Polymerization

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“On Water” Surface-initiated Polymerization of Hydrophobic Monomers

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Abstract: *We present the “on water” surface-initiated Cu-mediated controlled radical polymerization (“on water” SI-CuCRP) that converts hydrophobic monomers in aqueous reaction medium to polymer brushes at unparalleled speed and efficiency. The method allows the facile conversion of a variety of common monomers under most simple reaction conditions and with minimal monomer amounts to thick and homogeneous polymer brushes. The highly living character of the “on water” SI-CuCRP allowed the preparation of decablock (homo)polymer brushes and opens the pathway to sequentially controlled polymer brushes on solids.*

Controlled/living radical polymerizations (CRPs), have led to a revolution in polymer and surface chemistry for complex polymer and polymer brush synthesis.[1] Cu^0-mediated CRP (CuCRP) has attracted considerable attention because of its remarkable end group fidelity and high conversion rates.[2] Although the mechanistic details are still under debate (role and nature of the Cu^0 activator in single electron transfer-living radical polymerization (SET-LRP) and supplemental activator and reducing agent (SARA-ATRP)),[3] the versatility and robustness of CuCRP is now widely used to convert many vinyl monomers into functional polymers.[4]

Recently, we optimized the CuCRP for polymer brush synthesis via surface-initiated polymerization CuCRP (SI-CuCRP) by simply using a copper plate as the catalyst, a ligand and the monomer of choice but no additional $Cu^{I/II}$ sources.[5] The SI-CuCRP was found to be the fastest SI-CRP for many monomers, and resulted in very dense brushes and homogeneous brushes even on the wafer scale.[5a–c,6] Very recently, this method was also successfully adopted for SI-ATRP.[7] Analog to CuCRP in solution or SI-ATRP, the SI-CuCRP is significantly accelerated in water or aqueous solutions, hydrophilic monomers showed the highest brush layer growth rate (δ) and were remarkably oxygen tolerant.[5b,8] However, for the conversion of hydrophobic monomers such as many acrylates and methacrylates the SI-CuCRP was performed intuitively in organic solvents and required an inert atmosphere. Inspired by the findings of Sharpless et al.[9] that many organic reactions are substantially accelerated in water even if the reactants are water insoluble,[9,10] we tested the “on water” reaction condition for SI-CuCRP. In brief, a hydrophobic monomer (e.g. methyl methacrylate (MMA)) was mixed and stirred vigorously with water for about 5 min. The mixture was then allowed to stand for 30 min to obtain phase separation (Figure 1 a) before a copper ligand (1,1,4,7,7-pentamethyldiethylentriamin, PMDETA) was added to both phases, respectively. A SiO_2 substrate modified with a self-assembled monolayer bearing radical initiator

