Chain Extension of Stimuli-Responsive Polymer Brushes: A General Strategy to Overcome the Drawbacks of the "Grafting-To" Approach

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Stimuli-responsive polymer brushes are smart materials for the design of bio-interactive and responsive interfaces. The "grafting-to" approach is a convenient preparation procedure that allows the modification of surfaces with preformed and most notably well-defined functionalized macromolecules. However, the shortcoming of this approach is an intrinsic limitation of the grafting density, which in turn affects the stimuli-responsive properties of the brush system. Here, a general strategy to overcome this limitation and to simultaneously improve the switching behavior of a temperature-responsive poly(*N*-isopropylacrylamide) (PNiPAAm) brush is reported. A technically simple processing step is used in combination with the thermal azide–alkyne cycloaddition to perform the chain extension of alkyne-functionalized PNiPAAm brushes with azide-functionalized PNiPAAm molecules.

1. Introduction

Stimuli-responsive polymers are promising materials for the development of smart surfaces which reversibly change their physicochemical properties in response to an external signal. The structural diversity of those smart materials have gained increased interest over the last decades and offers a variety of opportunities for the fabrication of bio-interactive and responsive interfaces.[1–7] Polymer brushes are a specific example of stimuli-responsive thin films and involve macromolecules that are grafted chemically to a surface at sufficiently high grafting densities so that the polymer chains experience excluded volume repulsions and adopt a stretched conformation.[8–10] Upon external stimuli (changes in solvent quality, temperature, pH, ionic strength, mechanical stress, and/or electromagnetic field), the macromolecular chains of the brush may respond via conformational transformations and/or domain formation, resulting in the switching of the spatial distribution of functional groups within the ultrathin layer.[2,3] Especially water soluble temperature-responsive polymers, such as poly(*N*-isopropylacrylamide) (PNiPAAm) may be considered particularly intriguing as a platform for biotechnological engineering in terms of controlled protein adsorption, cell adhesion or cell harvesting.[11–16] They normally exhibit a lower critical solution temperature (LCST) and undergo a reversible phase transition from the hydrated to the hydrophobic state owing to changes in the solvent quality and temperature.[17–19] The temperature of this transition may depend on varying degrees on the nature, molar mass and architecture of the polymer, but also on its concentration.[20–23] The LCST of PNiPAAm (31–32 °C)[24–26] is not far from physiological temperatures and can be considerably increased by copolymerization.[21] In general covalently attached polymer chains can be prepared by either the "grafting-to"[27,28] or "grafting-from"[29,30] method. The first approach involves the chemical reaction of preformed, functionalized polymers on solid substrates having complementary functional groups, whereas the latter uses an in situ polymerization of the monomer of interest from an initiator grafted on a surface.[10] The primary advantage of the grafting-to method is a technically simple processing step consuming low quantities of an accurately characterized preformed polymer. However, the shortcoming of this approach is an intrinsic limitation of the grafting density, which generally depends on the molecular weight and diffusion kinetics of the attached macromolecule. With the grafting-from method rather high grafting densities can be obtained, but the effect of side reactions may be more important as compared to the bulk polymerization because of the high local concentration of polymer chains in the grafted layers. Hence, the grafting-from polymerization may lead to chain termination reactions and a broader molecular mass distribution.[10] The switching properties of a polymer brush are substantially determined by the

