ATR-IR Investigation of Solvent Interactions with Surface-Bound Polymers

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ABSTRACT: Solvent interactions with bulk and surface-bound polymer brushes are crucial for functionalities such as controlled friction and thermoresponsive adhesion. To study such interactions, the temperature-induced solvent-quality changes and the effect of surface tethering on the mechanical and tribological properties of poly(dodecyl methacrylate) (P12MA) brushes have been investigated by means of attenuated total reflection infrared spectroscopy (ATR-IR), as well as atomic force microscopy (AFM) and lateral force microscopy (LFM). These results have been compared with temperature-dependent UV–visible spectrophotometry (UV–vis) data for the corresponding bulk polymer solutions. The ATR-IR results clearly show that increasing temperature enhances ethanol uptake in P12MA, which results in film swelling. This is accompanied by a marked increase in both adhesion and friction. We have also shown that a combination of solvents, such as toluene and ethanol, can lead to a temperature-dependent solvent partitioning within the polymer brush. To our knowledge this is the first time preferential solvent uptake in a grafted-from brush has been monitored via in situ ATR-IR. Moreover, we have observed remarkably different behavior for polymer chains in solution compared to the behavior of similar chains bound to a surface. The presented findings on the temperature-dependent solvent interactions of surface-grafted P12MA reveal previously unknown solvation phenomena and open up a range of possible applications in the area of stimuli-responsive materials.

INTRODUCTION

Poly(n-alkyl methacrylates) (PnMA) constitute a versatile class of polymers that are produced on a very large scale.1–3 Upon varying the number of carbon units in the alkyl side groups (n), physical properties such as the glass-transition temperature (T_g) can be tailored to range from ~65 °C (P12MA) up to 133 °C (PMMA).4–7 Grafted from a surface and in the presence of a good, viscous solvent, P12MA (containing a 12-carbon side group) swells to a brush conformation that enables significant reduction of friction and wear in the boundary-lubrication regime.5,9 Traditionally, techniques that have been applied to study the swelling and collapse of polymer brushes include the surface forces apparatus (SFA),10 atomic force microscopy (AFM),11 liquid-cell ellipsometry,12 quartz-crystal microbalance (QCM),13 and neutron reflectometry.14 Although all these techniques provide valuable information about the combined behavior of polymer and solvent, they fail to distinguish between the brush and solvent contributions to the resulting physicochemical properties. To better understand the lubrication properties of P12MA, Espinosa et al.15 and Bielecki et al.16 studied P12MA brushes in various solvents using SFA and AFM, respectively. Their results indicate that solvent-quality-dependent swelling and consequent solvent confinement within the brush structure plays a critical role in the tribological and mechanical properties, although the exact solvent-brush interaction is not yet fully understood.

We have measured the spectroscopic characteristics of the polymer brush and the solvent independently, via in situ liquid-cell ATR-IR. Although, in the past, ATR-IR has been used to study the uptake of water and butanol in silicate-1 films,17 interactions of immobilized human serum18 or proteins,19 and the thermoresponsiveness of poly-N-isopropylacrylamide (PNIPAAm) in water20–22 to our knowledge, it has never been applied to study solvent–mixture interactions with grafted-from polymer brushes. By monitoring the spectroscopic features of the brush and the solvent individually, we can detect solvent-partitioning and preferential solvent uptake upon changing temperature. UV–vis, AFM, and lateral force microscopy (LFM) measurements complement the study to provide further insights into the bulk and surface-property changes. Our findings reveal a temperature-induced swelling of P12MA in ethanol, which is a poor solvent at room temperature. Additionally, in situ probing of the surface showed changes in both the adhesive and tribological behavior of the brush. We describe an approach to studying brush-solvent interactions and the study sheds new light on the temperature-dependent properties of P12MA.

