

Surface-Initiated Cu(0)-Mediated CRP for the Rapid and Controlled Synthesis of Quasi-3D Structured Polymer Brushes

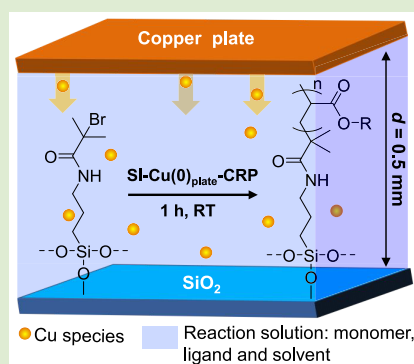
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ABSTRACT: Surface-initiated controlled radical polymerization mediated by Cu(0) plate (SI-Cu(0)_{plate}-CRP) is an extremely effective and versatile technique for the synthesis of functional polymer brushes from vinyl monomers on planar substrates. The advantages of SI-Cu(0)_{plate}-CRP in comparison to “classical” SI-CRP methods not only rely on the easy accessibility, handling, and recycling of the catalyst source, but also on the faster brush growth rates, and exceptionally high reinitiation efficiencies and grafting densities for the obtained brushes. The confined geometry of the SI-Cu(0)_{plate}-CRP reaction setup, with a Cu(0) plate placed in close proximity to the initiator bearing substrate, considerably simplifies the preparation of polymer brushes over large areas, and the fabrication of gradient, patterned and arrayed polymer brushes. In this viewpoint we summarize the recent developments and applications of SI-Cu(0)_{plate}-CRP, emphasizing its mechanism, advantages, and standing challenges.



The use of zerovalent copper for controlled radical polymerization (CRP) was initially reported by Matyjaszewski and co-workers in conjunction with classical atom transfer radical polymerization (ATRP) in 1997.¹ Later on, Cu(0)-mediated CRP (Cu(0)-CRP) was applied by Percec and co-workers for the synthesis of ultrahigh-molecular-weight polymers from various acrylates, methacrylates, and vinyl chloride.² Based on the proposed mechanism, this method was referred to as single-electron transfer living radical polymerization (SET-LRP),³ while subsequent insight into the involvement of Cu(0) in the polymerization led to the definition of its role as supplemental activator and reducing agent (SARA), while Cu(I)/Cu(II) derived from the metallic surface were identified as the main catalytically active species, according to the ATRP equilibrium.^{4–6} Haddleton et al. expanded the use of Cu(0)-CRP to the synthesis of high-molecular-weight polymers using Cu(0) powder generated in situ from Cu(I)Br/Me₆TREN within aqueous media.⁷ Due to these fundamental works, Cu(0)-CRP is now widely utilized to convert vinyl monomers into well-defined homo- and block copolymers.^{3,8–10}

Recently, Jordan et al. applied Cu(0)-CRP for the synthesis of polymer brushes from self-assembled monolayers (SAMs) of initiator adsorbates on planar substrates by using a copper plate as the only catalyst source, and introduced surface-initiated Cu(0) plate-mediated controlled radical polymerization (SI-Cu(0)_{plate}-CRP).^{11–15} In a SI-Cu(0)_{plate}-CRP setup, a Cu(0) plate is placed parallel at a typical distance (*d*) of 0.5

mm away from the initiator SAM, and also works as a cover for the confined polymerization chamber (Figure 1). In the presence of a ligand, copper species from the Cu(0) surface¹⁶ activate the initiator at the substrate and trigger the formation of uniform polymer brushes.^{11–19} Due to the confined geometry of the setup and the proximity of the metallic plate to the initiator SAM, SI-Cu(0)_{plate}-CRP is characterized by an extremely fast brush growth rate and a remarkably high tolerance to oxygen, even when large substrates are modified.¹³ Compared to the other SI-CRP methods, including those that make use of homogeneous catalytic systems,^{20–23} as well as Cu(0) powder and wires, the simple and straightforward setup of SI-Cu(0)_{plate}-CRP is advantageous.^{11,15} A simple variation of the distance between the copper plate and the initiating substrate by tilting one or both the surfaces, or the use of a patterned Cu(0) plate, enable the preparation of defined brush gradients and structured polymer films.^{11–13} Similarly easy is the fabrication of arrays of different polymer brushes on one substrate with the use of an intermediate mask.¹¹

This viewpoint aims to provide a first review on SI-Cu(0)_{plate}-CRP, critically assessing the recent advances and applications of this technique, while highlighting the opportunities and challenges for its future developments.