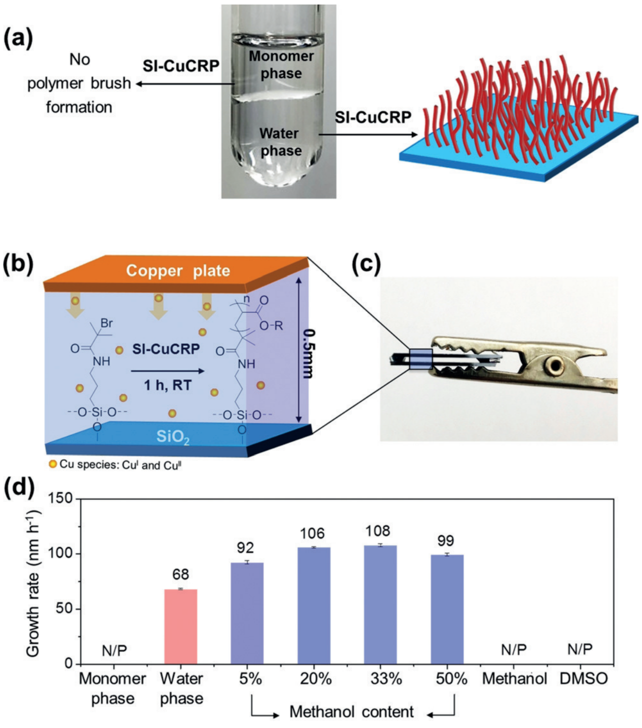

Figure 1. “On water” SI-CuCRP. a) Photograph of the two phases (“wet” monomer and water). Each phase was used separately for SI-CuCRP. While with the upper monomer phase no polymer brush was formed, use of the water phase (mainly water with minor amounts of monomer aggregates and unimers) formed homogeneous polymer brush layers at high growth rates. b) Schematic of the reaction scheme. c) Photograph of the experimental setup. Initiator modified substrate and copper plate are clamped and a thin layer of the reaction solution filling the gap ($D = 0.5$ mm). d) Typical PMMA brush growth rates from various solutions as indicated at ambient conditions. N/P: no polymer brush formation. The “methanol content” at x-axis is counted on pure water.

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function (2-bromoisobutyryl bromide, BIBB) was sandwiched with a copper plate at a distance of 0.5 mm. The gap was filled with either of both phases (Figure 1 b and c) and the assembly was left under ambient conditions for polymer brush growth by SI-CuCRP as reported before.[5,11]

Surprisingly, no polymer brush formation was observed using the organic phase. However, with the lower aqueous phase (mainly water with a tiny amount of monomer aggregates and dissolved monomer unimers) a homogeneous 68 nm thick PMMA brush was obtained in only 1 h reaction time (Figure 1 d). In further experiments, we found that the polymer brush growth rate (δ) can be increased by adding a small amount of methanol as a protic co-solvent following the arguments on the reaction acceleration for "on water" reactions (Figure 1 d).[9,10] The fastest PMMA brush growth rate of $\delta = 108\ \mathrm{nm\,h^{-1}}$ was found for a methanol:water ratio of 1:2 (v/v), further increase of the methanol content decreases the brush growth rate, and no polymerization was observed for pure methanol (or DMSO) as the reaction medium, which is in contrast to the SI-CuCRP at inert conditions (Figure S1). The water-methanol mixture (2:1, v/v, 1.5 mL) was used as the solvent for all of the following "on water" SI-CuCRP in this work, unless other solvent was specifically mentioned. It is noteworthy that the "on water" SI-CuCRP was conducted under the most simple experimental conditions. Neither the solvents, nor the monomers were deoxygenated, and the SI-CuCRP was performed at room temperature. The assembly was done on a benchtop under normal atmosphere (Figure 1 c). Analog to our previous report,[5a] this most simple methodology allows the preparation of polymer brushes of choice from hydrophobic vinyl monomers under ambient conditions and is basically scalable to any substrate size.[5b,17]

To establish a relationship between the initial monomer concentration and the rate of polymerization or brush growth rate (δ) we determined the critical solubility of monomers in the water-methanol mixture. An increasing amount (starting from 1 µL) of each monomer was added to the water-methanol mixture (1.5 mL), until phase separation was observed. Afterwards, the lower aqueous phase that contains water, methanol and a tiny amount of monomer was used for "on water" SI-CuCRP. The "on-water" SI-CuCRP was performed for 1 h at room temperature, the substrate was thoroughly cleaned and the thickness of resulting polymer brush was analyzed by ellipsometry. The results are summarized in Table 1 and compared to SI-CuCRP (pure DMSO as solvent, deoxygenated) and state-of-the-art SI-ATRP methods (eATRP and photoATRP, organic solvents, inert conditions).[18]

Although the polymer brush growth rate of SI-CuCRP in DMSO is already remarkable in comparison to photoATRP and eATRP,[18] the "on water" SI-CuCRP shows the highest polymer brush growth rates of any surface-initiated polymerization methods reported to date. The highest growth rate was observed for EA with $\delta = 462\ \mathrm{nm\,h^{-1}}$, which is nearly four times faster than SI-CuCRP in DMSO (Table 1). Only minor differences are noticeable for "on water" SI-CuCRP and SI-CuCRP in DMSO for MMA, but both show more than seven-folds higher δ as compared to SI-ATRP (i.e. $\delta_\mathrm{d} = 15\ \mathrm{nm\,h^{-1}}$).[13] Besides the extremely fast polymerization rate and high oxygen tolerance, the "on water" SI-CuCRP is also applicable to many other monomers that have not been converted to polymer brush layers by other SI-ATRP reactions such as EA, *t*BuMA, *i*BA and HA.

