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Adsorption and Desorption Behavior of Asphaltene on Polymer-Brush-Immobilized Surfaces

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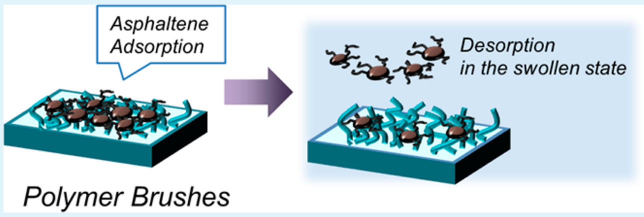
Supporting Information

ABSTRACT: The adsorption behavior of a model compound for surface-active component of asphaltenes, *N*-(1-hexylheptyl)-*N*′-(12-carboxylicdodecyl) perylene-3,4,9,10-tetracarboxylic bisimide (C5Pe), and detachment behavior of asphaltene deposit films for high-density polymer brushes were investigated. Zwitterionic poly(3-(*N*-2-methacryloyloxyethyl-*N*,*N*-dimethyl)ammonatopropanesulfonate (PMAPS) brushes and hydrophobic poly(*n*-hexyl methacrylate) (PHMA) brushes exhibit less C5Pe adsorption than poly(methyl methacrylate) (PMMA). The asphaltene deposit films on the PHMA brush detached in a model oil (toluene/*n*-heptane = 1/4 (v/v)), and the asphaltene films on the PMAPS brush detached in water. The antifouling character was explained by the interface free energy for the polymer-brush/asphaltenes (γ_{SA}) and polymer-brush/toluene (γ_{SO}).



KEYWORDS: *polymer brush, asphaltene, adsorption, antifouling, surface-initiated atom transfer radical polymerization, interface free energy*

INTRODUCTION

Asphaltenes are a component of crude oil that is insoluble in low-boiling paraffinic solvents (*n*-pentane or *n*-heptane) but soluble in aromatic solvents (toluene or benzene), and they are regarded as one of the major sources of pipeline fouling.[1] Suppression of asphaltene adsorption is a key technology in the petroleum industry and innovative approaches are needed. Asphaltenes consist of heterogeneous macromolecules with high degrees of aromaticity and polarity. This class of molecules has been reported to form colloidal aggregates in solution, stabilize water-in-oil emulsions, and adsorb onto solid−liquid and liquid−liquid interfaces.[2−4] The strong interaction between π-electrons in the aromatic cores, as well as the dipole of the heteroatoms, contribute to the strong adsorption to the interfaces. Asphaltene adsorption studies have been carried out on metal or glass substrates,[5,6] but systematic study on organic polymer surfaces has not been reported. Genzer et al. investigated asphaltene adsorption onto self-assembled monolayers (SAMs) of alkyl silane compounds.[7] The amount of strongly adsorbed asphaltenes at the liquid/SAMs interface was evaluated by removing the weakly adsorbed molecules through sonication in toluene. They concluded that the wettability of the substrates is not the leading factor for asphaltene adsorption, and that the thickness of the SAMs is most important. This phenomenon was attributed to the shielding of interactions between asphaltenes and the underlying polar silicon substrate by the long alkyl chain buffer layer. Sjöblom et al. monitored asphaltene adsorption onto chemically modified silica particles.[8] The amount of adsorption was larger for the more hydrophilic silica particles, indicating that the strong interaction between the asphaltenes and SiO_2 is responsible for the sludge formation.