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**EXPERIMENTAL SECTION**

**Materials and Sample Preparation. Reagents, Solvents, and Lubricants.** Dimethylchlorosilane (Sigma-Aldrich, Germany, 98%), 10-undecen-1-ol (Sigma-Aldrich, 98%), 2-bromo-2-methylpropionyl bromide (Sigma-Aldrich, 98%), and chloroplatinic acid hexahydrate (ABCR, Germany, 99.9%) were used as received. Lauryl methacrylate (LMA) (Acros Organics, 96%) was purified from hydroquinone monomethyl ether (MEHQ) inhibitor by passing it through a basic alumina column. 4,4′-dinitro-2,2′-bipyridine (dNbpy) and copper(II) bromide (CuBr, Sigma-Aldrich, 99%) were used as received. Copper(I) bromide (CuBr, Sigma-Aldrich) was purified by stirring in glacial acetic acid overnight, followed by filtration and washing with methanol and diethyl ether. Poly(lauryl methacrylate) (PLMA/P12MA) (Mn = 500,000, Mw = 290,000, Sigma-Aldrich) in a 25 wt % solution in toluene was used as received. Toluene (Fluka Analytics, Germany, 99.7%), ethanol (Fluka Analytics, 99.8%), and hexadecane (Sigma-Aldrich, 99%) were used as received from the manufacturers. Ultrapure water was used as dispensed from a TKA GenPure (TKA GmbH, Germany).

**Polymer Solutions.** For UV–vis measurements, P12MA in toluene was used as received from Sigma-Aldrich. Toluene–ethanol mixtures, containing 10 wt % of P12MA, with 34, 37, 38, and 41 wt % of ethanol were prepared by gravimetry. The final solutions were analyzed by nuclear magnetic resonance (NMR) spectroscopy to determine the precise concentrations.

**Surface-Bound Polymer-Brush Samples.** For ATR-IR measurements, two 6 mm thick, light-guiding silicon crystals, of dimensions 72 mm × 10 mm at the top sensing surface and a 45° angle of incidence toward the bottom surface, were piranha cleaned, rinsed with ultrapure Milli-Q water and dried under a nitrogen stream prior to use. One crystal was maintained in a pristine state and used to collect background measurements. A P12MA polymer brush was grafted onto the second ATR-IR silicon crystal using surface-initiated atom transfer radical polymerization (SI-ATRP). In brief, the sensing surface of the piranha-treated crystal (Harrick Plasma Cleaner/Sterilizer, Ossining, NY) was functionalized via a previously described surface-deposition protocol, using a solution of 11-(2-bromo-2-methylpropionyl)-dimethylchlorosilane (BPCS) initiator.

Subsequently, SI-ATRP was carried out under a nitrogen atmosphere. In detail, the dodecyl methacrylate monomer (12MA) was mixed with anisole in the ratio of 9:1 v/v. Then the ligand (dNbpy) was added to the mixture and dissolved. The solution was degassed by three freeze–thaw cycles and subsequently transferred though a cannula into a second flask containing copper(I) bromide and copper(II) bromide (reactant ratio monomer/dNbpy/CuBr/CuBr₂ = 150:1:5:1:0.01). The mixture was subsequently heated to 90 °C and maintained under stirring until a homogeneous dark-brown solution was formed. Finally, the solution was transferred via a cannula to a flask containing the BPCS-functionalized crystal and SI-ATRP was carried out for the necessary time at 110 °C. Exposing the flask to air terminated the polymerization.

Before characterization, the synthesized film was washed extensively with toluene and chloroform, and finally dried under a stream of nitrogen. A dry thickness of the P12MA brush of 68 nm was measured by means of spectroscopic ellipsometry (M200-F J.A. Woollam Co. Inc., Lincoln, NE). An approximate swollen thickness can be estimated from the swelling ratios reported for P12MA, prepared using the same synthesis method. The estimated swelling ratios are 15 and 1 for toluene and ethanol, respectively. Thus, swollen brush thicknesses of about 1000 nm in toluene and 68 nm in ethanol were assumed. Uniformity of P12MA films produced with this synthesis method was confirmed in earlier studies by Bielecki et al.

For AFM and LFM measurements, P12MA brushes of 80 nm dry thickness were grafted from initiator-functionalized silicon oxide substrates (P/B (100), Si-Mat Silicon Wafers, Germany) following the same protocol reported above for the ATR-IR sample functionalization.

**Methods and Instrumentation. Temperature-Controlled UV–Vis.** The turbidity of four different toluene-ethanol solutions of P12MA was measured at a wavelength of 410 nm using a temperature-controlled UV–visible spectrophotometer (V670 UV–visible spectrophotometer, JASCO Inc.) to study the temperature-dependent solubility in varying solvent environments. Using a Peltier unit, the samples were exposed to increasing and decreasing temperatures from 0 to 35 °C with a heating and cooling rate of 0.5 °C/min. Measurements were made every 0.5 °C and a resting period of 30 s was held at each measurement point to allow equilibration of the solution.