The polymer brush grafting density, as estimated from the saturated swelling ratio of polymer brush heights calculated to $0.42 \pm 0.03\ \mathrm{chains\,nm^{-2}}$ (Table 1 and Table S1) for a PMMA brush prepared by the "on water" SI-CuCRP. This is considerably denser than PMMA brushes prepared by state-of-art SI-ATRP methods with $0.28\ \mathrm{chains\,nm^{-2}}$ using a same characterization method.[17] The highest grafting density of $0.54 \pm 0.02\ \mathrm{chains\,nm^{-2}}$ for "on water" SI-CuCRP was determined for a PMA brush. Grafting densities for other hydrophobic monomers are higher but decreases with monomer size and reactivity (Table 1 and S1).

To determine the minimal monomer concentration needed for brush formation by the "on water" SI-CuCRP, four monomers (MA, MMA, EA and *t*BA) were selected for detailed studies (Figure 2 a). In comparison, SI-CuCRP in DMSO was performed using 1 mL monomer in 0.5 mL

Table 1: Polymer brush growth rate (δ) for "on water" SI-CuCRP, SI-CuCRP in DMSO and SI-ATRPs in organic solvents for various hydrophobic monomers.

Monomers[a]	MA	MMA	EA	*t*BA	*t*BuMA	*i*BuMA	*i*BA	HA	2-EHMA
"On water" SI-CuCRP δ [$\mathrm{nm\,h^{-1}}$][d]	273 ± 4	108 ± 1	462 ± 4	354 ± 4	112 ± 3	146 ± 2	405 ± 13	342 ± 4	186 ± 18
Swelling ratio in THF[d]	1.30 ± 0.04	1.36 ± 0.07	1.62 ± 0.05	2.62 ± 0.06	1.67 ± 0.08	1.77 ± 0.09	1.97 ± 0.04	2.88 ± 0.03	2.46 ± 0.3
Grafting density σ (chains $\mathrm{nm^{-2}}$)[d]	0.54 ± 0.02	0.42 ± 0.03	0.30 ± 0.01	0.10 ± 0.01	0.19 ± 0.01	0.18 ± 0.01	0.17 ± 0.01	0.08 ± 0.01	0.08 ± 0.01
SI-CuCRP in DMSO δ [$\mathrm{nm\,h^{-1}}$]	125 ± 2	83 ± 1	121 ± 1	197 ± 3	91 ± 3	35 ± 1	139 ± 1	159 ± 5	–[b]
SI-ATRP δ [$\mathrm{nm\,h^{-1}}$]	175[12]	15[13]	–[c]	9[14]	–[c]	60[15]	–[c]	–[c]	12[16]

[a] MA: methyl acrylate, MMA: methyl methacrylate, EA: ethyl acrylate, *t*BA: *tert*-butyl acrylate, *t*BuMA: *tert*-butyl methacrylate, *i*BuMA: isobutyl methacrylate, *i*BA: isobutyl acrylate, HA: hexyl acrylate, 2-EHMA: 2-ethylhexyl methacrylate. [b] Not soluble in DMSO. [c] No available data. [d] These values and errors were obtained by three measurements on the same sample.