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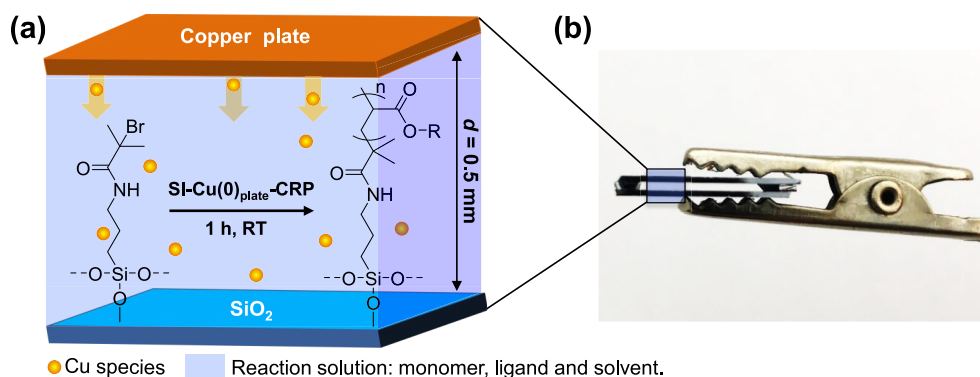


Figure 1. Typical setup for the synthesis of polymer brushes on planar substrates by SI-Cu(0)_{plate}-CRP. (a) Schematic of the reaction scheme. (b) Photograph of the experimental setup. An initiator-modified substrate and a copper plate are clamped, with a thin layer of the reaction solution filling the gap ($d = 0.5$ mm). Adapted with permission from ref 15. Copyright 2018 John Wiley and Sons.

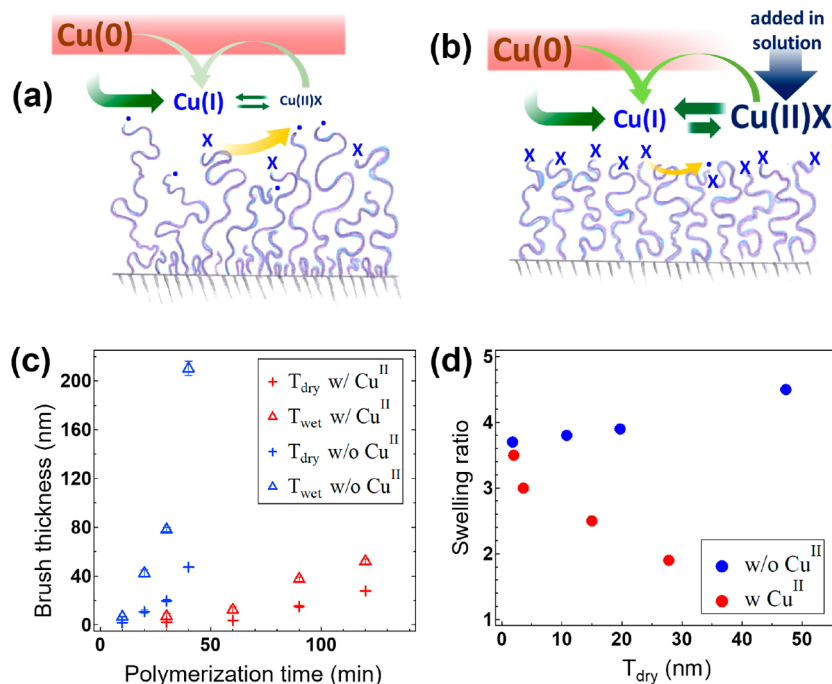


Figure 2. SI-Cu(0)_{plate}-CRP in the presence of only ligand (a) leads to the rapid growth of polymer brushes, although chain-termination reactions limit their grafting density (σ). When Cu(II) species are added (b), the brush growth rate decreases and chain termination reactions are suppressed. In (c), the values of brush thickness in dry (T_{dry}) and wet states (T_{wet}) measured with variable angle spectroscopic ellipsometry (VASE) at different polymerization times for poly[(oligoethylene glycol) acrylate] (POEGA) brushes are reported. The resulting swelling ratio (SR) is compared to the polymerization time in (d). When just ligand is added to the polymerization mixture, a progressive increase in brush swelling ratio indicates that the grafting density gradually decreases during the grafting process (blue markers). In contrast, when Cu(II) is externally added (red markers) the values of SR progressively decrease, suggesting that the POEGA brush density increases. Adapted with permission from ref 17. Copyright 2018 American Chemical Society.