**In Situ Attenuated Total Reflection.** Infrared spectra were collected using an attenuated total reflection (ATR) setup (Portman Instruments AG, Biel-Benken, Switzerland) with a Nicolet 5700 Fourier transform infrared spectrometer (Thermo Electron Corporation, Madison, WI). After inserting the light-guiding crystal in a Graseby-Specac advanced overhead “specallow” ATR system (P/N 1401 series), see the setup schematics in Figure 1 below, a peristaltic pump was used to feed fresh solvent at a constant rate. The temperature of the setup was controlled through a heatable top-plate for ATR units and measured via a PT-100 resistance element (FCS-23A, Shinko Technos CO., LTD Japan). Additionally, controlling the thermostat temperature, a thermometer (E910-650, Amarell GmbH, Germany) with a Pt 100 class A probe located at the top of the thermostat measured the temperature close to the sample.

It is important to note that the penetration depth of the infrared signal decays exponentially away from the surface of the silicon crystal, making ATR-IR a very surface-sensitive technique. The penetration depth, d, is described by eq 1, where n₁ and n₂ are the refractive indices of crystal and solvent, respectively, λ is the wavelength, and θ is the angle between the walls and top surface of the prism.

\[ d = \frac{\lambda}{2 \pi n_1 \sin^2 \left( \frac{\theta}{2} \right) - \left( \frac{n_2}{n_1} \right)^2} \]  

For a Si-crystal (n₁ = 3.4), with θ = 45°, and for a solvent n₂ = 1.4, the penetration depth d is about 200–550 nm over a transmission range between 4000 and 1500 cm⁻¹.

Knowing the characteristic values of d, the dry thickness of the P12MA coating was adjusted during synthesis to fall largely within the probed range in all solvent environments and for all temperatures.

To account for the temperature-dependent absorption of the light-guiding silicon crystal, background measurements were conducted using the pristine crystal for each solvent at the relevant temperatures of 25, 30, 45, and 60 °C. The measurements carried out in the presence of the coatings were compared to those from the bare configuration with corresponding solvent type and temperature. To eliminate any time-dependent behavior, reversibility was evaluated by cycling the temperature applied from 25 to 60 °C and back to 25 °C with appropriate resting periods to allow equilibration of the sample. The experiment was repeated by an additional heating and cooling cycle, in order to guarantee reproducibility of any temperature-dependent changes in the system studied.

Hydrocarbon stretches in the IR spectrum are present for all solvents used in this study as well as for the polymer brush investigated. However, the carbonyl groups in the polymer brush allowed us to identify the brush from the C=O stretches in the spectra. In the case of ethanol, the solvent exhibits a characteristic
hydroxyl stretch that uniquely identifies it. Ethanol has a boiling point of 78 °C and can therefore be used for tests up to 60 °C to assess solvent-dependent changes in the spectra upon changing temperature. Atomic and Lateral Force Microscopy. To study the temperature effects on the adhesive and lubricious properties of P12MA, atomic force microscopy (AFM) was used for indentation experiments and lateral force microscopy (LFM) for tribological characterization, using a MFP-3D atomic force microscope (Asylum Research, Santa Barbara, CA). The adhesion and tribological properties of both bare and brush-coated silicon surfaces were performed using a micrometer-scale colloidal silica probe and a dedicated temperature-controlled liquid-cell setup at temperatures ranging from 25 to 60 °C, i.e., well above the polymer’s bulk Tg of −65 °C.

For all measurements, AFM colloidal probes were produced by gluing silica spheres (Kromasil, Brewster, NY) of 9 μm diameter mounted on a reference cantilever of the same batch against a vertical wall. The deflection upon contact with the wall provides the sensitivity value of the probe-cantilever combination, which is necessary to convert the voltage recorded during lateral motion into a lateral force. The adhesion between the colloidal probes and the samples was measured by recording the pull-off force with a consequent retraction of the probe at a constant rate of 1 μm/s, following indentation at forces up to 17 nN. Between 24 and 59 force–distance measurements were performed for each sample.

