Scheme 1. Schematic Representation of (A) Keto Group Reduction at the PEEK Surface, (B) Anchoring of ATRP Initiator, and (C) SI-ATRP of MPS, MeOEGMA, and NIPAAm
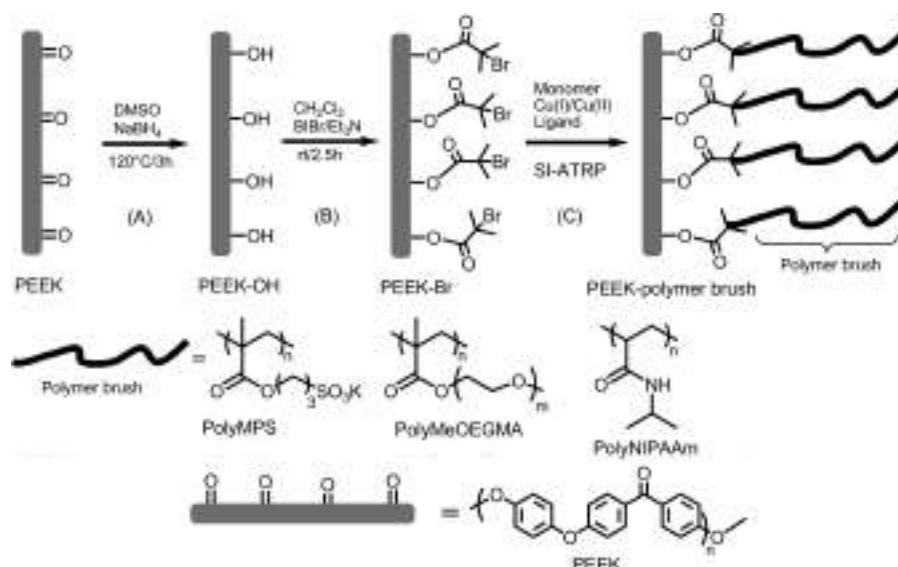
temperature with a commercial AFM Dimension 3100 (Veeco) controlled with a Nanoscope V, in tapping mode. Silicon cantilevers (Olympus) 160 μm long, 50 μm wide, and 4.6 μm thick with an integrated tip (tip radius < 10 nm) of a nominal spring constant of 42 N/m and a resonance frequency of 300 kHz were used. Typically the tip was scanned at a velocity of 0.5 Hz, and minimal applied forces were used when imaging. Topography and phase images were used to record the structures. Scanning electron microscopy (SEM) was performed with a LEO Gemini 1530 SEM with a resolution of 3.5 nm. ATR-IR spectra were recorded on neat films using a Nicolet FT-IR 730 spectrometer. Contact angle goniometry was performed on a drop shape analysis system (DSA 10-Mk2, Krüss GmbH, Germany) equipped with a thermostat chamber (TC3010/3410, Krüss GmbH, Germany), which in turn is connected to a Thermo Haake K 10/ThermoHaake DC 10 circulation system for the temperature control inside the chamber. The reported water CAs are the average of at least three individual measurements. The ellipsometric analysis was performed on a commercial ellipsometer (Nanofilm EP3-SE). All measurements were carried out at a wavelength of 532 nm. Each sample was measured at four angles of incidence (from 40° to 70°). XPS measurements were carried out using a Physical Electronics 5600 A instrument. The Mg Kα (1253.6 eV) X-ray source was operated at 300 W. A pass energy of 117.40 eV was used for the survey spectra. The spectra were recorded using a 45° take-off angle relative to the surface normal. The XPS scans were analyzed using the MultiPak 5.0 software.