Mechanism of SI-Cu(0)_{plate}-CRP. Although SI-Cu(0)_{plate}-CRP has been already proven to be an extremely efficient method for the controlled grafting of a large variety of monomers,^{11,15} its mechanism has not been completely understood yet. First attempts in describing the mechanism of polymerization have suggested that the catalytically active species regulating the grafting process must be Cu-based compounds formed or brought into solution, while the physical separation between the copper plate and the initiator bearing surface, intrinsic in the designed setup, prevents the metallic surface to directly participate in the activation/deactivation equilibria.¹¹ Due to the extremely fast brush growth rate recorded for compositionally different brushes, the formation

of nascent Cu(0) particles and their involvement as activators was initially hypothesized, following a similar mechanism to that described for SET-LRP² or Cu(0)-mediated reversible deactivation radical polymerization (Cu(0)-RDRP).⁷

However, recent studies have demonstrated the diffusion of Cu(I) species from the copper plate to the initiating surface, and thus suggested their role as the main activators during the surface-confined polymerization.¹² According to a subsequently proposed model,¹⁷ the mechanism of SI-Cu(0)_{plate}-CRP would be analogous to that described for SARA-ATRP,^{4,5,24} as the activation and deactivation processes are carried out by Cu(I)/Cu(II) species, while Cu(0) acts mainly as a reducing agent (RA) for Cu(II) to regenerate the Cu(I)

activators through comproportionation. However, the role of Cu(0) as a supplemental activator (SA), typically observed for polymerization in solution, would be totally hindered when initiator molecules are immobilized on a macroscopic substrate placed at a certain distance from the Cu(0) surface (Figure 1).

Generally, the availability of catalyst originating from the Cu(0) source is controlled by the composition of the polymerization mixture. Namely, the solvent, the concentration, and type of ligand, as well as the presence of externally added Cu(II) determine the amount of Cu species migrating from the metal plate to the medium and the rate of this process.¹⁷ While studying the SI-Cu(0)_{plate}-CRP of different acrylates and acrylamides in dimethyl sulfoxide (DMSO), the role of Cu(II) species was identified as 2-fold. On the one hand, Cu(II) triggers the generation of Cu(I)-based activator at the Cu(0) surface by comproportionation,^{2,4,24–27} as it was confirmed by monitoring the desorption of copper species from the metallic plate, alternatively with and without externally added Cu(II). On the other hand, it has been demonstrated that the presence of additional Cu(II)-based deactivator with respect to that generated through the ATRP equilibrium suppresses irreversible termination reactions (Figure 2a,b), which limits the thickness of brushes fabricated by SI-Cu(0)_{plate}-CRP and affects their structural and physicochemical properties.^{12,17} Without added Cu(II), the growth of polymer brushes proceeds relatively fast in DMSO (Figure 2c); however, this is accompanied by a progressive decrease in grafting density (σ), as indicated by an increase of the brush swelling ratio (SR, Figure 2d), presumably due to irreversible termination reactions (Figure 2a).

Hence, in the presence of externally added Cu(II) the grafting process is slower, as the concentration of surface-immobilized radicals is reduced in favor of dormant grafts (Figure 2b). Under these conditions, SI-Cu(0)_{plate}-CRP obeys to an activation–deactivation mechanism, while σ shows a progressive increase due to the growth of additional polymer chains from unreacted initiator functions at the substrate (Figure 2d).

Polymerization Setup. The advantage of using a copper plate placed in close proximity to the initiator bearing surface, instead of applying a copper wire or salt can be highlighted by comparing the growth rates recorded for compositionally different polymer brushes. As displayed in Figure 3, SI-Cu(0)_{plate}-CRP demonstrated the fastest polymerization process to yield brushes of different compositions, if compared to surface-initiated ATRP involving homogeneous catalytic systems, and processes exploiting a copper wire as source of catalyst.^{11,15} The rapid brush growth observed in SI-Cu(0)_{plate}-CRP is partly due to the geometry matching between the Cu(0) plate and the initiator substrate, which enables a fast and confined transport of catalyst to the initiator/dormant species. Moreover, since the concentration of Cu-based catalyst dissolved in the polymerization medium is overall extremely low, the frequency of activation/deactivation events results comparatively much slower compared to that generated by homogeneous catalytic systems applied in SI-ATRP, thus, ultimately suppressing the rate of irreversible termination reactions between surface-attached macroradicals.²⁸

As the availability of catalyst during SI-Cu(0)_{plate}-CRP is regulated by its diffusion from the copper plate toward the initiator-bearing substrate, the distance (d) between these two surfaces determines the rate of polymerization and influences its mechanism. Variation of d across a substrate, that is, by