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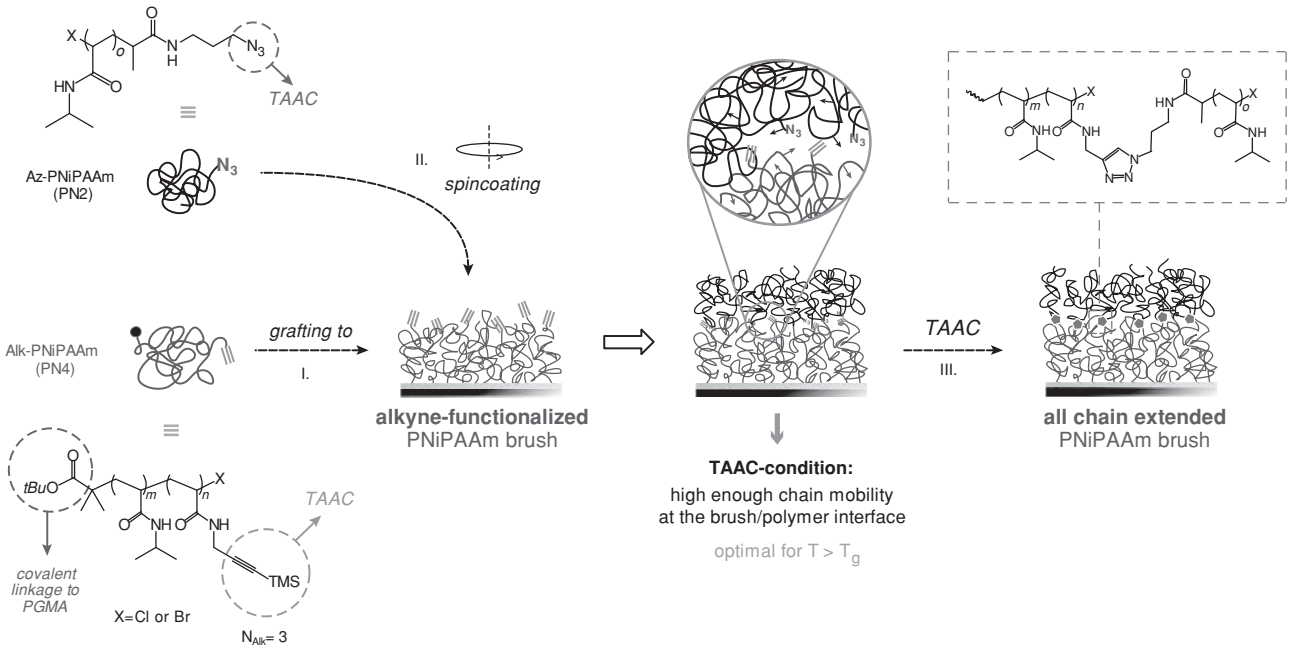
composition, grafting density, molecular weight and polydispersity of the attached macromolecules.[6] Because the grafting-to approach can address brush properties as e.g. polydispersity more precisely, it is desirable to extend its applicability. We recently presented a novel temperature-responsive polymer brush system with a terminal alkyne-functionality available for post-modification reactions via orthogonal "click" chemistry.[25] It was shown that every polymer chain, which was grafted to the substrate could be functionalized afterwards using an azide-modified low molecular weight organic compound. Hence we were motivated to expand and improve the properties of this new polymer brush system by introducing an azide-modified high molecular weight compound, that is a macromolecule, to the terminal end of the brush. This chain extension concept is a very smart way to prepare polymer brushes with high molecular weight, low polydispersity and moderate grafting densities. In addition it can increase simultaneously the switching sensitivity of temperature-responsive polymer brushes so that, e.g., modulation of interfacial (biological) processes can be triggered more effective. The versatile character of the presented concept offers high potential for the modification of any 2D or 3D (nanostructured) materials and thus can lead to stimuli-responsive systems with improved functional properties.

In this work the chain extension of alkyne-functionalized PNiPAAm brushes with azide-functionalized PNiPAAm molecules is presented for the first time. At the beginning we describe the thermal azide–alkyne cycloaddition (TAAC) to attach the azide-functionalized PNiPAAm covalently to the terminal end of functionalized polymer brushes with varying amounts of alkyne groups at the surface. The classical TAAC reaction, also known as Huisgen 1,3-dipolar cycloaddition of azides and alkynes,[31] was employed because it offers the ability to conduct the reaction without the use of additional reagents, solvents, or catalysts. Both van Hest and co-workers[32] as well as Hawker and co-workers[33] utilized these features to cross-link side-chain functional azide polymers covalently using small difunctional alkyne molecules and polymers containing both azides and alkynes randomly incorporated along the backbone, respectively. After a detailed analysis of the chain extension via TAAC we show how the temperature-responsive switching behavior of the alkyne-functionalized PNiPAAm brush can be improved after applying the chain extension.

2. Results and Discussion

2.1. Chain Extension of Polymer Brushes

Scheme 1 outlines the principle processing steps for the chain extension of alkyne-functionalized PNiPAAm (Alk-PNiPAAm) brushes[25] or polymer brushes generally. The basic component of this modular system is a bi-functionalized macromolecule which offers one chain end suitable for the grafting-to approach while the other free end remains active for post-modification reactions via click chemistry[34] or thermal azide–alkyne cycloaddition. In our previous studies we found out that PNiPAAm which was end-functionalized with a tert-butyl protected carboxylic group can be used for grafting to poly(glycidyl methacrylate) (PGMA) modified surfaces leading to well-defined polymer brush films with moderate grafting densities.[25] In addition it could be shown that during the grafting-to process of Alk-PNiPAAm (Scheme 1) ca. 60% of the trimethylsilyl (TMS) protecting groups were cleaved.[25] This effect led to free



Scheme 1. Preparation (I,II) of alkyne-functionalized PNiPAAm brushes and subsequent chain extension (III) with azide-functionalized PNiPAAm via thermal alkyne-azide cycloaddition (TAAC). The terminal alkyne groups of the polymer brush are drawn directly at the surface for clarity but are not necessarily located there and can have a depth distribution.