Reduction of PEEK Surface Carbonyl Groups to the Hydroxy Groups (PEEK−OH). A procedure reported by Noiset et al.[21] was used with slight modification to reduce carbonyl groups at the PEEK surface to hydroxy groups. A 50 mL Schlenk tube was equipped with a reflux condenser, argon inlet, and outlet. 30 mL of freshly distilled DMSO and 60 mg (0.0016 mol) of sodium borohydride were added to the Schlenck tube. The reaction mixture was heated at 120 °C under stirring until dissolution occurred. A 3 × 3 cm^2 piece of PEEK membrane was immersed in the gently stirred reaction mixture and heated at 120 °C for 3 h under argon. After removing from reaction mixture the PEEK membrane was successively immersed in stirred methanol for 15 min, in distilled water for 10 min, in 0.5 N HCl for 10 min, in water for 10 min, and in ethanol for 10 min. The membrane was then dried at 60 °C under vacuum for 2 h and stored under N$_2$. The PEEK membrane with surface hydroxy groups is referred to as PEEK−OH.

Immobilization of ATRP Initiator on the PEEK−OH Membrane Surface (PEEK−Br). A solution of 2-bromoisobutyryl bromide (BIBr) (0.185 mL, 3 mmol) and triethylamine (0.205 mL, 3 mmol) in dry dichloromethane (30 mL) was injected over a 3 × 3 cm^2 piece of PEEK−OH membrane under N$_2$ at room temperature and left to react for 2.5 h. The membrane was washed with dichloromethane followed by absolute ethanol and dried under a stream of N$_2$. The PEEK membrane with the initiator group anchored on the surface is referred to as PEEK−Br.

SI-ATRP on the Surface of the PEEK−Br Membrane. *PolyMPS Brush.* The sulfonate monomer MPS (17.29 g, 0.07 mol) was dissolved by stirring in 20 mL of methanol and 10 mL of water at room temperature. To this solution BiPy (0.651 g, 0.0042 mol) and Cu(II)Cl$_2$ (11.4 mg, 0.085 mmol) were added. The mixture was stirred and degassed by N$_2$ bubbling for an hour before Cu(I)Cl (165 mg, 1.67 mmol) was added. The mixture was degassed with N$_2$ bubbling for another 15 min. A 1 × 1 cm^2 piece of the PEEK−Br membrane was sealed in a Schlenk tube and degassed by four high-vacuum pump/N$_2$ refill cycles. The reaction mixture was transferred by a syringe into this Schlenk tube, adding enough to cover the membrane completely, and the mixture was left for 12 h under N$_2$ at room temperature. The samples were then removed and thoroughly rinsed with deionized water to yield the PEEK−polyMPS membrane.

PolyMeOEGMA Brush. Monomethoxy oilgo(ethylene glycol) methacrylate (MeOEGMA) (11 g, 37 mmol) was dissolved in water (11 mL) at 30 °C. To this solution BiPy (160 mg, 1.0 mmol) and Cu(II)Br$_2$ (9 mg, 0.042 mmol) were added. The mixture was stirred and degassed by N$_2$ bubbling for 1 h before Cu(I)Cl (41 mg, 0.42 mmol) was added. The polymerization (for 6 h at 30 °C) and purification conditions were analogous to the polyMPS brush, yielding the PEEK−polyMeOEGMA membrane.

PolyNIPAAm Brush. NIPAAm (2.5 g, 22.1 mmol) was dissolved by stirring in a solvent mixture of 5 mL of methanol and 5 mL of water at room temperature. To this solution PMDETA (0.138 g, 0.8 mmol) was added. The mixture was stirred and degassed by N$_2$ bubbling for an hour before Cu(I)Br (0.032 g, 0.22 mmol) was added. The polymerization (for 6 h at room temperature) and purification conditions were analogous to the polyMPS brush, except the samples were additionally washed with methanol, yielding the PEEK−polyNIPAAm membrane.

Exploiting the Surface Charge: Electrostatic Interaction of PEEK–PolyMPS and Rhodamine 6G. Strips of pristine PEEK and PEEK–polyMPS membranes were immersed in 0.1 mM aqueous solution of Rhodamine 6G for 2 h. Both the membranes were washed with plenty of water before taking a photograph.