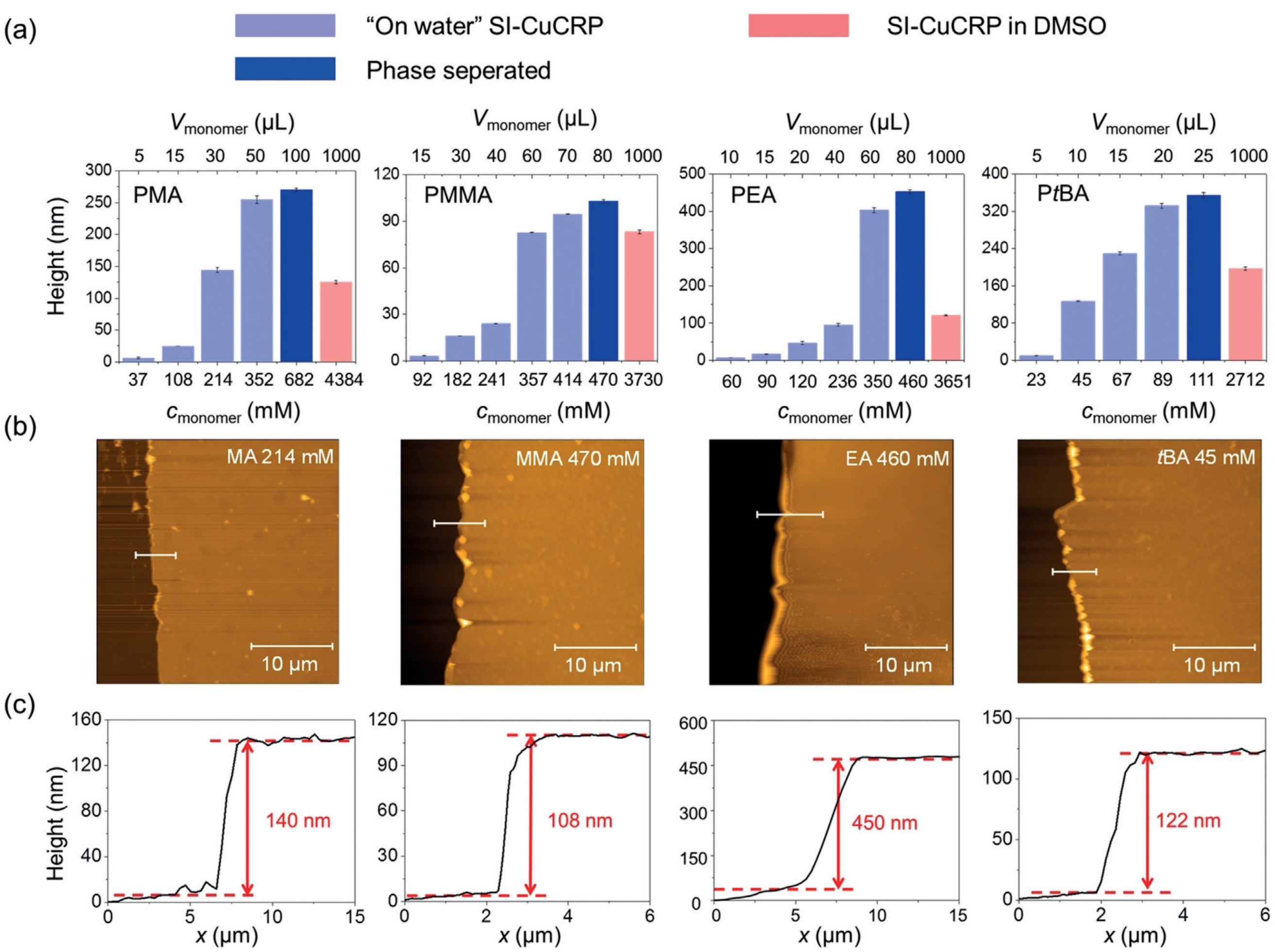

Figure 2. a) Comparison of the "on water" SI-CuCRP (blue) and SI-CuCRP in DMSO (red) for the respective monomer concentrations. b) AFM topographic scans and high profiles taken at purposely inflicted scratches of the polymer brush layer.

DMSO (Figure 2a, red color). The results indicate that various polymer brushes (from tens to hundreds of nm) can be obtained via the "on water" SI-CuCRP by the variation of the monomer content down to a few microliter. Remarkably, a brush growth rate of $\delta = 265\ \text{nm}\,\text{h}^{-1}$ for MA was observed using only 352 mmol (50 µL) of the monomer. The SI-CuCRP in DMSO, in contrast, shows only $\delta = 127\ \text{nm}\,\text{h}^{-1}$ and more than ten-folds (4384 mmol) of the monomer is required. Similar findings were made with the other monomers (MMA, EA and *t*BA, Figure 2a). In Figure 2b, typical AFM topographic scans and height profiles of the prepared brush layers are shown. Besides the remarkable brush thickness, the scans reveal the formation of very smooth, uniform and defect free polymer brush layers. Since the polymerization is strictly confined in the space between copper plate and silicon substrate, the actual reaction volume is only ca. $v = 30\ \text{mm}^3$ ($v = l \times w \times h$, where $l = 10$ mm, $w = 6$ mm, $h = 0.5$ mm). Therefore, the actual amount of for example, MA as the monomer required in the "on water" SI-CuCRP to prepare a 265 nm thick PMA brush on a 60 mm^2 substrate is only around 1 µL. In view of the potential scalability of the "on water" SI-CuCRP to modify cm^2 or even m^2 of a planar surface with polymer brushes[5b] or if expensive monomers has to be used, the efficiency of the "on water" SI-CuCRP is very advantageous.