Table 1. Characteristics of the PNiPAAm polymers used in this study: functional groups at/near the chain ends (α,ω), number of alkyne groups per chain (N_{Alk}), number average molecular weight (M_N), polydispersity index (PDI) and glass transition temperature (T_g).

Polymer	α	ω	N_{Alk}[a)]	M_N[a)] [g/mol]	M_N[b)] [g/mol]	PDI[b)]	T_g [°C]
PN*	COOH	–	–	94 000	–	1.30	–
PN1	COOH	–	–	48 900	97 700	1.28	140
PN2	N_3	–	–	35 000	68 600	1.26	140
PN3	COO*tBu*	–	–	42 300	82 900	1.20	139
PN4	COO*tBu*	C≡C-TMS	3	48 300	107 000	1.32	143

[a)]Determined by ^{1}H-NMR; [b)]Determined by GPC; *Obtained from a commercial source.

reactive alkyne groups in the brush which are able to react with any azide-functionalized component and consequently also with azide-terminated PNiPAAm (Az-PNiPAAm, PN2) via TAAC, which is presented in this paper. In principle also bi-functionalized macromolecules with two terminal functionalities, such as an azide group and a carboxyl group, can be used within this strategy. As already mentioned the TAAC offers the ability to conduct the reaction without the use of additional reagents, solvents, or catalysts. To reach high conversion the reaction is traditionally run at elevated temperatures, typically above 70 °C.[34] For the chain extension of the Alk-PNiPAAm brushes with Az-PNiPAAm this circumstance is beneficial because high temperatures are required to realize high chain mobility at the interface between the polymer brush and the spin coated polymer film (TAAC-condition, Scheme 1). Only in this case the probability for alkyne and azide groups to collide (local diffusion process) and react is high enough and finally leads to the formation of the desired disubstituted 1,2,3-triazole. Although the TAAC can produce both regioisomers, that is 1,2- and 1,4-disubstituted triazoles,[34] we suggest due to steric reasons that the formation of the 1,4-disubstituted 1,2,3-triazole might be favored. The TAAC-condition is fulfilled for a temperature above the glass transition temperatures (T_g) of the involved polymers. Therefore, the TAAC was carried out at 150 °C, which was sufficiently above the T_g of the functionalized PNiPAAm (**Table 1**). Non-reacted Az-PNiPAAm could be easily removed from the brush surface by extraction in water. To have comparable start conditions in the TAAC-experiments only polymer brushes with grafting densities (σ) between 0.17–0.18 nm^{-2} were used (Supporting Information).

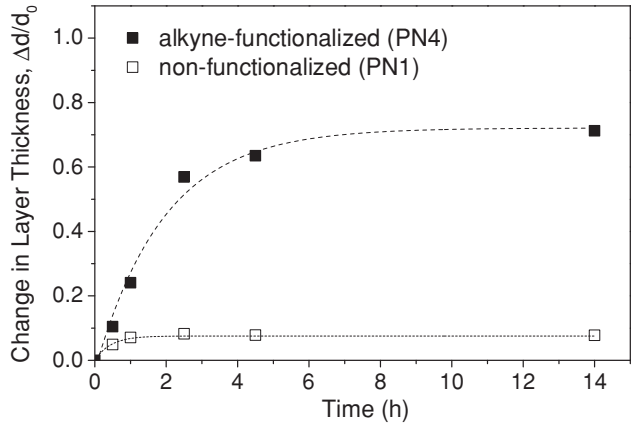


Figure 1. Relative change in layer thickness after chain extension of alkyne- and non-functionalized PNiPAAm brushes with Az-PNiPAAm (PN2) via TAAC as a function of time. The grafting densities for the PNiPAAm brushes are σ = 0.17–0.18 nm^{-2}. Lines are drawn to guide the eye.

