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Surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) using a copper plate†

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Surface engineering with polymer brushes has become one of the most versatile techniques to tailor surface properties of substrates for a broad variety of (bio-) technological applications. We report on a new facile approach to prepare defined and dense polymer brushes on planar substrates by surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) of numerous vinyl monomers using a copper plate at room temperature. The fabrication of a variety of homo-, block, gradient and patterned polymer brushes as well as polymer brush arrays is demonstrated. The SI-CuCRP was found to be strictly surface-confined, of highly living character, proceeds remarkably fast and results in polymer brushes of very high grafting densities. The brush layer thickness can be modulated by the polymerization time or by the distance of the copper plate to the modified substrate. As the copper plate can be reused multiple times, no additional copper salts are added and only minimal amount of chemicals is needed, the simple and low-cost experimental conditions allows researchers from various fields to prepare tailored polymer brush surfaces for their needs.

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Introduction

Polymer brushes on solids have emerged as one of the most versatile coatings to introduce chemical functions, control the surface-free energy and friction, modulate bioadhesion, introduce physical and chemical contrasts and to design adaptive interfaces.^{1–3} As a sufficiently high chain grafting density must be achieved to take full advantage of the polymer brush characteristics,⁴ surface-initiated polymerization (SIP) of small monomers using a self-assembled monolayer (SAM) as an initiator is advantageous⁵ and allows the preparation of patterned or gradient polymer brushes.^{6–8} Consequently, all polymerization types have been adopted for SIP, but most extensively the surface-initiated atom transfer radical polymerization (SI-ATRP).^{9,10} One of the drawbacks of SI-ATRP was the need of high amount of the toxic and staining copper. However, this could be significantly improved by employing chemical (A(R)GET), electrochemical (eATRP)¹¹ or photochemical processes (*i.e.* PSI-ATRP)^{12,13} to constantly convert Cu^{II} to the instable Cu^I species in the catalytic cycle.^{10,14} The latest development in SI-ATRP was the sacrificial-anode ATRP (sa-ATRP) by Huck *et al.*¹⁵ An interesting alternative to ATRP is the single-electron transfer living radical polymerization (SET-LRP)

developed by Percec *et al.*¹⁶ In contrast to ATRP, the SET-LRP uses only catalytic amounts of nascent Cu⁰ to generate radicals from organic halides and most importantly, only a ligand but no additional Cu salts is needed. The SET-LRP is of highly living nature, very fast, yields high molar mass polymers from a broad variety of monomers and proceeds at room temperature.¹⁷ Recent studies on the mechanism of SET-LRP reported on the absence of radical combination and high end group fidelity.¹⁸ Subsequently, the “supplemental activator and a reducing agent-ATRP” (SARA-ATRP) has been reported by Matyjaszewski *et al.*^{19,20} along with a different view on the mechanism of the catalytic cycle. In this article, we will use the descriptive term surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) for the here presented polymerization in order to distinguish this polymerization from the various ATRP types that are mediated by added copper halide catalysts. This is to emphasize that in our reaction system the only source of copper is the plate spaced at a macroscopic distance away from the surface-bonded initiator.

While, Cu⁰ mediated living or controlled radical polymerizations are now frequently used for polymerization in solution,²¹ only two examples demonstrated the versatility of *e.g.* surface-initiated SET-LRP (SI-SET-LRP) for the preparation of polymer brushes. Walters *et al.*²² prepared poly(amino(meth)acrylate) brushes on silicon substrates with Cu⁰ powder and found significantly reduced reaction times at low temperatures as compared to SI-ATRP. Huang *et al.*²³ prepared poly(2-hydroxyethyl acrylate) polymer carpets²⁴ from functionalized graphene using a copper wire as the catalyst. This improved the

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initiator to the solution in order to control the surface-polymerization by a sufficient deactivator concentration. However, Cu^0 -mediated CRP such as SET-LRP is able to produce ultrahigh molar mass polymers in significantly shorter polymerization times as compared to ATRP using very low amounts of initiators. This was largely attributed to its near-complete suppression of termination reactions by combination or transfer.^{16,17} In fact, despite numerous attempts, we could not isolate any detectable amount of polymer from the supernatant solution by precipitation and closer analysis of solution by gel permeation chromatography (GPC) only gave an elution peak for the monomer but no traces of formed oligomers or polymers could be detected. From this, we can only conclude that the SI-CuCRP is surface confined and radical transfer reactions from the surface-initiated polymerization into the solution do not occur.