Antifouling Evaluation: Growth of E. coli *Bacteria on the Surface of Pristine PEEK and PEEK–PolyMeOEGMA.* Bacterial strain from *E. coli*–BL12 (DE3) was defrosted, transferred into 250 μL of SOC medium, and incubated for 1 h at 37 °C. LB-Agar (Luria/Miller) medium (40 g/L) was prepared, sterilized at 121 °C for 5 min, and poured into Petri dishes. During cooling of the medium, sterile strips of pristine PEEK and PEEK–polyMeOEGMA were gently immersed in the medium, and 20 μL of bacteria was spread at the surface and incubated overnight at 37 °C. The incubated strips of PEEK and PEEK–polyMeOEGMA membranes were washed with PBS buffer (phosphate buffer saline, pH 7.5) before subjecting to SEM imaging.

Thermally Responsive Switching between Hydrophilicity and Hydrophobicity of PEEK–PolyNIPAAm: Measurement of Static Water Contact Angles above and below the LCST. A PEEK–polyNIPAAm membrane, mounted on a glass slide, was placed in the thermostat chamber. Static water contact angle measurements were carried out at 0, 25, and 40 °C. The sample was equilibrated at each temperature for 20 min. Five sample positions were measured at each temperature.

Results and Discussion

Immobilization of ATRP Initiator and Subsequent Polymer Brush Growth by SI-ATRP. The covalent immobilization of the ATRP initiator at the PEEK membrane surface was achieved in a two-step process (Scheme 1). In the first step the keto groups at the PEEK surface were subjected to sodium borohydride-assisted reduction in DMSO, which resulted in surface hydroxy groups (PEEK–OH). The extent of the keto-to-hydroxy group transformation under the comparable conditions has been extensively studied by Noiset et al. They confirmed by XPS analysis that after selective reduction of the benzophenone motif at the PEEK surface with NaBH₄ in DMSO at 120 °C for 3 h the 10 outermost atomic layers consisted mainly (75–85%) of hydroxylated units.[20] These hydroxy groups at the PEEK–OH surface were reacted in the second step with 2-bromoisobutyryl bromide (BIBr) in the presence of equivalent amounts of triethylamine, which acts as HBr scavenger during the acid bromide/PEEK–OH esterification reaction. The reaction was carried out in dichloromethane and yielded PEEK membranes with surface immobilized 2-bromoisobutyryl groups (PEEK–Br) well suited for SI-ATRP. Subsequently, polymer brushes were grown at the surface of the PEEK–Br membranes by SI-ATRP of MPS, MeOEGMA, and NIPAAm under aqueous ATRP conditions (Scheme 1).

Surface Charaterization. After SI-ATRP, a change in surface morphology was evident in both AFM and SEM images (Figure 1). For the AFM analysis, the phase images are given as insets to height images. There was no difference in the surface topography of pristine PEEK and PEEK–Br; therefore, AFM and SEM images of pristine PEEK are omitted. PEEK–Br showed a fibrous topography in AFM and SEM images (Figure 1A). After the SI-ATRP of MPS and MeOEGMA the PEEK–polyMPS and PEEK–polyMeOEGMA surfaces lost the fibrous topography of PEEK–Br (Figure 1B,C), whereas the surface retained the traces of fibrous topography after SI-ATRP of NIPAAm
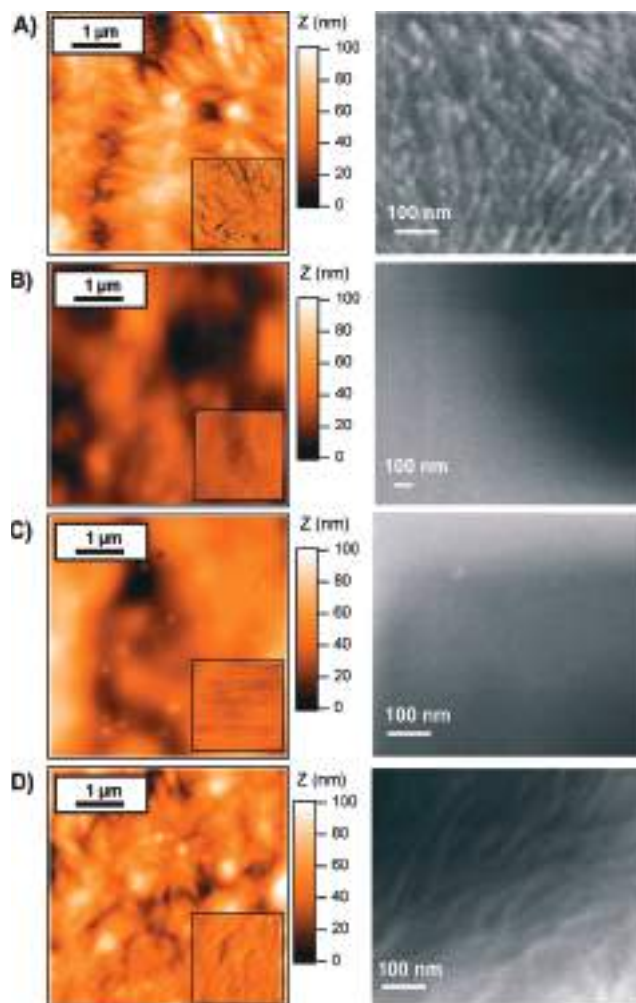