The chain extension with Az-PNiPAAm (PN2) via TAAC was analyzed as a function of time for an alkyne-functionalized PNiPAAm brush (PN4) with 3 alkyne groups per polymer chain (N_{Alk}), whereas a non-functionalized PNiPAAm brush (PN1) with no alkyne groups served as a reference sample (**Figure 1**). The relative change in the dry film thickness ($\Delta d/d_0$) was chosen as criterion to compare the results of the TAAC, and showed a maximum change of 71% (Δd = 9.6 nm) for the Alk-PNiPAAm brush PN4, while the control sample PN1 reached a maximum of 7% (Δd = 0.8 nm) (**Table 2**). The saturation level is already reached after approximately 5 h of reaction time and varies only slightly afterwards. Interestingly we observed almost constant values for the control sample (PN1) after the TAAC (Figure 1) at any time. Therefore we checked a possible side reaction of the Az-PNiPAAm with the PGMA-anchoring layer in a further control experiment and could identify a grafting-to-like behavior, which we think to be the explanation for this observation (Supporting Information).

The surface roughness and morphology of the Alk-PNiPAAm brush was studied by AFM and revealed a homogeneous well-defined surface before and after the chain extension with Az-PNiPAAm without any phase separation or segregation effects (Supporting Information).

As the primary grafting density (σ_0) of the Alk-PNiPAAm brush does not change during the TAAC reaction, the grafting density of the attached Az-PNiPAAm (σ_{PN2}) can be calculated according to:

$$\sigma_{PN_2} = \frac{N_A \Delta d \rho_{PNiPAAm}}{M_{PN2}} \quad (1)$$

Table 2. Characteristics of alkyne- and non-functionalized PNiPAAm brushes before and after chain extension with Az-PNiPAAm (PN2) via TAAC reaction for 14 h: grafting density (σ_o) and layer thickness (d_0) of brush before TAAC; layer thickness (d_{TAAC}) and absolute change (Δd) of brush after TAAC, as well as grafting density of Az-PNiPAAm attached to brush ends (σ_{PN2}).

Brush	alkyne-functionalized	σ_0 [nm^{-2}]	d_0 [nm]	d_{TAAC} [nm]	Δd [nm]	σ_{PN2} [nm^{-2}]
PN4	+	0.18	13.4	23.0	9.6	0.18
PN1	–	0.17	12.8	13.6	0.8	–

using Avogadro's number (N_A), the absolute change in layer thickness (Δd), the bulk density of PNiPAAm ($\rho_{PNiPAAm}$) and the molecular weight of the attached Az-PNiPAAm (M_{PN2}). Thus one can estimate how many chains of the Alk-PNiPAAm brushes are maximally extended. The summarized results (Table 2) reveal that every chain ($\sigma_{PN2} = \sigma_0$) of the Alk-PNiPAAm brush having three alkyne groups per chain was extended. The attachment of a further Az-PNiPAAm macromolecule per chain should be in principle possible due to residual reactive alkyne groups ($N_{Alk} = 3$). However, this is prevented by an increasing diffusion barrier which is built up from afore attached and closely packed P2 chains (self-limiting effect).

For the Alk-PNiPAAm brush where every chain was extended, the effective molecular weight of the elongated polymer chain (M_{TAAC}) can be calculated with the effective total layer thickness (d_{TAAC}) according to:

$$M_{TAAC} = \frac{N_A d_{TAAC} \rho_{PNiPAAm}}{\sigma_0} \quad (2)$$

Using Equation 2 an effective molar mass of 84 000 g/mol was calculated which is in a very good agreement with the sum of the M_N-values of the involved polymers PN4 and PN2, that is 83 300 g/mol. In a further control experiment we grafted commercial COOH-terminated PNiPAAm (PN, Table 1) with a comparable molecular weight of 94 000 g/mol to a PGMA-modified silicon wafer and reached a maximum grafting density of only 0.09 nm^{-2} (Supporting Information). This findings demonstrate clearly, that the obstacle of limited grafting density of grafting-to brushes can be overcome by exploiting the presented general strategy of chain extension.