Upon moving the probe 20 μm laterally across the surface, the torsion of the cantilever indicates the friction experienced during the motion. The frictional force corresponding to a lateral sliding velocity of 10 μm/s was calculated according to eq 2, where Ff(trace) is the lateral force in one direction and Ff(retrace) in the opposite sliding direction.

\[ F_f = \frac{F_f(\text{trace}) - F_f(\text{retrace})}{2} \]  

(2)

By varying the normal load exerted by the probe, its effect on the friction force between the probe and the surface can be evaluated. This procedure was carried out for bare as well as P12MA-coated silicon wafers, and was repeated for more than eight friction loops for every measurement point, for three different positions on each sample per temperature.

## RESULTS AND DISCUSSION

P12MA is readily soluble in nonpolar solvents, such as toluene, at room temperature. Due to a polarity mismatch, ethanol is considered a poor solvent and does not solubilize the polymer at ambient temperatures. We studied the solubility of P12MA in binary solvent mixtures of toluene and ethanol as a function of temperature, in order to identify the conditions under which it can be solubilized in the presence of ethanol. We also investigated the impact that surface grafting has on solubility by means of ATR-IR. This novel approach was crucial, because, although optical (ellipsometry, neutron reflectometry, TlnAS) and mechanical (AFM, QCM) techniques provide information on the combined solvent-brush properties, ATR-IR can provide invaluable information on chemical interactions and can separate the contributions of each individual component.11–13

Polymer-Brush Solubility in Solution. Visual inspection of P12MA (10 wt %) in an ethanol–toluene mixture (40:60) showed a transition from a translucent suspension of polymer aggregates to a clear solution upon heating from room temperature to temperatures above 35 °C, indicating a change in polymer–solvent interactions. These qualitative observations are quantitatively confirmed by the UV–vis spectrophotometry results shown in Figure 2. The data shows the suspension transmittance at 410 nm as a function of temperature for P12MA in toluene with ethanol contents ranging from 34 wt % to 41 wt %. For all suspensions there is a transition temperature at which the suspension becomes a clear solution (i.e., the cloud-point), indicating full solubilization of the polymer. It can be seen that increasing ethanol concentration increases the temperature required to achieve solvation of P12MA in the solvent mixture, both upon heating and cooling.

Post-experimental NMR analysis provided the exact composition of the solvent mixtures, enabling us to establish an accurate correlation between the transition temperature (50% transmittance) and the solvent composition. Figure 3 shows a linear relation between the transition temperature and the ethanol concentration in the range of solvent mixtures tested, upon both heating and cooling. A similar linear trend for a narrow concentration range and a minor hysteresis between heating and cooling curves is expected, as previously reported for PMMA solutions.27

Solvent Uptake of Surface-Attached Polymer Brushes. In order to investigate in more detail the microscopic origin of the transition for P12MA in the mixtures and to examine whether surface tethering within a brush assembly modifies the
solvent- and temperature-dependent solubility behavior of the polymer, we carried out ATR-IR investigations on P12MA brushes grafted on silicon wafers, as described in the Methods section. We focused on a mixture of 40 wt % ethanol in toluene, and on the pure ethanol and pure toluene cases as controls. We recorded IR spectra at 25, 30, 45, and 60 °C, cycling the temperature range. To correct for the background, we first collected spectra of the bare silicon crystal in each of the solvents or solvent mixtures and used these to correct spectra of the P12MA-coated crystal in the corresponding solvents. The absorbance (Abs) was determined from sample and background intensities according to eq 3 below.

\[
\text{Abs}_i = \log \left( \frac{\text{intensity}_{\text{sample}}(i)}{\text{intensity}_{\text{background}}(i)} \right)
\]

where \(i\) corresponds to each of the selected temperatures. The following relevant IR-spectroscopic features were tracked in the collected spectra: the hydrocarbon CH\(_2\) and CH\(_3\) stretches between 2950 and 2850 cm\(^{-1}\), a distinct carbonyl stretch at 1730 cm\(^{-1}\), and a broad hydroxyl stretch at 3350 cm\(^{-1}\), which allowed interactions involving ethanol to be followed unambiguously.