One useful approach for modifying surface physicochemical properties is to tether organic polymers to the substrate. The lubrication and antifouling properties of the polymer chain grafted surfaces have been demonstrated.[9,10] The polymer chains are immobilized on the substrate by covalent bonds and are not detached by friction and solvent exposure. Surface-initiated controlled radical polymerization techniques have been applied to achieve well-defined surface-tethered polymer layers with high grafting density. Solvated polymer brushes show unique physical properties in organic solvents, including extremely low coefficient of friction and resistance to adhesion of foreign objects such as proteins.[11,12] The unique surface

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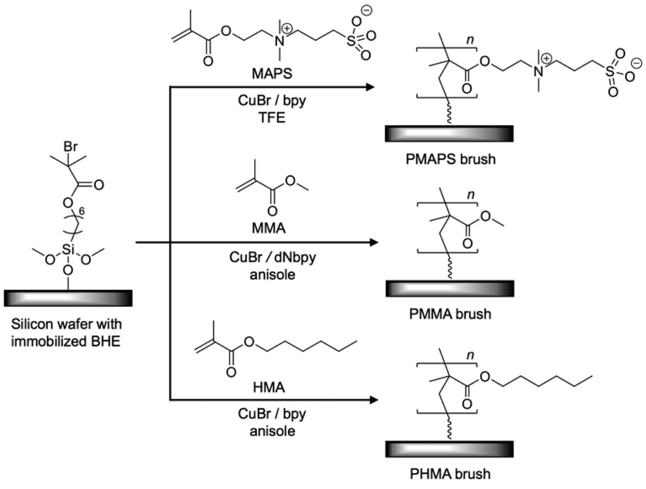
properties are due to the osmotic pressure between closely spaced chains, which serves to extend the chains from the substrate and minimize interaction between foreign objects and the substrate. Material design utilizing surface-tethered polymer brushes provides a potential route to effectively control asphaltene adsorption, and is anticipated to be viable as an antifouling coating for petroleum transportation facilities.[13] In this paper, we report the adsorption behavior of C5Pe and detachment behavior of asphaltene deposit films on a surface coated with high-density polymer brush. C5Pe is a model compound for surface-active component of asphaltene. We focus on the effect of the chemical structure of polymer brushes and interface free energy for the polymer-brush/asphaltene (γ_{SA}) and polymer-brush/toluene (γ_{SO}) on the C5Pe adsorption and asphaltene deposit film detachment behaviors.

EXPERIMENTAL SECTION

Materials. *n*-Heptane (>99%) and toluene (99%) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and used as received. Deionized water was purified with a NanoPure Water system (Millipore Inc.). *N*-(1-Hexylheptyl)-*N*′-(12-carboxylicdodecyl) perylene-3,4,9,10-tetracarboxylic bisimide (C5Pe; see the Supporting Information, Figure S1) was synthesized and used for adsorption test.[14] Natural asphaltenes were extracted from a vacuum residual oil on the basis of the IP143 standard. A vacuum residual oil was mixed with *n*-heptane in a 1:40 weight ratio followed by stirring for 24 h. The mixture was filtered, and the residue was washed with *n*-heptane using a Soxhlet apparatus for 24 h. The residue was washed with toluene using a Soxhlet apparatus for 24 h, and the extractions were dried under reduced pressure to give natural asphaltenes in a shiny, dark solid.

Preparation of Polymer Brush. The preparation procedure and chemical structure of the polymer brushes used here are illustrated in Scheme 1. Three polymer brushes were prepared: (1) poly(3-(*N*-2-methacryloyloxyethyl-*N*,*N*-dimethyl)ammonatopropanesulfonate (PMAPS), a zwitterionic poly(sulfobetaine); (2) poly(methyl methacrylate) (PMMA), a water insoluble but weakly hydrophobic polymer; and (3) poly(*n*-hexyl methacrylate) (PHMA), a hydrophobic aliphatic polymer. Surface-initiated atom transfer radical polymerization (SI-ATRP) was carried out with (2-bromo-2-methyl)-propionyloxyhexyl triethoxysilane (BHE)-immobilized silicon wafers in the presence of ethyl 2-bromoisobutylate (EB) coupled with CuBr and ligands (2,2′-bipyridine (bpy) for PMAPS and PHMA, and 4,4′-dinonyl-2,2′-bipyridyl (dNbpy) for PMMA). The detailed polymer brush preparation procedures were previously reported.[15,16] The molecular weight of the polymers grown from substrate was estimated based on the molecular weight of the free-polymer grown in solution from free-initiator.[15,17] The grafting density, σ, was evaluated based on the thickness and molecular weight of the grafted polymer chains.[18] Characteristics of the polymer brush samples are summarized in Table 1.