Repetitive use of copper plate and reaction solution

As the monomer is only consumed for the formation of the polymer brush, the monomer consumption must be low and should allow a repetitive use of the same reaction solution. Moreover, the catalyst reservoir from the plate is infinite and thus also the plate should be reusable multiple times. We performed five successive experiments using the same copper plate and reaction solution. For each new initiator-modified substrate, almost identical PMMA brush layer thicknesses were determined (Fig. 2).

Even after the 5th reaction we could not isolate PMMA from the solution and the solution showed no coloring by Cu salts as typical for SI-ATRP. UV-vis spectroscopy of the supernatant solution (Fig. 2b) confirmed the optical appearance of the solution as only minor traces of solubilized Cu could be detected, causing a broad but very weak adsorption from 500–800 nm. In contrast, SET-LRP catalyzed by a copper wire do cause a coloring of the reaction solution by copper salts as reported by Percec *et al.*¹⁸ and in own experiments as described below, probably because of the constant stirring to maintain a sufficient concentration of $\text{Cu}^{0/1}$ in the proximity of the surface. With the copper plate directly facing the substrate and no agitation, the diffusion of activating and deactivating

copper species in the confined volume is apparently sufficient to maintain the (SI)-CuCRP catalytic circle. The significant reduction of the copper load of the reaction solution is of relevance for the preparation of polymer brushes to be used in a biomedical context.

We also investigated the influence of the oxidation of the copper plate upon its catalytic activity to get first insights on the identity of the main activator (Cu^0 and/or Cu^1). Freshly cleaned copper plates as well as plates exposed to oxygen plasma for various times were used in identical SI-CuCRP experiments. All plates were able to efficiently catalyze the SI-CuCRP beyond reported brush growth rates for SI-ATRP. However, a stronger oxidation of the plate resulted in a noticeable reduction of its catalytic activity (Fig. S2†). Interestingly, we also observed that immediately after the SI-CuCRP the oxidized copper plate surfaces that were in contact with the reaction solution, appeared as if freshly etched/reduced to Cu^0 , indicating a conversion of the copper oxide layer to elemental copper or the deposition of Cu^0 as reported by Percec.³¹

Patterned and gradient polymer brushes by SI-CuCRP

Since, the SI-CuCRP appears to be surface confined and uses a SAM of surface bound initiators, the preparation of patterned polymer brushes is straightforward with patterned initiator-SAMs. As apparent from Fig. 3a–f, patterned PMMA brushes could be readily produced with patterns of various shapes and on various scales. For all cases, PMMA brush formation only occurred on initiator-covered surface areas. After 1.5 h reaction time, the dry PMMA brush thickness was found to be 110 nm which is in agreement with our SI-CuCRP experiments for homogeneous brush preparation (Fig. 1b).

To alter the surface properties continuously, brush gradients are ideally suited. Recently, Huck and Zhou demonstrated the use of a metal plate facing an initiator-functionalized planar substrate to control the brush height on a macroscopic scale. The plates were used either as a working electrode in eATRP¹¹ or as a sacrificial anode in saATRP.¹⁵ In both cases brush gradients were created and the brush height decreased linear with the distance to the facing metal. For SI-CuCRP the copper plate spacing should also influence the height of a