Figure 1. AFM (left column) and SEM (right column) images of (A) PEEK–Br, (B) PEEK–polyMPS, (C) PEEK–polyMeOEG-MA, and (D) PEEK–polyNIPAAm.

(Figure 1D), even though the edges were softer. The reduction of the fibrous features after SI-ATRP is explained by the formation of an amorphous and dense polymer brush layer, which levels out topographic height differences of the PEEK–Br surface. An ellipsometric analysis of the surface also supported a higher brush thickness for polyMPS and polyMeOEGMA (274 and 80 nm) compared to polyNI-PAAm (40 nm).

After characterizing the changes in surface topography, ATR-IR was employed to analyze the surface chemical composition. Within the resolution of the method the ATR-IR spectra of PEEK, PEEK–OH, and PEEK–Br were identical. However, after the growth of polyMPS and poly-MeOEGMA brushes the carbonyl stretch vibration bands appeared at 1724 and 1727 cm^{-1} in the ATR-IR spectra of PEEK–polyMPS and PEEK–polyMeOEGMA, which correspond to the ester linkage in these brushes (Figure 2A). On the contrary, no additional carbonyl group was observed in the ATR-IR spectrum of PEEK–polyNIPAAm, and the expected carbonyl band of the amide group could not be resolved as the aromatic keto group of the PEEK membrane absorbs in the same spectral range (Figure 2A).

Furthermore, the polyMPS brush showed a symmetric sulfonate stretching band around 1047 cm^{-1} in the ATR-IR spectrum of PEEK–polyMPS (Figure 2B). With the
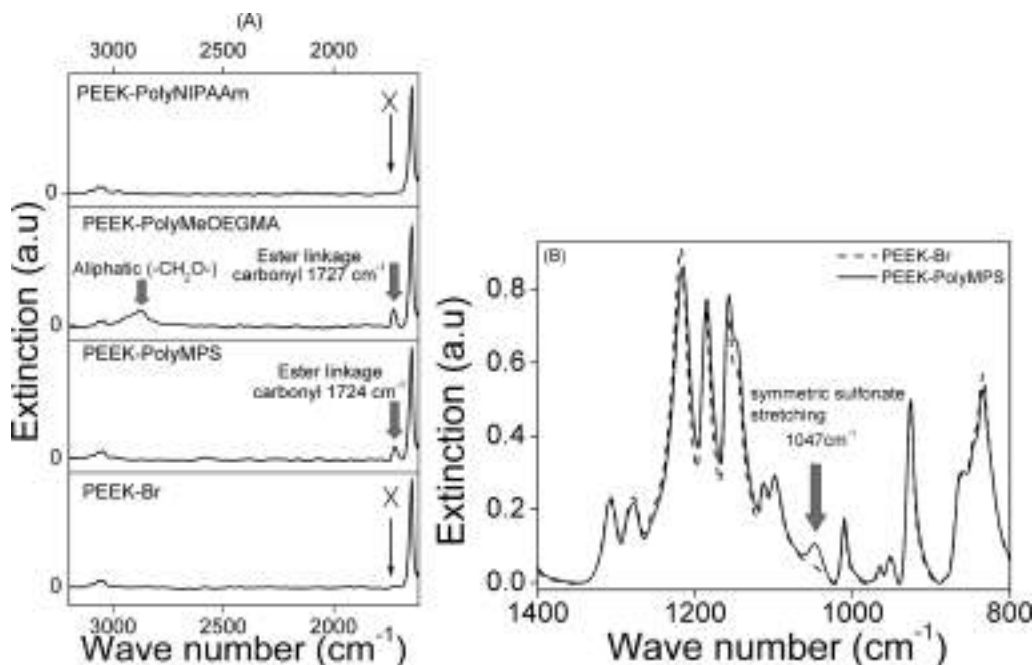
Figure 2. ATR-IR monitoring of surface chemical modification of PEEK by SI-ATRP.