2.2. Chain Extension of Binary Brushes

The amount of available alkyne groups on the brush surface can also be altered by the number of alkyne-containing polymer chains within the brush layer. For this alternative option we prepared binary polymer brushes consisting of non-functionalized PNiPAAm PN3 (Table 1) with defined amounts (ϕ_{PN4}) of alkyne functionalized PNiPAAm PN4 (**Figure 2**A). Both polymers were mixed prior to spin coating whereas it is assumed that the molar ratio in solution was transferred to the resulting brush film on the PGMA-modified surface. After chain extension via TAAC and removal of unreacted Az-PNiPAAm, a linear increase in the final layer thickness of the brush film with increasing amounts of PN4 can be observed (Figure 2B). However for the pure non-functionalized PNiPAAm brush (ϕ_{PN4} = 0) a relative change in the layer thickness of 15% is observed, which we attribute to the grafting-to-like behavior of the

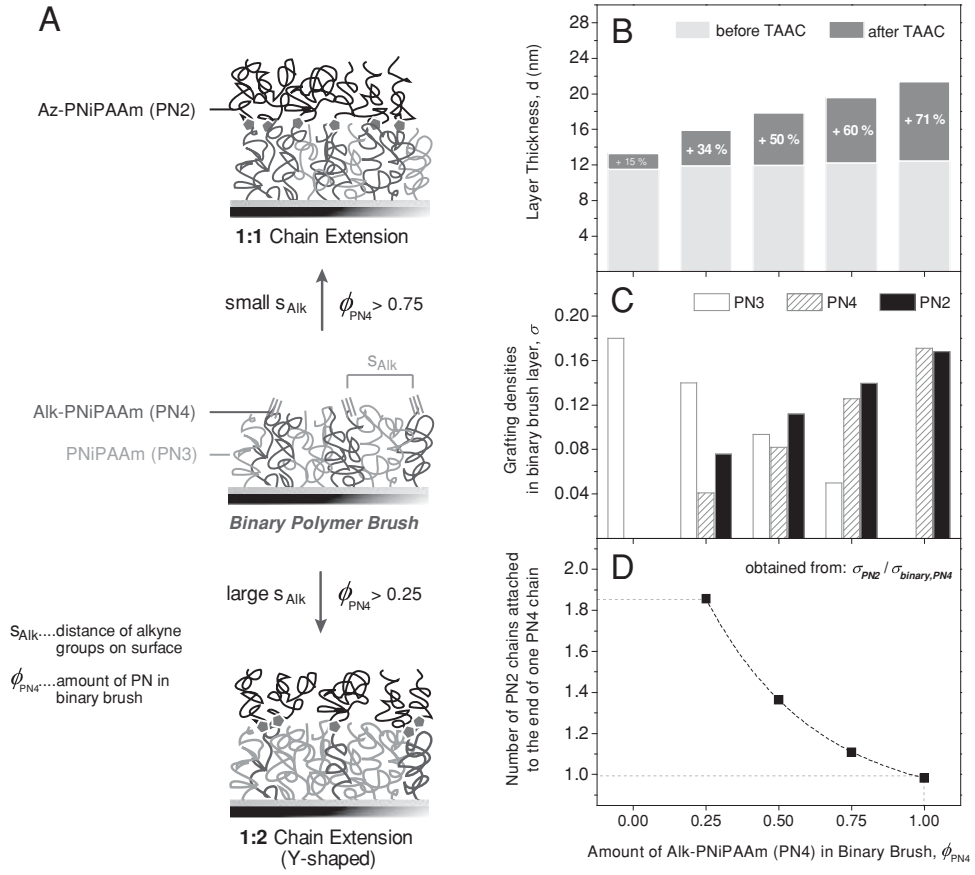


Figure 2. Chain extension of binary polymer brushes with Az-PNiPAAm (PN2) via TAAC reaction as a function of the amount of Alk-PNiPAAm (PN4) in the system. A) Schematic representation. B) Layer thickness before and after TAAC. C) Calculated grafting densities of polymers in brush layer. D) Number of PN2 chains attached to the end of one PN4 chain in the binary brush system.

Az-PNiPAAm (Supporting Information) as mentioned before in the text. To estimate how many chains of the alkyne-functionalized PNiPAAm chains of the binary brush were extended, we again calculated the grafting density of the attached Az-PNiPAAm (σ_{PN2}) according to Equation 1. Then the resulting values were compared to the grafting densities (σ_{binary}) of PN3 and PN4 forming the binary brush (Figure 2C), which can be obtained from:

$$\sigma_{binary} = \frac{N_A d_{o,binary} \rho_{PNiPAAm}}{M_{PN4(PN3)}} \phi_{PN4(PN3)} \quad (3)$$