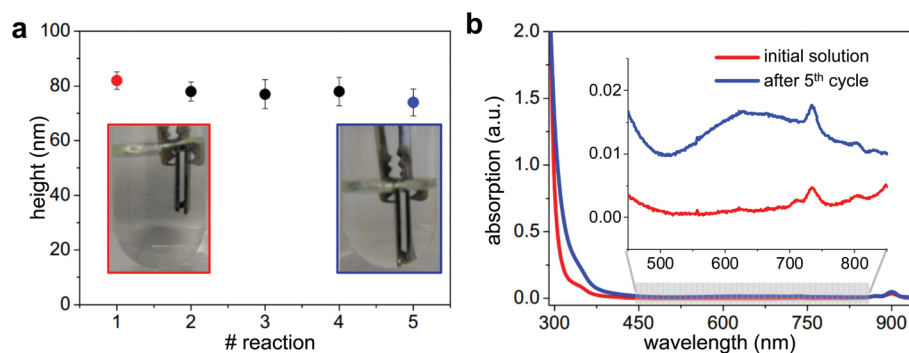


Fig. 2 Reuse of the reaction solution and the copper plate. SI-CuCRP (1 h, r.t., 2 mL MMA, 36.8 μL PMDETA in 1 mL DMSO, $D = 0.5$ mm). (a) PMMA brush layer thickness for five consecutive experiments. Insets show clear reaction solution after 1st and 5th reaction. (b) UV-vis spectra of initial reaction solution (red) and after 5th reaction (blue).



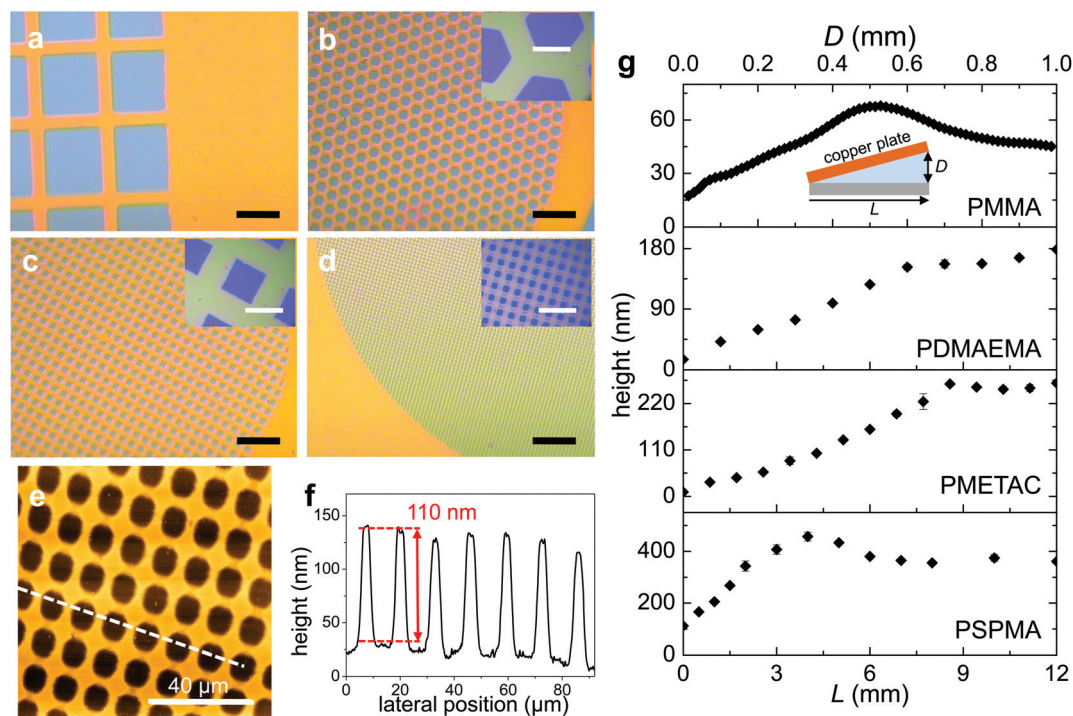


Fig. 3 (a)–(d) Optical micrographs and magnifications (insets) of patterned PMMA brushes with scale bars of 300 μm (black) and 40 μm (white). The SI-CuCRP of MMA was carried out for 1.5 h at r. t. (e) AFM scan (z : 160 nm) and (f) height analysis along the indicated line in (e). (g) Macroscopic polymer brush gradients prepared from MMA, DMAEMA, METAC and SPMA with a tilted copper plate for 1 h at r. t.