incorporation of $-CH_2-O-$ linkages on the surface, a change in the aliphatic $-CH$ region was observed for the polyMeOEGMA brush (Figure 2A).

Successful initiator immobilization and subsequent polymer grafting were further ascertained by XPS measurements. While reducing the surface keto groups into hydroxy groups, there is no change in the atomic concentration of the PEEK elements and no new element is incorporated; hence, no change was observed in XPS. After reacting PEEK−OH with BIBr, the successful anchoring of the ATRP initiator was indicated by the appearance of a Br 3d core level absorption between 70 and 75 eV and for Br 3p between 182 and 198 eV (Figure 3B and inset). Except for the observation of bromine in the high-resolution XPS spectrum, the surface chemical composition (see Table 1) was similar to that of pristine PEEK. The experimentally determined atomic concentration of Br was also less than the theoretical value. This is consistent with the fact that only the hydroxy groups on the outermost surface have been converted to the initiator species and that the depth of surface modification is just at the margin of the XPS sampling depth of ∼4 nm at a 45° take-off angle relative to the surface normal.

The XPS survey scan of the PEEK−polyMPS surface revealed the presence of sulfur (S 2s: 233.6 eV; S 2p: 170.9 eV) and potassium (K 2s: 379.7 eV; K 2p: 295.4 eV) incorporated onto the surface through the sulfonate groups (Figure 3C). The grafting of polyMPS was further evident from the surface chemical composition that matched that of the bulk polyMPS (see Table 1). Furthermore, the C 1s high-resolution scan of PEEK−polyMPS surface could be fitted by three peak components attributable to the aliphatic carbon (C−C/C−H), the ester carbonyl carbon (O−C=O), and the carbon linked to the sulfonate group (C−S), corresponding to binding energies at 285.3, 286.8, and 289.1 eV, respectively (Figure 3D).