Scheme 1. Preparation Procedure and Chemical Structure of the Polymer Brushes Fabricated on Silicon Wafer



Adsorption Test of C5Pe. C5Pe was dissolved in toluene to obtain a 0.2 mg/mL C5Pe in toluene solution. To ensure complete dissolution of C5Pe, the solution was sonicated for 10 min, and filtered by a 0.45 μm polytetrafluoroethylene filter before its use. The polymer brushes were immersed in the C5Pe toluene solution for 24 h, and were subsequently lifted up from the solution. During drying, the polymer brush surface was fixed vertically with respect to the ground. The C5Pe adsorbed on the polymer brush surfaces was observed by the fluorescence microscopy. The polymer brushes were subsequently sonicated in pure toluene for 10 min two times. The relative amount of C5Pe adsorption on the polymer brush surfaces was evaluated by the maximum absorption intensity at 527 nm of the C5Pe toluene solution in the ultraviolet−visible (UV−vis) adsorption spectra.

Detachment Test of Asphaltene Deposit Films. A 1.0 wt % toluene solution of the extracted natural asphaltenes was deposited on the polymer brushes and dried in air. The asphaltene films were immersed and shaken in a model oil (toluene/*n*-heptane = 1/4 (v/v)) or pure water for 20 min. The detachability was evaluated through visual observation.

Measurements. The number-averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the free-polymer were estimated by size exclusion chromatography (SEC) using a Shimadzu HPLC system equipped with a multiangle light-scattering detector (MALS, Wyatt Technology DAWN-EOS, 30 mW GaAs linearly polarized laser, wavelength λ = 690 nm) and a refractive index detector (Shimadzu RID-10A, tungsten lamp, wavelength 470−950 nm). The Rayleigh ratio at a scattering angle of 90° was based on that of pure toluene at a wavelength of 632.8 nm at 25 °C. SEC setup was followed by previous reports.[15,16] The thickness of the polymer brushes immobilized on a silicon wafer in air (the relative humidity was ca. 45%) was determined by a MASS-102 spectroscopic ellipsometer (Five Lab Inc.) with a xenon arc lamp (wavelength 380−890 nm) at a fixed incident angle of 70°. The static contact angles were recorded with a DSA10 Mk2 (Krüss, Inc.) drop shape analysis system equipped with a video camera. A 2.0 μL droplet was placed on the surface using a microsyringe to measure the static contact angle in ambient air at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an PHI 5000 VersaProbe II (Physical Electronics Inc., Chanhassen, MN) at 1×10^{-9} Pa using a monochromatic Al K_α X-ray source operated at 150 W. All of the XPS data were collected at a takeoff angle of 45°, and a low-energy (25 eV) electron flood gun was used to minimize sample charging. The high-resolution spectra of the C_{1s}, O_{1s}, N_{1s}, and S_{2p} regions were acquired at analyzer pass energies of 25.0 eV. Fluorescence microscopy images were observed with a Nikon Eclipse E400 microscope (Nikon Co., Ltd.) equipped with a Nikon G-2A filter and a Nikon DS-5 M digital camera. The light source was a C-SHG1 super high-pressure mercury lamp. UV−vis absorption spectroscopy was performed on a Shimadzu UV-3600 UV−vis−NIR spectrophotometer in a wavelength range of 400−580 nm at room temperature.

RESULTS AND DISCUSSION

XPS spectra of the polymer brushes revealed a large decrease in silicon peak intensity with respect to the initiator immobilized substrate. The surface atomic ratios of carbon, oxygen, nitrogen, and sulfur correspond well with the theoretical values calculated from the atomic composition of the polymer brushes, which indicates that the surface is homogeneously covered with the polymer brushes.