brush formed at the opposite substrate location as the copper plate is the only of the transition metal. Analog to the experiments described above, SI-CuCRP was performed with a tilted copper plate (plate-substrate distance, D , from 0 to 1 mm over a length of 12 mm). Fig. 3g gives the brush thickness development as a function of D for MMA in DMSO (for other monomers in MeOH–water). As apparent from the plots, in all cases, D had a strong influence on the brush height and macroscopic brush gradients were obtained. Interestingly, for SI-CuCRP the brush thickness increases roughly linear with D until a maximum is reached and levels or decrease again. In contrast, for eATRP and saATRP, the brush height scales *opposite* with the distance to the facing metal plate. This must be accounted to a different reaction mechanism of SI-ATRP and SI-CuCRP or identity of the main activator which is discussed below.^{18,20} The different dependency of the brush height as a function of D for the various monomers is somewhat expectable because of the different polymerization rate for each monomer as well as the different polarity of the reaction solutions because of the different polar monomers. Remarkable is the formation of a 457 nm thick PSPMA brush at room temperature within 1 h at $D = 0.33$ mm.

SI-CuCRP with various monomers

To demonstrate the general applicability of SI-CuCRP, the reaction was studied for a broad variety of monomers including styrenics, methacrylates, acrylamides and charged monomers. In contrast to the procedure described above, a MeOH–water

mixture was used as the solvent for water soluble monomers and to further accelerate the polymerization (Table 1).

The SI-CuCRP readily converted all monomers to polymer brushes at surprisingly high brush growth rates. As apparent from Table 1, the polymerization is further accelerated in

Table 1 Polymer brush layer thicknesses obtained by SI-CuCRP with various monomers. Hydrophobic monomers were polymerized in DMSO, all others in a MeOH–water (0.5 mL : 1 mL) for 1 h at room temperature at $D = 0.5$ mm

Monomer ^a	Solvent	δd^b (nm h ⁻¹)	$\theta_s^{\text{water } c}$ (°)
S	DMSO	31	89 ± 2
4VP	DMSO	56	62 ± 6
MMA	DMSO	80	74 ± 2
<i>t</i> BuMA	DMSO	85	92 ± 5
HEMA	MeOH–H ₂ O	140	65 ± 4
DMAEMA	MeOH–H ₂ O	200	83 ± 3
NIPAM	MeOH–H ₂ O	190	65 ± 4
METAC	MeOH–H ₂ O	180	10 ± 1
SPMA	MeOH–H ₂ O	270	10 ± 2
OEGMA ₄₇₅	MeOH–H ₂ O	106	44 ± 2
IPOx	MeOH–H ₂ O	40	75 ± 1

^a S: styrene, 4VP: 4-vinylpyridine, MMA: methyl methacrylate, *t*BuMA: *tert*-butyl methacrylate, HEMA: 2-hydroxyethyl methacrylate, DMAEMA: 2-(dimethylamino)ethyl methacrylate, NIPAM: *N*-isopropylacrylamide, METAC: methacryloxyethyltrimethylammonium chloride, SPMA: 3-sulfopropyl methacrylate potassium salt, OEGMA: oligo(ethylene glycol) methyl ether methacrylate, IPOx: 2-isopropenyl-2-oxazoline. ^b δd : brush growth rate. ^c θ_s^{water} : average static water contact angle from 5 individual measurements on randomly selected locations.



aqueous environments. Again, we neither see formation of polymer in solution nor a noticeable coloring of the supernatant liquid. Noteworthy is the fast polymerization of the bulky OEGMA macromonomer to a 53 nm bottle-brush brush within 30 min which calculates to $\delta d = 106 \text{ nm h}^{-1}$ that is more than ten folds faster as reported for SI-ATRP ($\delta d = 8.75 \text{ nm h}^{-1}$).³² In contrast to ATRP, SI-CuCRP was also able to polymerize IPOx. To date, IPOx could be polymerized either by free radical,³³ living anionic^{33,34} or group-transfer polymerization.³⁵ Own attempts with various ATRP recipes resulted in only oligomeric products (unpublished). The accessibility of structurally defined PIPOx by the (SI-)CuCRP poses an interesting alternative and opens a facile route to defined molecular brushes based on poly(2-oxazoline)s.