The XPS analysis of the PEEK−polyMeOEGMA surface showed a higher oxygen content than the pristine PEEK surface (Figure 3E and Table 1). Successful grafting was confirmed by agreement of the theoretical and experimentally
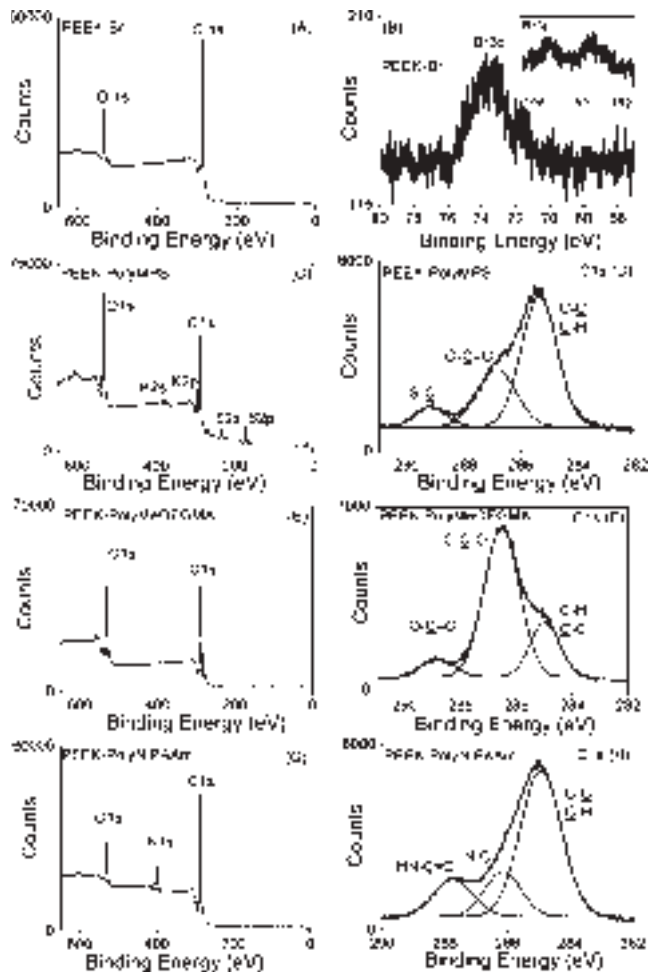
Figure 3. XPS analysis of the modified PEEK surfaces.

determined surface chemical composition (Table 1). The C 1s high-resolution scan of PEEK−polyMeOEGMA could be fitted by three peak components of aliphatic (C−C/C−H), ether (C−O), and ester (O−C=O) carbons corresponding to

Table 1. Water Contact Angles and XPS Surface Atomic Concentrations[a]

sample	static CA (deg)	XPS surface atomic concentration (%)					
		C	O	Br	N	S(2s,2p)	K(2s,2p)
PEEK	93 ± 3	86	14				
		86.4	*13.6*				
PEEK−Br	65 ± 2	86	13	1			
		82.1	*14.3*	*3.5*			
PEEK−polyMPS	∼0	48	30			6, 6	5, 5
		50.0	*35.7*			*7.1*	*7.1*
PEEK−polyMeOEGMA	57 ± 2	68	32				
		70.0	*30.0*				
PEEK−polyNIPAAm	65 ± 2	76	13		11		
		75.0	*12.5*		*12.5*		

[a] Theoretical atomic concentrations are shown in italics beneath the experimental values.

binding energies of 284.9, 286.5, and 288.8 eV, respectively (Figure 3F).

The survey scan of the PEEK−polyNIPAAm surface showed the signal for incorporated nitrogen at 400.8 eV (Figure 3G). The experimentally determined surface chemical composition of PEEK−polyNIPAAM corresponds to that of the theoretical chemical composition of a pure polyNIPAAm film (Table 1). The C 1s high-resolution scan of PEEK−polyNIPAAm could be fitted by three peak components of aliphatic (C−*C*/C−H), C–N and amide (NH−*C*=O) carbons corresponding to binding energies of 284.9, 286.16, and 287.7 eV (Figure 3H).

The growth of polymer brushes also resulted in a change in surface polarity. Static water contact angles of the PEEK brush surfaces determined at room temperature are given in Table 1. The PEEK−polyMPS surface exhibited a high hydrophilicity, and the water contact angle was ∼0°. The static water contact angle of PEEK−polyMeOEGMA (57°) was consistent with the literature values where poly(ethylene oxide) was immobilized onto a fluorinated ethylene−propylene copolymer surface.[47] Similarly, the water contact angle of the PEEK−polyNIPAAm surfaces (65°) was comparable to the reported literature value, where a polyNIPAAm brush was grown on the surface of a silicon wafer or gold via SI-ATRP.[48,49]