The current challenge in polymer brush synthesis is the preparation of brushes with high sequential control. For this, the "livingness" of the surface-bound polymer chain in SIP reactions must be very high because the total amount of active chains are by orders of magnitude lower as compared to polymerizations in solution if solid substrates of low surface area have to be modified. Thus, termination reactions by radical combination, disproportionation and chain transfer reaction in surface confined polymerizations prevented the preparation of block copolymer brushes of high order (high local concentration of active chains, very low total number). In fact, the highest block numbers for block copolymer brushes prepared by living anionic polymerization is diblock reported by Advincula et al.[19] and for SI-CRP a pentablock prepared with SI-CuCRP.[5b]

To challenge the end group fidelity and robustness of the "on water" SI-CuCRP, three acrylates were chosen to prepare multiblock (homo)polymer brushes via consecutive SI-CuCRP (Figure 3a). In solution, the average degree of polymerization (P_n) for each block is typically kept low ($P_n \approx 10$[20] to avoid highly viscous reaction solutions and allow

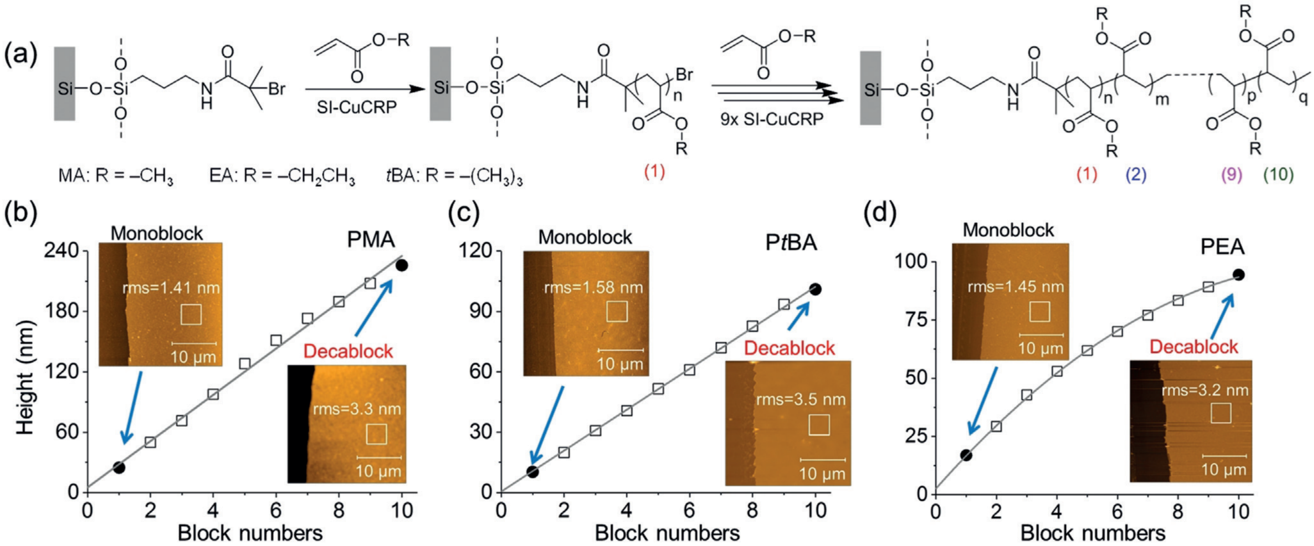

Figure 3. a) Sequential polymerization of decablock (homo)polymer brushes via "on water" SI-CuCRP. AFM and ellipsometry data for SI-CuCRP of b) 108 mmol MA, c) 23 mmol *t*BA and d) 90 mmol EA in water-methanol (2:1, v/v) mixture. ☐ Ellipsometry data; ● AFM data.

good accessibility of the active chain end for sequential monomer addition. For surface-initiated polymerizations coiling is not really an issue, as the active polymer chain end is enriched in the upper brush region because of chain stretching. However, for analytical reasons we allowed only 10–20 nm brush layer growth (controlled by the monomer content) for each consecutive step to stay within a thickness range where a reliable comparison of the analytical data is given (ellipsometry and AFM).