The hydroxyl stretch at 3350 cm\(^{-1}\), which appears negative due to the pure-ethanol background, recorded while flowing a solvent mixture of 40 wt % ethanol in toluene over the P12MA-coated ATR-IR crystal (Figure 4), reveals a significant absorbance increase upon increasing temperature. A decrease of the peak intensity upon cooling back to 25 °C demonstrated that the effect was completely reversible. Upon repeated heating and cooling cycles, the intensity changes were reproducible and the peak positions overlapped upon reaching the same temperature during both heating and cooling procedures. This increased OH-absorbance results from an increased ethanol concentration at the sensing surface (i.e., within the range of the evanescent field). The peak-intensity change suggests that ethanol penetrates and swells the P12MA layer to a greater extent with increasing temperature, and upon cooling retreats from the collapsing brush structure. Similar swelling phenomena have also been observed when studying thickness and mass changes in temperature-responsive PNIPAM brushes by means of ellipsometry, but ATR-IR yields additional information on composition close to the surface.\(^{28}\)

To confirm the swelling of the brush, the carbonyl peak at 1730 cm\(^{-1}\), a signal that is solely due to the presence of P12MA at the sensing surface, was measured. Ethanol penetration also leads to an intensity reduction in signals from the swelling brush structure, as can be seen in a reproducible reduction in carbonyl peak intensity (Figure 5).

Changes in peak intensity from brush (C=O) and the ethanol-containing solvent (OH) can be used individually to investigate solvent partitioning and preferential solvation effects—normally a nontrivial task for surface-bound polymers.\(^{29–32}\) The schematic in Figure 6a shows P12MA in 100% ethanol, a poor solvent at room temperature, in a collapsed state.\(^{33}\) Figure 6b shows how the addition of toluene, a good solvent, can improve the solvent environment and allow the brush to swell, as measured for a P12MA in solution using UV–vis. Assuming that toluene preferentially solvates the brush in a solvent mixture, a semistretched brush configuration is expected. Such a semistretched brush structure is expected for ethanol, a poor solvent at room temperature, in a collapsed state.\(^{33}\) Figure 6c shows how the addition of toluene, a good solvent, can improve the solvent environment and allow the brush to swell, as measured for a P12MA in solution using UV–vis. Assuming that toluene preferentially solvates the brush in a solvent mixture, a semistretched brush configuration is expected. Such a semistretched brush structure is expected for
binary solvent-mixtures of varying quality from theoretical thermodynamic calculations.\(^{34}\) Upon heating the pure ethanol environment, depicted in Figure 6c, changes in the hydroxyl peak clearly indicate ingress of ethanol into the brush structure in a pure ethanol environment. As mentioned earlier, the carbonyl peak intensity gradually decreases, indicative of swelling and reduction of brush presence at the sensing surface. Studies on PNIPAM using neutron reflectometry and liquid-cell ellipsometry have shown that temperature-induced solvent-quality-dependent swelling initially occurs in the outermost layers, swelling the collapsed layer from the outside inward.\(^{12,35}\)

However, compared to the pure ethanol environment, when heating the brush in an ethanol–toluene mixture the changes in peak intensity for the OH signal are more pronounced than the changes in the C=O signal. Such divergent behavior is an indication of solvent partitioning and preferential solvent uptake, as has been reported for brushes in solvent mixtures using small-angle neutron reflectometry.\(^{32}\) The carbonyl peak intensity change upon heating is smaller in a solvent mixture, as the already partially stretched brush only undergoes minor swelling. The black dots in Figure 6d depict the increased presence of ethanol upon heating for the mixed solvent environment, as indicated by the stronger hydroxyl peak intensity change with increasing temperature ethanol is also able to access the already swollen structure of the brush, thereby reaching closer to the sensing surface.

To provide a more quantitative illustration of the solvation effects, we integrated both the hydroxyl and carbonyl peaks, from 3050 to 3554 cm\(^{-1}\) and from 1714 to 1747 cm\(^{-1}\), respectively, at each temperature in each solvent mixture used, as shown in Figure 7. For the hydroxyl peak, the integrated intensity measured at 25 °C, representing a maximum intensity obtained from measuring the area below the zero line, shown as a histogram of the probability distribution in Figure 9. The increase in adhesion with increasing temperature, which appears to follow a linear trend. Increasing mobility and flexibility of the polymer can in fact lead to the probe experiencing a larger contact area, i.e., an increase in the number of chain-probe contacts. With increasing temperature and improved solvent quality, the polymer chains are more flexible and thus can remain more easily attached to the retracting probe.