The presented characterization data fully confirm the change in surface chemical composition of PEEK, which corresponds to the respective polymer brush after subjecting PEEK−Br to SI-ATRP. This in turn accounts for the efficient accessibility of hydroxy groups on the PEEK−OH surface and also for the high effectiveness of the covalently anchored 2-bromoisobutyryl groups on the PEEK−Br surface as initiators for subsequent polymer brush growth via SI-ATRP. The efficient SI-ATRP resulted in a thick and dense polymer brush layer evident from the XPS analysis (Figure 3 and Table 1), which shows the complete transformation of the surface chemical nature of PEEK to the respective brush and which is further documented by the macroscopic properties investigated below (Figure 4). Set aside the fundamental research on SI-ATRP, the access to functional materials by a combination of commercial PEEK and simple preparation methods for well-defined polymer brushes is of high technological relevance.

Demonstration of Properties Imparted to the PEEK Surface by Polymer Brushes. After characterizing the surface chemical composition, the surface properties of pristine PEEK was compared with the PEEK brushes (Figure 4).

The growth of polyMPS bearing sulfonate groups resulted in a negatively charged PEEK surface. This negatively charged PEEK−polyMPS surface immediately stained red when immersed in a 0.1 mM aqueous solution of positively charged Rhodamine 6G (Figure 4A.II), while the pristine PEEK retained its original color after an immersion time of 2 h (Figure 4A.I). Such surface property shows the potential for manipulation of electrostatic interactions at the PEEK surface.[50]

Surfaces coated with poly(ethylene glycol) (PEG) or oligo(ethylene glycol) are known to prevent bioadhesion of proteins or living cells and bacteria.[51,52] The growth of the polyMeOEGMA brush in analogy to PEG also rendered the PEEK surface antifouling (Figure 4B), which was demonstrated by exposing PEEK−polyMeOEGMA to a culture medium of *E. coli*−BL12 (DE3) bacteria. While a significant number of bacteria attached to the surface of pristine PEEK (Figure 4B.I), no bacteria adhered to the PEEK−polyMeOEGMA surface (Figure 4B.II). This result is potentially important in the field of biomedical devices where PEEK is employed as structural implant material.

PolyNIPAAm grafted on solid substrates is known to result in temperature-dependent surface properties.[53] In this respect the thermally responsive polarity change of PEEK−polyNIPAAm surface was demonstrated by measuring water CAs at temperatures below and above the critical transition temperature (T_c around 32 °C) of polyNIPAAm, where the film converts from the swollen to the collapsed state.[48,54] A change in the static water droplet profile can be seen when the temperature was elevated from 0 to 25 °C and then to 40 °C with water CAs of 42°, 64°, and 87°. In contrast, the CA measured on pristine PEEK under identical conditions did not show any significant temperature dependence. The molecular mechanism of the thermally responsive polarity of a PNIPAAm thin film is discussed in the literature to involve a reversible switching from intermolecular hydrogen bonding between polyNIPAAm chains and water molecules below the LCST in solution or the T_c in hydrogel networks (left) to intramolecular hydrogen bonding between C=O