The composition and corresponding adsorption behavior of asphaltenes vary widely and depend on the crude oil producing

Table 1. Characterization of the Polymer Brush Samples

					surface free energy[c] (mJ/m^2)		
polymer brushes	M_n[a] (g/mol)	M_w/M_n[a]	thickness[b] (nm)	σ (chains/nm^2)	γ_{SV}	γ_{SV}^{d}	γ_{SV}^{p}
PMAPS	145 800	1.34	33.1	0.18	71.8	28.5	43.3
PMMA	35 400	1.17	24.4	0.49	42.4	35.3	7.1
PHMA	59 000	1.34	27.6	0.28	30.0	28.5	1.5

[a] Estimated by size exclusion chromatography (SEC) equipped with a multiangle light-scattering detector (MALS) using 200 mM NaCl aqueous solution as an eluent for PMAPS, and tetrahydrofuran as an eluent for PMMA and PHMA. [b] Thickness in dry state estimated by imaging ellipsometer. [c] Determined from contact angles of 2 μL of water and 1 μL of diiodomethane droplets by the Owens−Wendt method using the following parameters: γ_{LV}^{d} (water) = 21.8, γ_{LV}^{p} (water) = 51.0, γ_{LV}^{d} (diiodomethane) = 49.5, γ_{LV}^{p} (diiodomethane) = 1.3 mJ/m^2.

location. For fundamental research into asphaltene adsorption, a model compound is necessary. In addition, the fluorescent intensity of natural asphaltene is too weak to evaluate the adsorption amount through fluorescent microscopy observation. C5Pe was synthesized and used for adsorption test.[14] Prior works have demonstrated that the alkylated perylene core with carboxylic acid group is soluble in toluene and precipitates upon addition of *n*-heptane, is highly interfacially active, and slowly aggregates in mixed solution of toluene and *n*-heptane.[19] These behaviors are consistent with the general behavior of natural asphaltenes and indicate that C5Pe can be regarded as a model compound for the surface-active component of asphaltenes.[19,20] C5Pe also has strong fluorescent intensity, which provides a means to directly visualize adsorption amount. The C5Pe adsorption behavior correlates well with the asphaltene attachment/detachment and the asphaltene deposition trends because the surface-active components exist at the interface of the asphaltene deposit and it is the primary adsorption of the surface-active component that triggers the subsequent asphaltene deposition. In other words, C5Pe provides a useful signal for onset of asphaltene deposition behavior, but is not necessarily valid to study later stages of fouling behavior. For the adsorption test, the polymer brushes were immersed in a 0.2 mg/mL toluene solution of C5Pe for 24 h. The polymer brushes were lifted from the solution and dried. Fluorescence microscopy images of the polymer brushes after the C5Pe adsorption test are shown in Figure 1a.

The PMAPS brushes and PHMA brushes show less C5Pe adsorption than the PMMA brushes, which are densely covered with the C5Pe molecules. Weakly adsorbed C5Pe was removed by sonication in toluene for 10 min, and the adsorbed quantity of C5Pe was evaluated with UV−vis absorption spectroscopy. The amount of strongly adsorbed C5Pe decreased in the following order: PMMA > PHMA > PMAPS. The adsorption behavior may be attributed to the differences in interfacial energy between the polymer brushes and toluene or asphaltene. The interfacial free energies of polymer-brush/asphaltene (γ_{SA}), polymer-brush/toluene (γ_{SO}), and polymer-brush/water (γ_{SW}) were determined by the extended Fowkes equation (Table 2).[21]

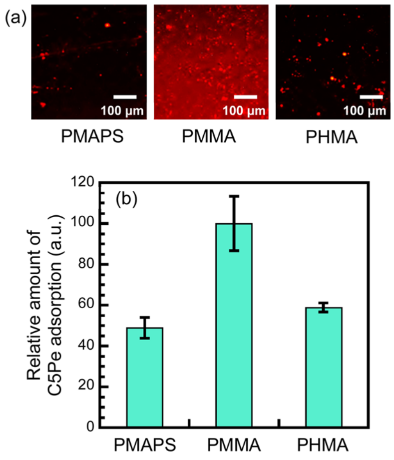


Figure 1. (a) Fluorescence microscopy images of the polymer brush surfaces after C5Pe adsorption test. (b) Relative amount of C5Pe adsorption onto the polymer brush surfaces.