The first "on water" SI-CuCRP step of MA was performed as mentioned above (1 h, RT, water: methanol = 2:1, $c(\mathrm{MA}) = 108$ mmol), the substrates were also thoroughly cleaned with good solvents (see experimental) and then analyzed to give a PMA brush with a thickness of ca. 25 nm (AFM, ellipsometry and XPS, Figure S2 and Table S2) and a root-mean-square roughness of RMS = 1.41 nm (determined from the square marked area shown in Figure 3b). For the second and all following steps, the same substrate but fresh reaction solution was used. The thickness development of the PMA brush with each step is shown in Figure 3b. After 10 polymerization, cleaning and characterization steps, a 225 nm thick and homogeneous PMA brush was obtained (total reaction time: 10 h). The thickness increased strictly linear with each polymerization step. However, a slight increase of the roughness for the (homo)decablock brush of RMS = 3.3 nm was noticeable. This can be accounted to chain termination but also to polymer chain degrafting because of the repeated swelling and collapse of the brush layer (treatment with good solvents in the cleaning procedure and drying before analysis). Degrafting of dense polymer brushes has been observed before and is due to the high mechanochemical forces in a stretched brush.[5b,21] To the best of our knowledge this is the first report of a high-order block copolymer brush on a planar substrate and indicates a surprising robustness and high livingness of the "on water" SI-CuCRP method. Please note that the entire procedure took several days because of the sample preparation, cleaning procedure and characterization by AFM, ellipsometry and XPS during which the sample was repeatedly exposed to various environments (various solvents, air, vacuum). The same robustness was observed using *t*BA as the monomer for P*t*BA homodecablocks (Figure 3c). Only for EA (Figure 3d), a slower brush growth rate is noticeable from the 4th block on. Nevertheless, chain extension was still observable.

Currently, we cannot fully explain why the counterintuitive approach of the "on water" SI-CuCRP show such remarkably high growth rates but in the view of the work by Sharpless et al.[9] and the later work on "on water" organic reactions,[9,10,22] the formation of monomer aggregates in the aqueous phase and the beneficial role (activation) of hydrogen-bonding by interfacial water might play a substantial role. This can include activation of the vinyl monomer for radical chain addition, beneficial water–Cu-catalyst interactions, modulation of the Cu-catalyst redox cycle ($\mathrm{Cu^0/Cu^I/Cu^{II}}$ species). Following existing hypotheses[9,10,22] we suggest a tentative scheme in Figure 4 for further discussions.

In conclusion, we present the "on water" surface-initiated Cu-mediated controlled radical polymerization ("on water" SI-CuCRP) that converts hydrophobic monomers in aqueous

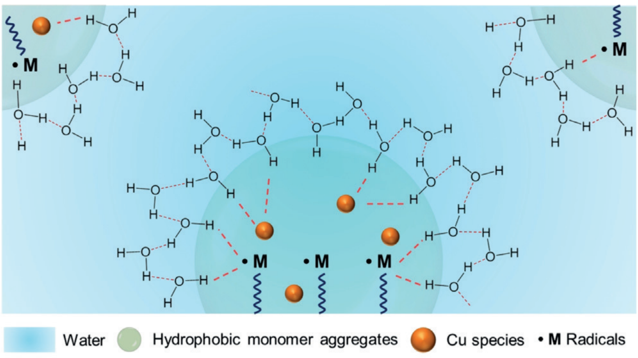

Figure 4. Tentative scheme for the "on water" SI-CuCRP.

reaction medium to polymer brushes at unparalleled speed and efficiency. The method allows the facile conversion of a variety of common monomers under most simple reaction conditions and with minimal monomer amounts to thick and homogeneous polymer brushes. The highly living character of the "on water" SI-CuCRP allowed the preparation of decablock (homo)polymer brushes and opens the pathway to a precise sequence control of grafted polymers on solids.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: "on water" reaction · controlled radical polymerization · polymer brush · polymer film · surface-initiated polymerization

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