To investigate the effect of the dimensionality/shape of the bulk copper catalyst, we performed SI-CuCRP with a copper plate and a wire that was wrapped around the magnetic stir bar at the bottom of the reaction vial as for SET-LRP. Furthermore, SI-ATRP were performed using the same initiator, solvent, monomers, temperature and reaction time for direct comparison (Fig. 4). For all monomer types the SI-CuCRP catalyzed by a copper plate is by far the fastest surface-initiated polymerization. Matching the shape of the copper catalyst to the planar substrate not only facilitates the synthetic procedure but also strongly increases the brush growth rate as the comparison to SI-CuCRP or SI-SET-LRP catalyzed by a copper wire demonstrates. Surely, the much larger distance of the wire to the substrate surface can be accounted for the much lower brush thicknesses obtained in this setting. The SI-CuCRP catalyzed by the copper plate outperforms the SI-ATRP by nearly one order of magnitude for MMA. Differences are smaller for NIPAM (1.6 fold) and SPMA (3 fold). Noteworthy is the fast conversion of styrenics (4VP, S by 3.5 and 8 fold, respectively) with an initiator tailored for methacrylates.

The fast conversion of vinyl monomers to polymer brushes poses the question if the SI-CuCRP is really a controlled/living polymerization, because the total amount of deactivator (CuBr/L and CuBr_2/L) is limited by the initiator SAM and thus extremely low. As no coupled controlled radical polymerization reaction in solution was enabled by the addition of sacrificial initiator, analysis of the average molar mass and

dispersity of free polymer and estimation of the grafting density using the brush scaling laws⁴ was not possible. Hence, we prepared a PNIPAM brush on a larger substrate (approx. 4 cm^2) with a dry thickness of $220 \pm 5 \text{ nm}$ (AFM) and an optical thickness of $230 \pm 8 \text{ nm}$ (ellipsometry). The polymer brush was detached from the substrate by KOH and analyzed by GPC. The determined number average molar mass was with $M_n = 207 \text{ kg mol}^{-1}$ very high and the dispersity with $D = 1.07$ very low. This indicates that the SI-CuCRP is not only ultrafast but also highly controlled if not living. For this sample, the PNIPAM brush grafting density, σ , calculates to $0.81\text{--}0.85 \text{ chains nm}^{-2}$ which is, to the best of our knowledge, one of the highest reported grafting densities obtained by any surface-initiated polymerization. In comparison, Zhu *et al.*³⁶ reported a maximum density of $0.61 \text{ PNIPAAm chains nm}^{-2}$ prepared from a dense, preassembled silane-SAM ($9.0 \text{ initiators nm}^{-2}$) and consecutive SI-ATRP. In a recent and very detailed study, Genzer *et al.*³⁷ investigated degrafted PMMA brushes prepared by SI-ATRP and found typical grafting densities between $0.47\text{--}0.58 \text{ chains nm}^{-2}$.

Block copolymer brushes

The controlled/living character of SI-CuCRP is further evidenced by the successful preparation of block copolymer brushes. Exploiting the reported high end group fidelity of Cu^0 mediated CRP,¹⁸ we prepared block copolymer brushes by consecutive SI-CuCRP of OEGMA₄₇₅ and SPMA with HEMA (Fig. 5). For all experiments homogeneous brush coatings were found. The brush thickness increase by the second PHEMA block was also found to be uniform with a slightly lower increase from the PSPMA to the P(SPMA-*b*-HEMA). Currently, further studies are underway to elucidate the limits of SI-CuCRP to prepare functional multiblocks and repetitive brush extension experiments as in solution, this or similar polymerization types proved to be feasible to prepare high-order multiblock copolymers.^{38,39}

Polymer brush arrays from microliter volumes

The experimental setup of two facing plates defining a very small reaction space and the minimal monomer consumption offers the possibility to prepare polymer brushes from tiny amounts of chemicals. Inspired by the experiments from Zhou and Huck,¹⁵ we prepared a similar simple setup with a PDMS mask ($D = 0.5 \text{ mm}$) forming seven channels that were filled with approx. $20 \mu\text{L}$ reaction solution (Fig. 6). After 1 h, the SI-CuCRP resulted in an array of seven polymer brush areas on one substrate in a single reaction step. While for saATRP already remarkable thick brush layers are reported,¹⁵ the SI-CuCRP outperforms saATRP for all investigated monomers (e.g. saATRP gave a 30 nm thick PMETAC brush, SI-CuCRP a 180 nm thick brush (6 fold)). Please note that as the SI-CuCRP is not restricted to aqueous reaction media and in this example, polymer brushes from aqueous solution as well as DMSO were synthesized in parallel on the same substrate.