Table 2. Interfacial Free Energies of Prepared Polymer Brush Samples

	interface free energy[a] (mJ/m^2)		
polymer brushes	γ_{SA}	γ_{SO}	γ_{SW}
PMAPS	36.5	43.3	0.8
PMMA	4.3	7.5	21.7
PHMA	1.4	1.5	35.5

[a] γ_{SA}, γ_{SO}, and γ_{SW} are the polymer-brush/asphaltene, polymer-brush/toluene, and polymer-brush/water interface free energies, respectively, as determined by the extended Fowkes equation using the following parameters: γ_{LV}^{d} (water) = 21.8, γ_{LV}^{p} (water) = 51.0, γ_{LV}^{d} (toluene) = 28.4, γ_{LV}^{d} (asphaltene) = 40.7, γ_{LV}^{p} (asphaltene) = 0.4. γ_{LV}^{d} and γ_{LV}^{p} for asphaltene were evaluated from contact angles of water and diiodomethane droplets on the asphaltene deposit film by the Owens−Wendt method.

The calculation procedure is provided in the Supporting Information. For the PHMA brush, γ_{SA} is smaller, whereas for the PMAPS brush, γ_{SA} is largest. Despite showing the largest amount of strongly adsorbed C5Pe, the PMMA brush shows an intermediate value of γ_{SA}. This trend can be explained by comparison of γ_{SA} to the γ_{SO}. For the PHMA brush, γ_{SO} is smaller and of similar magnitude to γ_{SA}. In this case, the solvent (toluene) wets the PHMA brush, leading to effective suppression of the C5Pe adsorption. For the PMMA brush and PMAPS brushes, $\gamma_{SO} > \gamma_{SA}$, indicating that C5Pe adsorption is preferred over solvent wetting.

The surface free energy of the PMAPS brush is significantly higher than that for the other polymer brushes. Strong interaction between the charged sulfobetaine groups and C5Pe is expected to promote significant C5Pe adsorption.[22] However, the hydrophilic PMAPS brush is able to efficiently inhibit the C5Pe adsorption process. This trend is attributed to the presence of a hydrated layer at the PMAPS brush/toluene interface. The hydrophilic polyelectrolyte chains immediately adsorb water. When immersed in toluene, a slight amount of dissolved water preferentially segregates at the PMAPS brush/toluene interface, which results in a hydrated polymer brush layer. The hydrated layer prevents penetration of the adsorbent because of the extremely low interface energy of the PMAPS brush/water interface.

The detachability of the deposited film of asphaltene was examined with a detachment test in solvent. For the detachment experiments, natural asphaltenes were extracted from a vacuum residual oil on the basis of the IP143 standard because the model compound for surface-active component of asphaltenes, C5Pe, does not form a deposited film. The appearances of the deposited films on the polymer brush surfaces after washing are shown in Figure 2. The asphaltene film rigidly attaches to the polymer brush surface in dry state. The asphaltene films on the PHMA brush detach in the model oil, whereas the asphaltene films remain adhered to the PMAPS and PMMA brushes. On the other hand, the asphaltene films on the PMAPS brush detach in water, whereas the asphaltene films remain adhered to the PHMA and PMMA brushes. The detachment phenomenon of the deposited asphaltene films is attributed to the low interface free energy in the respective solvent. The PHMA brush has a low interface free energy for the model oil, and because of the high mobility and low density of the swollen brush chains, the interface tension will be lower than in the dry state. A similar mechanism may be used for the hydrophilic PMAPS brushes in water. The interface free energies clearly dictate the asphaltene adsorption behavior; however, the chain dynamics and swelling state of the polymer brushes should have a larger effect on adsorption of foreign objects.[12,23] More detailed study of these effects will be the focus of future work.