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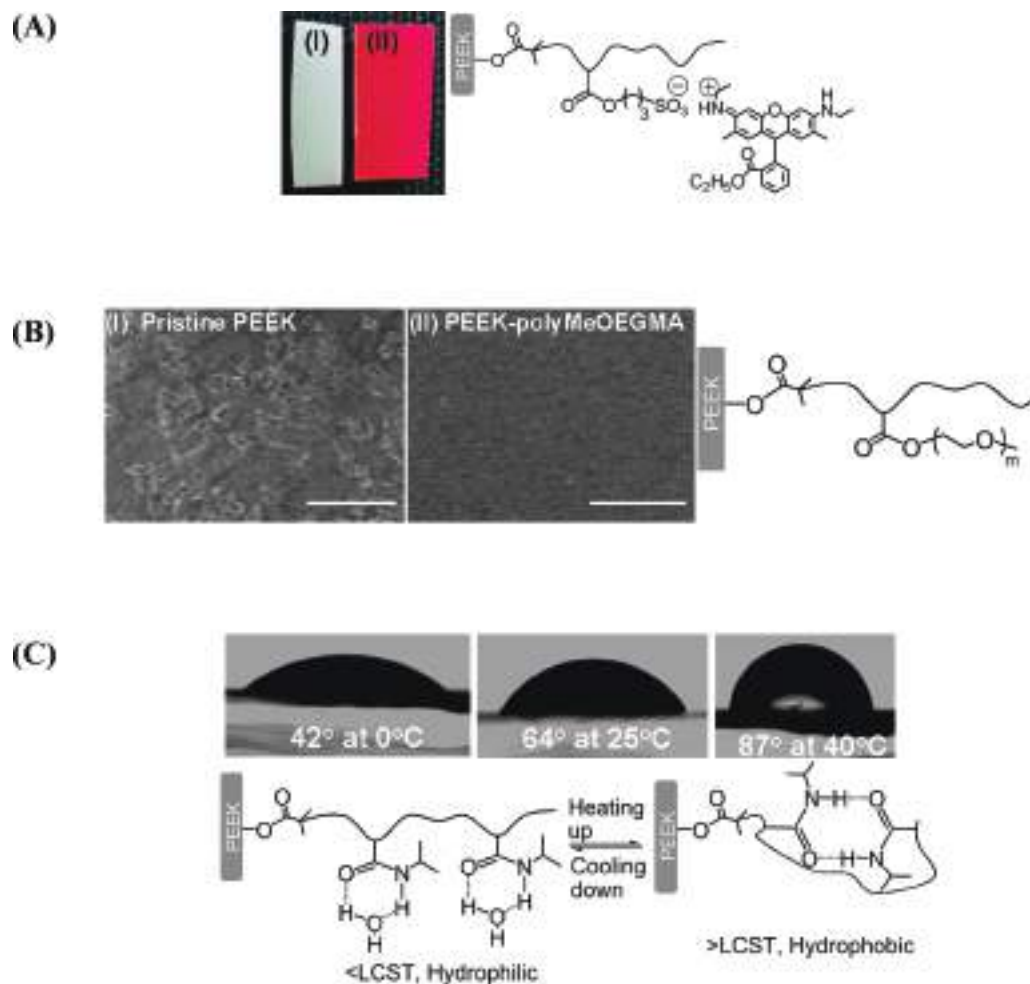
Figure 4. Demonstration of changes in surface properties of PEEK after growing polymer brushes via SI-ATRP. (A) Electrostatic interaction of prinstine PEEK (I) and PEEK−polyMPS (II) with Rhodamine 6G in aqueous solution. (B) SEM images of pristine PEEK (I) and PEEK−polyMeOEGMA (II) surfaces previously exposed to an *E. coli* bacteria culture. The scale bars in both images are 10 μm. (C) Water droplet profiles on the PEEK−polyNIPAAm surface at 0, 25, and 40 °C corresponding to water CAs of 42°, 64°, and 87° (above). The proposed molecular mechanism of the thermally responsive polarity change of a PNIPAAm thin film depicts a switching between intermolecular (<LCST) and intramolecular (>LCST) hydrogen bonding in polyNIPAAm (below).

and N−H groups in PNIPAAm chains (right) above the transition temperature. The mechanism is also schematically presented in Figure 4C.[55]

Conclusions

The surface of poly(ether ether ketone) (PEEK) was successfully functionalized with polymer brushes grown by surface-initiated atom transfer radical polymerization (SI-ATRP), which enables precise control over the PEEK surface properties like electrostatic interactions, antifouling character, or a thermally responsive polarity. At the PEEK surface SI-ATRP, which has emerged as a highly versatile and powerful tool for controlling the materials surface properties, could be achieved in a convenient two-step wet-chemical process by first anchoring covalently a 2-bromoisobutyryl group as initiator followed by the growth of polymer brushes by SI-ATRP. This simple process holds great technological potential for scale-up and industrial application, in particular due to the possibility of specifically tuning the PEEK surface properties via careful selection from a plethora of functional monomers.

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