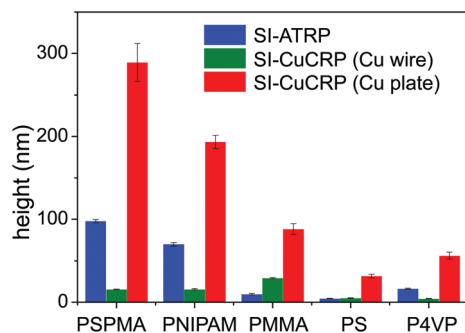


Fig. 4 Comparison of SI-ATRP, SI-CuCRP (SI-SET-LRP) catalyzed by a copper wire and SI-CuCRP using a copper plate for several monomers.



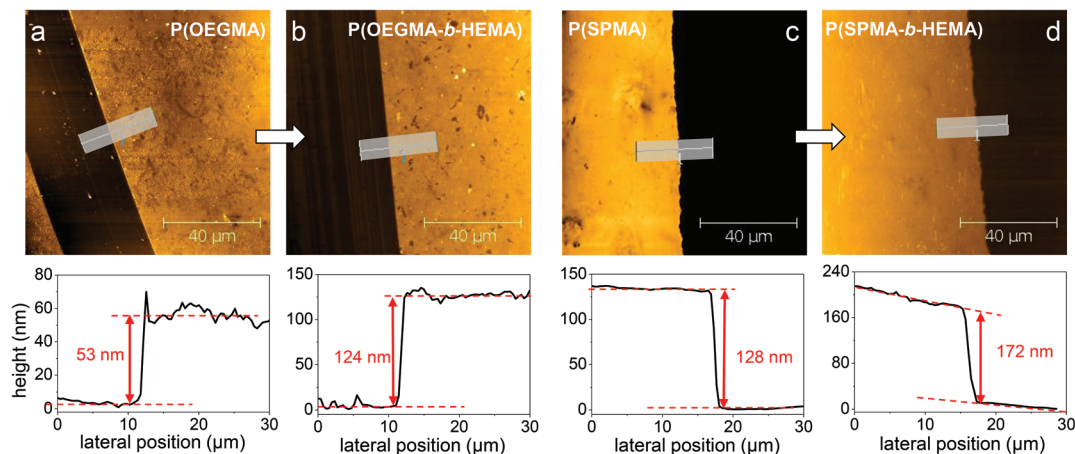


Fig. 5 Preparation of block copolymer brushes by consecutive SI-CuCRP. (a) A P(OEGMA) brush was prepared within 30 min at r.t., cleaned and a scratch defect inflicted into the layer. Layer thickness was evaluated from the area at the rim indicated in grey (upper picture, x,y : 100 μm , z = 80 nm). Polymer brush thickness is indicated in the respective height analysis shown below. (b) The same sample was subjected to a second SI-CuCRP (30 min) using HEMA to yield P(OEGMA-*b*-HEMA) of d = 124 nm. (c) Accordingly, a P(SPMA) brush (d = 128 nm) was converted to (d) a P(SPMA-*b*-HEMA) block copolymer brush (d = 172 nm).