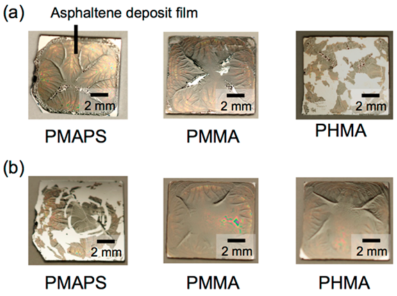


Figure 2. Appearances of asphaltene deposit film on the polymer brushes after immersing and shaking in (a) a model oil (toluene/*n*-heptane = 1/4 (v/v)) and (b) water.

■ CONCLUSIONS

The adsorption behavior of a model compound for the surface-active component of asphaltenes, and attachment/detachment behavior of asphaltene deposit films, for different polymer brush surfaces has been systematically investigated. The C5Pe has a significant affinity for the PMMA brushes, whereas the PMAPS brushes and PHMA brushes prevent C5Pe adsorption. The C5Pe adsorption suppression is explained by the interface free energy for polymer-brush/asphaltene (γ_{SA}) and polymer-brush/toluene (γ_{SO}). Natural asphaltene films deposited on the PHMA and PMAPS brushes easily detach after immersion in oil or water, respectively. The behavior is explained on the basis of the wetting of the liquids into the polymer-brush/asphaltene interface because of the low polymer-brush/liquid interface free energy. The antiasphaltene fouling property of the polymer brushes provides a new antifouling strategy for the petroleum industry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Chemical structure of C5Pe and preparation procedure; calculation of surface and interface free energy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Leontaritis, K. J.; Mansoori, G. A. Asphaltene Deposition: A Survey of Field Experiences and Research Approaches. *J. Pet. Sci. Eng.* **1988**, *1*, 229−239.

(2) Takanohashi, T.; Sato, S.; Saito, I.; Tanaka, R. Molecular Dynamics Simulation of the Heat-Induced Relaxation of Asphaltene Aggregates. *Energy Fuels* **2002**, *17*, 135−139.

(3) Yarranton, H. W.; Hussein, H.; Masliyah, J. H. Water-in-Hydrocarbon Emulsions Stabilized by Asphaltenes at Low Concentrations. *J. Colloid Interface Sci.* **2000**, *228*, 52−63.

(4) Gabrienko, A. A.; Lai, C. H.; Kazarian, S. G. In Situ Chemical Imaging of Asphaltene Precipitation from Crude Oil Induced by *n*-Heptane. *Energy Fuels* **2014**, *28*, 964−971.

(5) Alboudwarej, H.; Pole, D.; Svrcek, W. Y.; Yarranton, H. W. Adsorption of Asphaltenes on Metals. *Ind. Eng. Chem. Res.* **2005**, *44*, 5585−5592.

(6) Akhlaq, M. S.; Götze, P.; Kessel, D.; Dornow, W. Adsorption of Crude Oil Colloids on Glass Plates: Measurements of Contact Angles and the Factors Influencing Glass Surface Properties. *Colloids Surf., A* **1997**, *126*, 25−32.

(7) Turgman-Cohen, S.; Fischer, D. A.; Kilpatrick, P. K.; Genzer, J. Asphaltene Adsorption onto Self-Assembled Monolayers of Alkyltrichlorosilanes of Varying Chain Length. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1347−1357.

(8) Hannisdal, A.; Ese, M. H.; Hemmingsen, P. V.; Sjöblom, J. Particle-Stabilized Emulsions: Effect of Heavy Crude Oil Components Pre-Adsorbed onto Stabilizing Solids. *Colloids Surf., A* **2006**, *276*, 45−58.

(9) Klein, J.; Kumacheva, E.; Mahalu, D.; Perahia, D.; Fetters, L. J. Reduction of Frictional Forces between Solid Surfaces Bearing Polymer Brushes. *Nature* **1994**, *370*, 634−636.