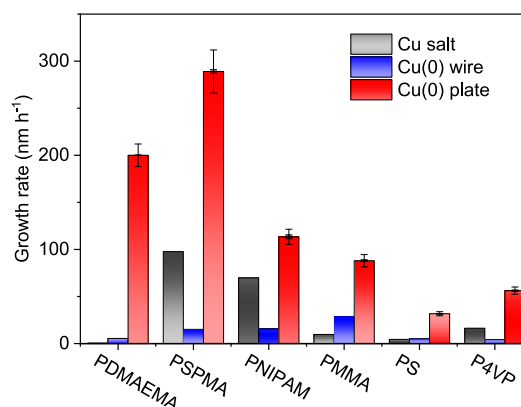


Figure 3. Comparison of brush growth rates during SI-CRP for various monomers by applying Cu salt (i.e., SI-ATRP), Cu(0) wire, and Cu(0) plate. Growth rates for the grafting of PDMAEMA by using Cu salts and Cu(0) wire are obtained from ref 29 and the other values from ref 11. PDMAEMA: poly(2-(dimethylamino)ethyl methacrylate); PSPMA: poly(3-sulfopropyl methacrylate potassium salt); PNIPAM: poly(*N*-isopropylacrylamide); PMMA: poly(methyl methacrylate); PS: poly(styrene); P4VP: poly(4-vinylpyridine).

tilting the copper plate, results in the formation of brush gradients and elucidates the effects played by d under different polymerization conditions.¹² As shown in Figure 4a, in the absence of externally added Cu(II), the brush thickness increases with d , whereas an opposite trend is observed when Cu(II) is added. In the former case, a relatively high concentration of activator species reaches the initiator SAM in areas where d is low (Figure 4a), causing a locally high radical concentration, which leads to termination reactions and limits brush thickness. Under these conditions, a gradual increment in d along the substrate is accompanied by a progressive reduction of catalyst concentration (Figure 4b,c) and a simultaneous increase in brush thickness.²⁸

In contrast, upon addition of Cu(II) the brush thickness decreases along with the gradual increment in d . A faster brush growth is accomplished in areas where d is relatively low, due to the high concentration of activators (through diffusion and comproportionation), while the surface concentration of dormant species progressively increases by rising the distance to the copper plate, significantly slowing down the polymerization process. Thus, it is clear that through a local tuning of the diffusion of copper species via, for example, varying the degree of tilt of the Cu plate overlying the initiating surface, a precise structuring of polymer brush films can be achieved.

As an example, the steepness of brush gradients can be directly tuned by varying the degree of tilt of the copper plate (Figure 4d). Brush layers showing just a slight variation in thickness are obtained when the maximum distance between the copper and the initiating surfaces (d_{\max}) is 0.5 mm, while the thickness gradient becomes increasingly steeper by rising d_{\max} to 2 mm. Alternatively, while keeping a constant d_{\max} of 1 mm, an increment in the polymerization time from 30 to 90 min provides a longer time for Cu species to diffuse toward the initiating surface, and enables the formation of brush films with a more uniform thickness (Figure 4e).

It is also important to emphasize that the concentration of Cu species dissolving from the copper surface is extremely low, that is, in the order of a few ppm.¹⁷ Hence, a copper plate can be reused multiple times, generating several polymer brush surfaces with identical characteristics.¹¹ Moreover, the low