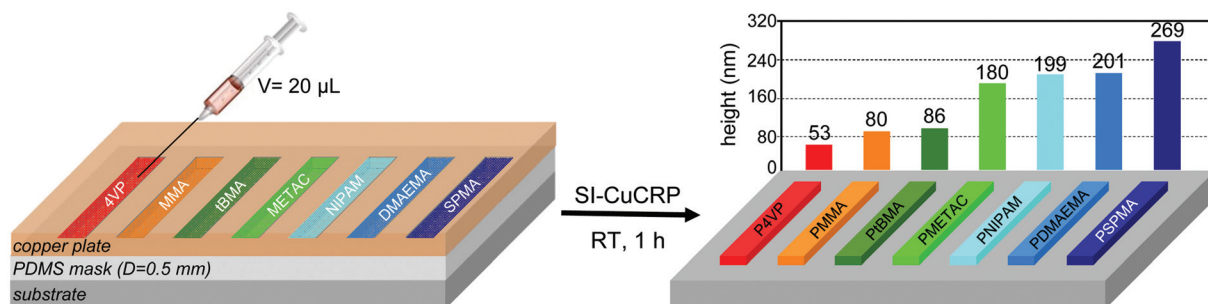


Fig. 6 Fabrication of a polymer brush array by SI-CuCRP using a crosslinked PDMS layer as a mask and spacer (D = 0.5 mm) between the substrate and the copper plate with MMA and *t*BuMA in DMSO, NIPAM, 4VP, DMAEMA, METAC and SPMA in methanol–water. The individual cavities have approx. a V = 20 μL . Brush thicknesses were evaluated by AFM (average of 3–5 measurements) at the rim of the brush areas defined by the mask.

Considerations on the mechanism of SI-CuCRP

As shown in Fig. 1a, the initiator for the polymerization is a surface bonded typical ATRP initiator SAM (APTES-BiBB). The solution contains only the solvent (DMSO or water), the vinyl monomer as well as the ligand (PMDTA). The only source of copper is the plate spaced typically 0.5 mm away from the initiator-SAM. This means, that copper species first have to diffuse over a large distance in order to react with the alkyl halide initiator and start the polymerization. For this, the observed efficiency and speed of the brush formation is very surprising as the copper concentration in the solution is extremely low⁴⁰ although enhanced⁴¹ by the PMDTA ligand. The observed absence of transfer reactions only partially explain the observed high polymer brush growth rate (Please note, that all SI-CuCRP reactions are carried out at room temperature within 30–60 min). Even more surprising is the observed control or even living character of the SI-CuCRP as evidenced by the formation of block copolymers (Fig. 5) and the very high molar mass and low dispersity as found for the degrafted polymer brushes. At the same time, the obtained grafting

density is very high which might indicate that not a bulky copper complex, but a small nascent Cu^0 species first reacts with the initiator-SAM and start the SI-CuCRP. The experiments with tilted copper plates (Fig. 3g) show that direct contact of the copper (or copper oxide) with the initiator-SAM is not favorable for the polymerization as brushes are significantly thinner at D = 0. Larger distances between the bulk copper catalyst and the initiator are also unfavorable as the same experiments show as well as the experiments with a copper wire wrapped around the stir bar at the bottom of the reaction vial (Fig. 4). This might again indicate, that the main activator for SI-CuCRP is produced in the solution and in equilibrium that is dependent on the distance to the solid copper catalyst. In any case, the bulk copper itself can not be the catalyst.

In case SI-CuCRP is following a similar mechanism as described for SET-LRP with nascent Cu^0 as the activator its reported extremely high reactivity¹⁶ could explain our observations. For the initiation of SI-CuCRP following the SET-LRP mechanism,¹⁸ nascent Cu^0 has to react with the APTES-BiBB initiator SAM to CuBr/L and initiates the living radical