(10) Kobayashi, M.; Terayama, Y.; Yamaguchi, H.; Terada, M.; Murakami, D.; IshiharaK.; Takahara, A. Wettability and Antifouling Behavior on the Surfaces of Superhydrophilic Polymer Brushes. *Langmuir* **2012**, *28*, 7212−7222.

(11) Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T. Structure and Properties of High-Density Polymer Brushes Prepared by Surface-Initiated Living Radical Polymerization. In *Surface-Initiated Polymerization I*; Jordan, R., Ed.; Springer: Berlin, 2006; Chapter 63, pp 1−45.

(12) Kobayashi, M.; Terayama, Y.; Kikuchi, M.; Takahara, A. Chain Dimensions and Surface Characterization of Superhydrophilic Polymer Brushes with Zwitterion Side Groups. *Soft Matter* **2013**, *9*, 5138−5148.

(13) Dunderdale, G. J.; Urata, C.; Miranda, D. F.; Hozumi, A. Large-Scale and Environmentally Friendly Synthesis of pH-Responsive Oil-Repellent Polymer Brush Surfaces under Ambient Conditions. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11864−11868.

(14) Holman, M. W.; Liu, R. C.; Adams, D. M. Single-Molecule Spectroscopy of Interfacial Electron Transfer. *J. Am. Chem. Soc.* **2003**, *125*, 12649−12654.

(15) Terayama, Y.; Kikuchi, M.; Kobayashi, M.; Takahara, A. Well-Defined Poly(sulfobetaine) Brushes Prepared by Surface-Initiated

ATRP Using a Fluoroalcohol and Ionic Liquids as the Solvents. *Macromolecules* **2011**, *44*, 104−111.

(16) Ishikawa, T.; Kobayashi, M.; Takahara, A. Macroscopic Frictional Properties of Poly(1-(2-methacryloyloxy)ethyl-3-butyl Imidazolium Bis(trifluoromethanesulfonyl)-imide) Brush Surfaces in an Ionic Liquid. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1120−1128.

(17) Kobayashi, M.; Terada, M.; Terayama, Y.; Kikuchi, M.; Takahara, A. Direct Synthesis of Well-Defined Poly[{2-(methacryloyloxy)ethyl}trimethylammonium chloride] Brush via Surface-Initiated Atom Transfer Radical Polymerization in Fluoroalcohol. *Macromolecules* **2010**, *43*, 8409−8415.

(18) Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. Controlled Synthesis of Polymer Brushes by "Living" Free Radical Polymerization Techniques. *Macromolecules* **1999**, *32*, 1424−1431.

(19) Wang, J.; Opedal, N. T.; Lu, Q.; Xu, Z.; Zeng, H.; Sjöblom, J. Probing Molecular Interactions of an Asphaltene Model Compound in Organic Solvents Using a Surface Forces Apparatus (SFA). *Energy Fuels* **2012**, *26*, 2591−2599.

(20) Wang, J.; Lu, Q.; Harbottle, D.; Sjöblom, J.; Xu, Z.; Zeng, H. Molecular Interactions of a Polyaromatic Surfactant C5Pe in Aqueous Solutions Studied by a Surface Forces Apparatus. *J. Phys. Chem. B* **2012**, *116*, 11187−11196.

(21) Fowkes, F. M. Additivity of Intermolecular Forces at Interfaces. I. Determination of the Contribution to Surface and Interfacial Tensions of Dispersion Forces in Various Liquids. *J. Phys. Chem.* **1963**, *67*, 2538−2541.

(22) Nordgård, E. L.; Sørland, G.; Sjöblom, J. Behavior of Asphaltene Model Compounds at W/O Interfaces. *Langmuir* **2010**, *26*, 2352−2360.

(23) Michailidou, V. N.; Loppinet, B.; Vo, C. D.; Rühe, J.; Tauer, K.; Fytas, G. Observation of Slow Down of Polystyrene Nanogels Diffusivities in Contact with Swollen Polystyrene Brushes. *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2008**, *26*, 35−41.