From UV–vis measurements of free polymer chains, we assume that in the case of a pure ethanol environment, the brush is in a collapsed state at 25 °C, while a solvent mixture of ethanol and toluene (40 and 60 wt %, respectively) leads to a partially stretched brush configuration at the same temperature due to the toluene being a good solvent.\(^{13,31}\) Therefore, the carbonyl peak intensity value at 25 °C is assumed to be 1, representing a maximum intensity obtained from measuring the brush layer being either collapsed in ethanol or partially stretched in the presence of toluene. Consequently, eq 5 describes the normalized peak intensity changes (NIC\(_{C=O}\)) for the carbonyl peak.

\[
\text{NIC}_{C=O}(i) = \frac{\text{Abs}_i}{\text{Abs}_{25^\circ C}}
\]

**Adhesive and Frictional Properties of Swelling Brushes.** AFM and LFM experiments were carried out in order to study the effects of temperature-induced solvent interactions on adhesion and friction properties of a P12MA coating. The interaction between a spherical probe and the surface-bound polymer in pure ethanol was studied upon changes in temperature, via AFM nanoindentation. Upon retraction of the probe, force–indentation curves, shown in Figure 8, show increased adhesion with increasing temperature.

Not only does the maximum pull-off force increase with increasing temperature (Figure 8), but also the distance to full detachment increases from about 120 nm to nearly 400 nm. Experiments in ethanol-toluene solvent mixtures could not be carried out due to incompatibility of the sample cell with toluene.

The adhesion energy has been quantified by integration over the area below the zero line, shown as a histogram of the probability distribution in Figure 9. The increase in adhesion energy can be explained through an increased contact area, a mechanism that has been previously observed for comparable polymer-brush structures.\(^{65,67}\) The inset displays an increase in the mean adhesion with increasing temperature, which appears to follow a linear trend. Increasing mobility and flexibility of the polymer can in fact lead to the probe experiencing a larger contact area, i.e., an increase in the number of chain-probe contacts. With increasing temperature and improved solvent quality, the polymer chains are more flexible and thus can remain more easily attached to the retracting probe.
normal forces an intersection is expected at about 110 nN.

P12MA in ethanol at room temperature. For increasing temperatures, $\mu$ decreases, and upon extrapolation to higher temperatures led to ethanol uptake and swelling of P12MA. The clear transition temperature measured via UV-vis for P12MA in solution could not be identified for surface-bound brushes. However, preferential solvation and solvent partitioning was identified via the changes in normalized peak intensity. Mechanical characterization of the brushes via AFM and LFM showed increased adhesion but also reduced load-dependent friction, deduced from the two-term equation, upon temperature-induced swelling of the brush.

Our current results show that ATR-IR studies can provide new insights into the interaction of surface-tethered polymers with their environment to help develop tailored polymer-solvent combinations for application as stimuli-responsive materials for controlled-friction behavior and switchable adhesion.

## SUMMARY AND CONCLUSIONS

We have studied the temperature-dependent properties of P12MA in ethanol, toluene, and their mixtures, with an emphasis on the solvent interactions of surface-bound brushes. ATR-IR was employed to investigate the effects of partitioning solvents and preferential solvation within the brush upon swelling and deswelling caused by temperature changes. While standard bulk UV-vis showed that solvent quality in ethanol-toluene mixtures could be improved upon increasing temperature, ATR-IR in liquid allowed measuring specific solvent-brush interactions in situ, enabling a more detailed analysis in the case of P12MA brushes. Specifically, improved solvent quality at higher temperatures led to ethanol uptake and swelling of P12MA. The clear transition temperature measured via UV-vis for P12MA in solution could not be identified for surface-bound brushes. However, preferential solvation and solvent partitioning was identified via the changes in normalized peak intensity. Mechanical characterization of the brushes via AFM and LFM showed increased adhesion but also reduced load-dependent friction, deduced from the two-term equation, upon temperature-induced swelling of the brush.

Our current results show that ATR-IR studies can provide new insights into the interaction of surface-tethered polymers with their environment to help develop tailored polymer-solvent combinations for application as stimuli-responsive materials for controlled-friction behavior and switchable adhesion.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

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ABBREVIATIONS

P12MA, poly(dodecyl methacrylate); UV−vis, UV−visible spectrophotometry; ATR-IR, attenuated total reflection infrared spectroscopy; AFM, atomic force microscopy; LFM, lateral force microscopy

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