using the final layer thickness ($d_{0,binary}$). For the pure Alk-PNiPAAm brush ($\phi_{PN4} = 1$) with a grafting density of 0.17 nm^{-2} an 1:1 chain extension ($\sigma_{PN2}/\sigma_{binary,PN4} \approx 1$) could be found again (Figure 2C,D) and reveals the very good reproducibility of the TAAC reaction in conjunction with this modular polymer brush system. Interestingly for a decreasing amount of PN4 inside the binary brush an increasing $\sigma_{PN2}/\sigma_{PN4}$-ratio can be found with a maximum value of ≈2 for $\phi_{PN4} = 0.25$ (Figure 2D). Due to the higher distance between reactive alkyne groups on the surface (s_{Alk}, Figure 2A) a less pronounced self-limiting effect occurs and further Az-PNiPAAm chains have an easier access to the remaining alkyne groups in the same polymer chain. According to this we assume that more than one Az-PNiPAAm macromolecule can be attached to a single Alk-PNiPAAm chain (N_{Alk} = 3), which leads to a 2:1 chain extension and finally Y-shaped polymer brushes (Figure 2A).

Although this binary polymer brush with alkyne functionality consists only of PNiPAAm species we believe that this strategy can be transformed easily to other water soluble binary brush systems like PAA/PNiPAAm[35] or P2VP/PNiPAAm[36] to create novel bio-interactive and responsive interfaces. In addition the use of azide- or thiol-functionalized biopolymers, such as polypeptides or polynucleotides, in combination with the presented strategy can facilitate the development of novel bio-conjugated polymer brushes with unique properties.

2.3. Temperature Responsive Switching Behavior

The temperature-responsive switching behavior of an Alk-PNiPAAm brush with a grafting density of 0.18 nm^{-2} was investigated before and after the extension of every brush chain ($\sigma_{PN2} = \sigma_0$) with Az-PNiPAAm via TAAC (**Figure 3**, **Table 3**). For this, we performed two heating/cooling cycles from 15 °C to 40 °C with steps of 0.5 °C and applied an effective medium approach to determine the in situ layer thickness (d_{H2O}), refractive index ($n_{632.8}$) and water content inside the polymer brush.[25] The not extended Alk-PNiPAAm brush offers a swollen film thickness of 62.1 nm at 15 °C, while in the collapsed state (T = 40 °C) a value of 17.3 nm is obtained (Figure 3A). After the chain