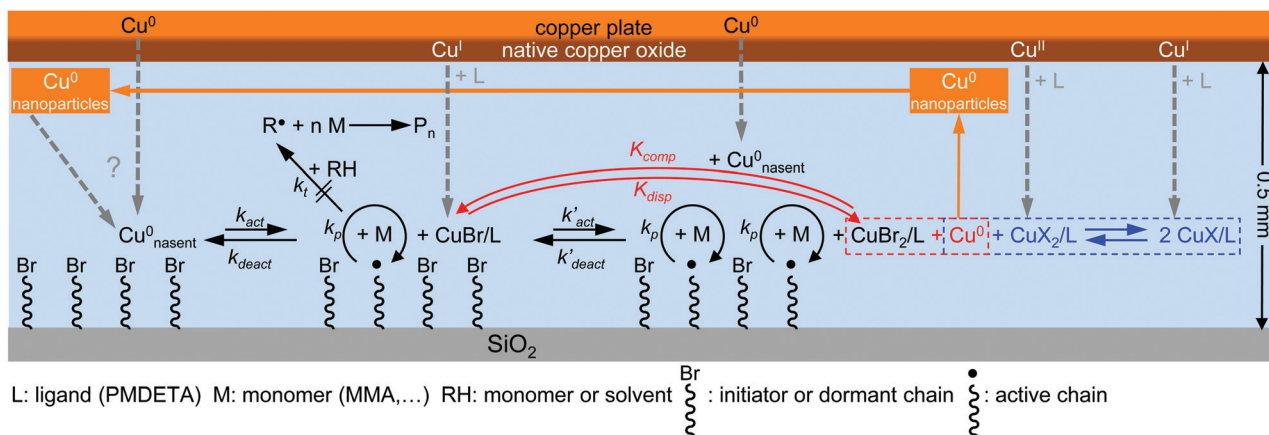


Fig. 7 Preliminary mechanism of SI-CuCRP mediated by a copper plate based on the current mechanisms for the Cu(0)-mediated SARA-ATRP and SET-LRP.

polymerization in equilibrium with Cu^0 and a surface tethered P-Br dormant species with $k_{\text{act}} \ll k_{\text{deact}}$ (Fig. 7). At the same time, CuBr/L can act as an activator by reaction with a new initiator or dormant P-Br to CuBr_2/L with $k'_{\text{act}} \ll k'_{\text{deact}}$. Additionally, the unstable CuBr/L can disproportionate to CuBr_2/L and Cu^0 (as outlined in red in Fig. 7).⁴² The absence of radical transfer is incorporated in a proposed reaction mechanism. Recently, Percec³¹ investigated the surface of copper wires used for SET-LRP and found evidence for the formation of Cu nanoparticles and associated changes of the copper wire surface. Indeed, we also see significant changes of areas of the copper plate that were in contact with the solution (experiments with oxidized plates, Fig. S2†) as they appear to be freshly reduced right after the SI-CuCRP. This indicates conversion of the copper oxides during the reaction and/or surface reconstruction by re-deposition of elemental copper.³¹ The formation of Cu nanoparticles is included in our scheme although we have currently no direct evidence of the formation of such particles in SI-CuCRP. Following the SARA-ATRP mechanism, the SI-CuCRP might also start with a $\text{Cu}^{\text{I}}\text{X/L}$ species as the activator and start the catalytic cycle. They could also participate in an additional redox reaction as proposed in Fig. 7 (blue). On the other hand, our experiments with increasingly oxidized copper plates clearly show that an increase of the copper oxide coating of the plate is not beneficial for SI-CuCRP.

At this point, it is unclear which copper species is the main or sole initial activator in SI-CuCRP and which mechanism is applicable. Currently, we perform experiments to elucidate the reasons for the surprising speed and at the same time high control of SI-CuCRP.

Conclusions

A new method for surface-initiated polymerization using $\text{Cu}(0)$ -mediated controlled radical polymerization (SI-CuCRP)

with a copper plate is described. The SI-CuCRP was found to be the fastest surface-initiated controlled/living radical polymerization reported to date and results in very dense polymer brushes. The simple experimental setup and reaction conditions allow the facile synthesis of defined brush layers at room temperature of unparalleled thicknesses within 1 h at room temperature. The reaction was found to be surface confined and monomers exclusively converted to grafted polymer chains, the reaction volume can be significantly minimized and the reaction solution reused multiple times. Overall minimal amounts of chemicals are needed. The copper load and thus, contamination of the polymer layers was found to be significantly reduced even if compared to a reaction with a copper wire used as the catalyst. The versatility of SI-CuCRP allows the preparation of brushes from a broad variety of monomers in organic solvents and aqueous media. This can also be performed in parallel on the same substrate to prepare polymer brush arrays for high-throughput experimentation. Currently, experiments are ongoing to elucidate the mechanism of the SI-CuCRP and to address the question how the SI-CuCRP is initiated and why it is so fast and efficient.

The fast, facile and very versatile SI-CuCRP mediated by a copper plate should allow researchers from various disciplines to prepare defined polymer brush layers by their own and is therefore expected to have a significant impact on future research and technology related to the tailoring and design of interfaces.

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