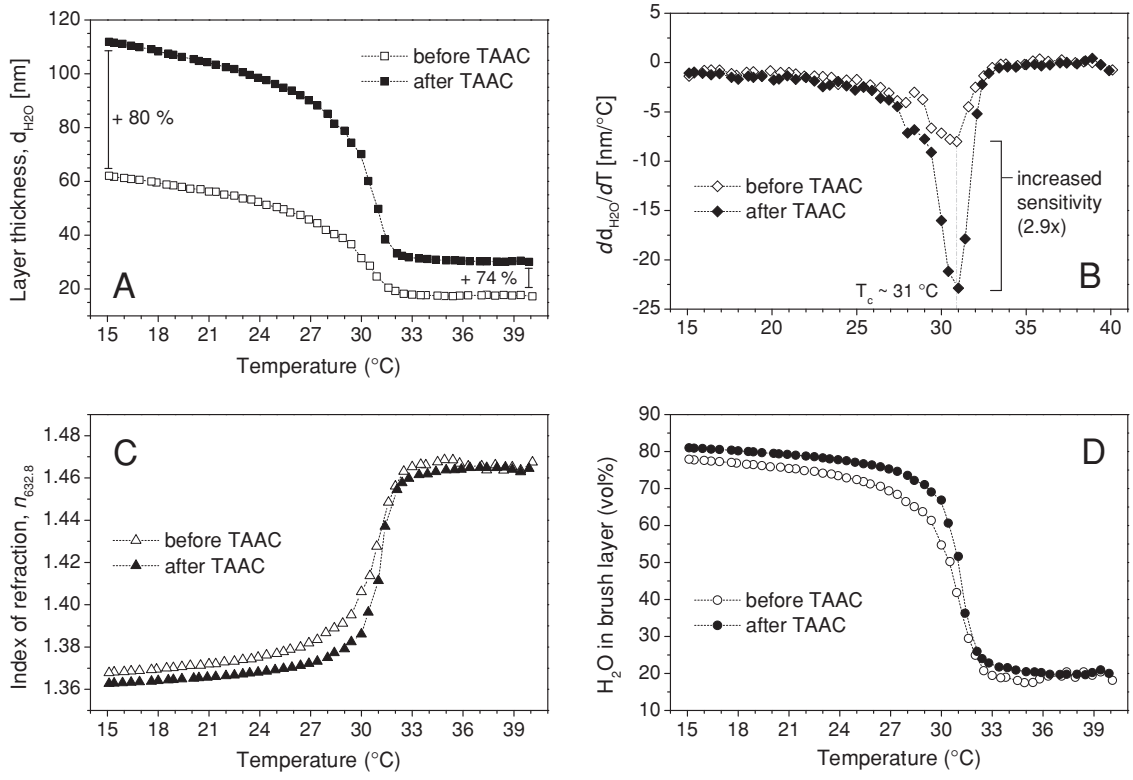


Figure 3. Temperature-responsive switching behavior (in situ) of the investigated Alk-PNiPAAm brush (PN4, N_{Alk} = 3) before and after an extension of every chain with Az-PNiPAAm (PN2) via TAAC. A) Brush layer thickness. B) Determination of T_c from the first derivative of the brush layer thickness. C) Refractive index of the brush layer. D) Water fraction inside the brush layer. The grafting density for the PNiPAAm brush is σ = 0.18 nm^{-2}. For better clarity only the second cooling cycle is displayed (for all cycles see Supporting Information).

Table 3. Properties of the investigated Alk-PNiPAAm brush (PN4, N_{Alk} = 3) before and after an extension of every chain with Az-PNiPAAm (via TAAC), in dry state and in situ: layer thickness (d), refractive index ($n_{632.8}$), water content in brush layer (H_2O), swelling ratio ($SR = d_{H2O}/d$) and absolute change in layer thickness (Δd). The grafting density for the PNiPAAm brush is $\sigma = 0.18$ nm^{-2}.

	condition	d [nm]	$n_{632.8}$	H_2O [vol%]	SR	Δd [nm]
before TAAC	dry state	13.4	1.493	–	–	–
	in situ (15 °C)	62.1	1.368	77.9 ± 0.1	4.6	–
	in situ (40 °C)	17.3	1.468	20.4 ± 0.3	1.3	–
after TAAC	dry state	23.0	1.498	–	–	9.5
	in situ (15 °C)	111.9	1.363	81.0 ± 0.1	4.9	49.8
	in situ (40 °C)	30.1	1.464	20.0 ± 0.2	1.3	12.8

extension the swollen and collapsed layer thickness increases by 80% and 74%, respectively. Concerning the switching amplitude ($d_{H2O,15\ °C}$-$d_{H2O,40\ °C}$) of the temperature-responsive polymer brush an improvement from 44.8 nm to 81.8 nm (+83%) is obtained. At the characteristic phase transition an increased sensitivity can be observed whereas the critical temperature (T_c) of 31 °C remains constant (Figure 3B). As a result an enhanced flexibility of the brush system is achieved, which should be beneficial for further studies of interfacial processes like protein adsorption or cell adhesion. Both the refractive indices (Figure 3C) and water fractions in the brush layer (Figure 3D), as well as the swelling ratios (Table 3) vary only slightly over the whole measured temperature range. Thus, it indicates that the characteristic swelling properties of PNiPAAm in water are preserved after chain extension via TAAC.

We think that this strategy of chain extension can be generally transferred to other polymers or polymer brush systems if the TAAC-conditions are fulfilled.

3. Conclusions

In this work we have shown a straightforward strategy to overcome a main handicap of the grafting-to approach in terms of limited grafting densities, which is especially significant when grafting end-functionalized polymers of high molecular weight. For this we used a convenient preparation procedure which employs the thermal azide–alkyne cycloaddition with the aim to attach azide-functionalized PNiPAAm chains to the terminal end of alkyne-functionalized PNiPAAm brushes. For an Alk-PNiPAAm brush having three alkyne groups per chain a full chain extension was observed. The number of alkyne groups at the surface could be altered by the composition of binary brushes composed of non-functionalized and alkyne-functionalized PNiPAAm. The decreased surface density of alkyne groups led to the effect that more than one Az-PNiPAAm macromolecule could be attached to a single Alk-PNiPAAm chain of the binary brush, if the amount of alkyne-functionalized polymer chains was lower than 25%. Furthermore, the temperature-responsiveness of the Alk-PNiPAAm brush was improved after an extension of every chain of the prior brush with Az-PNiPAAm via TAAC. Here a remarkable increase in the swollen and collapsed layer thicknesses, as well as the switching amplitude was found. Simultaneously a higher sensitivity in the range of the characteristic phase transition of 31 °C was observed, while the principle swelling properties of PNiPAAm in water were preserved. The concept of chain extension in conjunction with functionalized polymer brushes represents a significant progress in comparison to the current state-of-the-art and enables the development of novel bio-interactive and responsive interfaces in a simple manner. We are convinced that this strategy can readily be transferred to other (water soluble) binary brush systems and will notably augment the potential of the grafting-to approach.

4. Experimental Section

Materials: Poly(glycidyl methacrylate) (PGMA, M_N = 17 500 g/mol, M_W/M_N = 1.70) and carboxy-terminated PNiPAAm (PN, M_N = 94 000 g/mol, M_W/M_N = 1.30) were purchased from Polymer Source, Inc. (Canada). Absolute ethanol (EtOH, 99.8%) and hydrogen peroxide (H_2O_2, 33%) were acquired from Merck. Tetrahydrofuran (THF, 99.98%), chloroform ($CHCl_3$, 99%+) and ammonium hydroxide (NH_4OH, 25%) were purchased from Acros Organics. Purified water (H_2O) was used from a Milli-Q Direct 8 system from EMD Milipore Corporation. All chemicals were used as received if not otherwise specifically noted. Highly polished single-crystal silicon wafers of {100} orientation (Si-Mat Silicon Materials, Germany) were used as a substrate.

Synthesis of Functionalized PNiPAAm: Mono-functionalized PNiPAAm with a terminal carboxy group (PN1), azide group (PN2) or tert-butyl protected carboxy group (PN3), as well as bi-functionalized PNiPAAm with tert-butyl protected carboxy- and alkyne-functionality (PN4) were synthesized as described previously.[25,37] A brief description of the synthesis and characterization of the functionalized polymers is given in the Supporting Information.

Preparation and Chain Extension of Polymer Brushes: Silicon substrates were treated with EtOH in an ultrasonic bath for 15 min and dried with a stream of nitrogen. Afterwards they were exposed to a cleaning solution of $NH_4OH/H_2O_2/H_2O$ (1:1:6, v/v/v) at 70 °C for 20 min, rinsed twice with H_2O and dried with a stream of nitrogen. Next a thin layer of PGMA (≈2 nm) was deposited by spin coating (Spin 150, SPS Coating) a PGMA solution in $CHCl_3$ (0.3 mg/mL) with subsequent annealing at 100 °C in a vacuum oven for 20 min to react the silanol groups of the substrate with a fraction of the epoxy groups of PGMA, thus forming an anchoring layer equipped with the remaining epoxy groups for the following grafting-to process.[38] Afterwards, a filtered solution of functionalized polymer(s) in THF (9 mg/mL) was spin coated onto the PGMA layer and subsequently annealed at 150 °C in a vacuum oven for 15 h. To remove non-covalently bonded polymer, the resulting films were immersed first in H_2O then extracted in H_2O overnight, rinsed with EtOH and dried in a stream of nitrogen. For the chain extension of the alkyne-functionalized polymer brushes via TAAC a filtered solution of azide-terminated PNiPAAm (P2) in THF (9 mg/mL) was spin coated onto the brush films and annealed at 150 °C in a vacuum oven. To remove non-reacted polymer, the same extraction protocol was used.

Spectroscopic Ellipsometry: A spectroscopic ellipsometer (alpha-SE, Woollam Co., Inc., Lincoln NE, USA) equipped with a rotating compensator was used to measure the ellipsometric data Δ (relative phase shift) and $\tan\Psi$ (relative amplitude ratio) of the brush films in the dry state as well as in-situ in purified H_2O within a batch cuvette (TSL Spectrosil, Hellma, Muellheim, Germany).[39] All measurements were performed between 370 and 900 nm at an angle of incidence Φ_0 of 70°, which is close to the Brewster angle of silicon. For the monitoring of the temperature-sensitive swelling/deswelling of the polymer brushes, the temperature of the cell was adjusted by a home-built heating stage equipped with test-Point software, and the actual temperature at the

brush surface was controlled. Heating and cooling cycles for each sample were performed between 15 and 40 °C with a heating/cooling rate of 0.2 °C/s, and up to two cycles were measured. To evaluate the refractive index and thickness of the brush films in dry state and in situ, a multilayer-box-model consisting of silicon, silicon dioxide, anchoring layer PGMA, and a polymer brush was assumed.[25] The volume fraction of water inside the swollen/collapsed polymer brush layer was modeled by an effective medium approach (EMA) according to Bruggeman.[40] All data were acquired and analyzed using CompleteEASE software package (version 4.46).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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