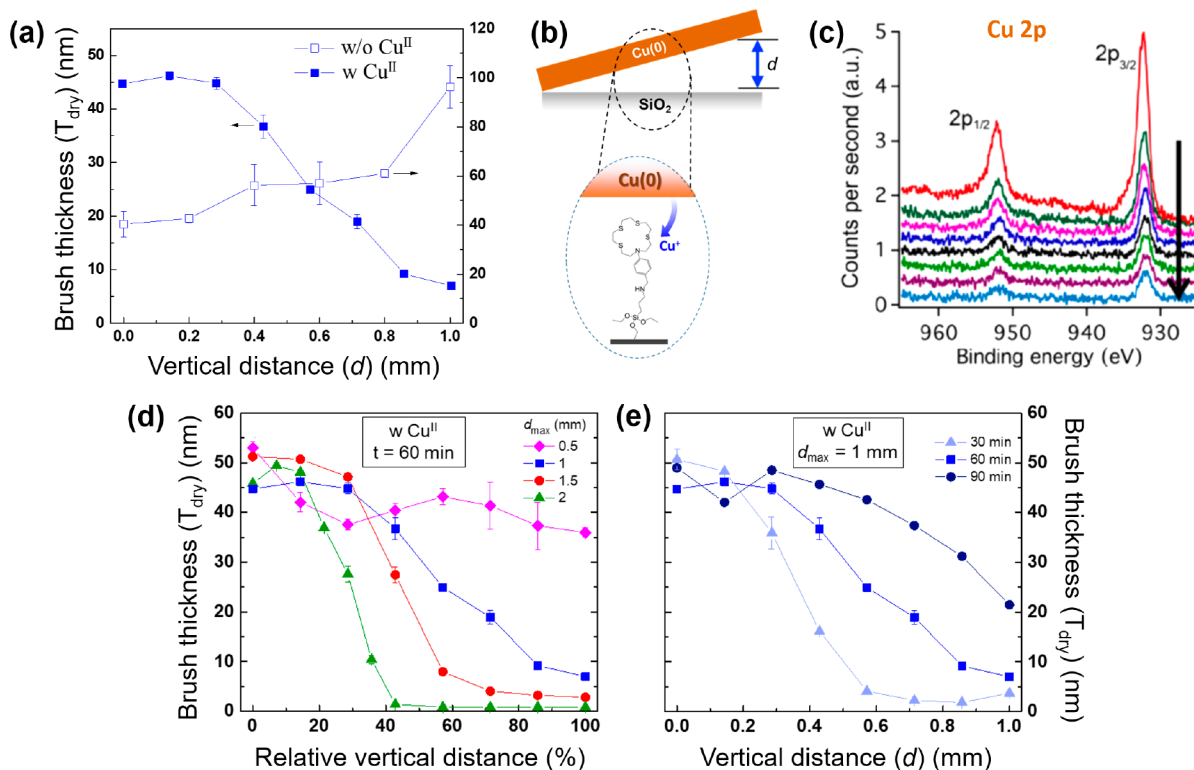


Figure 4. Dry thickness (T_{dry}) measured by VASE on POEGA brushes along gradients as a function of d . POEGA brush gradients were prepared by SI-Cu(0)_{plate}-CRP with and without addition of Cu(II). (b) A Cu(I)-selective ligand (CSL) on a silicon oxide substrate is applied in a setup similar to that used for SI-Cu(0)_{plate}-CRP for immobilizing Cu(I) species diffusing to the surface from the copper plate. X-ray photoelectron spectroscopy (XPS) is subsequently applied to estimate the surface concentration of Cu(I) species. In (c) the Cu 2p signals measured with XPS along a CSL monolayer on silicon oxide are shown; the arrow indicates the increased distance (d) from the Cu plate, from $d = 0.1$ mm (red profile) to $d = 0.8$ mm (light blue profile). (d) POEGA brush gradients synthesized by SI-Cu(0)_{plate}-CRP with externally added Cu(II) and applying different degrees of tilt of the copper plate, indicated as a fraction of the maximum distance d_{max} . (e) POEGA brush gradients synthesized by SI-Cu(0)_{plate}-CRP with added Cu(II) applying different polymerization times. Panels (a), (d), and (e) are adapted with permission from ref 17. Copyright 2018 American Chemical Society. Panels (b), (c), and (e) are adapted with permission from ref 12. Copyright 2017 American Chemical Society.

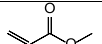
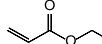
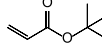
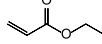
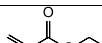
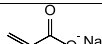
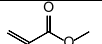
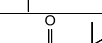
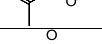
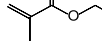
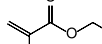
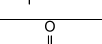
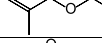
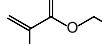
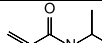
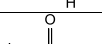
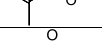
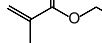
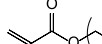
amount of Cu species involved during SI-Cu(0)_{plate}-CRP substantially reduces contamination by Cu of the subsequently formed brushes, easing their direct application within biological environments.³⁰

Monomer Compatibility. SI-Cu(0)_{plate}-CRP converts a broad variety of vinyl monomers to high-molar-mass homo- and block copolymer brushes with high grafting density under ambient conditions (Table 1). Hydrophilic monomers showed extremely fast polymerization kinetics (with brush growth rates up to 300 nm h⁻¹), including 2-hydroxyethyl methacrylate (HEMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), *N*-isopropylacrylamide (NIPAM), (methacryloyloxy)ethyl trimethylammonium chloride (METAC), and 3-sulfopropyl methacrylate potassium salt (SPMA). Noteworthy, grafting of poly(oligoethylene glycol) methacrylate (POEGMA) displayed a brush growth rate (δd) of 106 nm h⁻¹,¹¹ faster than classical SI-ATRP^{31,32} and comparable to the fastest photoinduced ATRP performed under UV irradiation.³³ The synthesis of poly(2-isopropenyl-2-oxazoline) (PIPOx) by SI-Cu(0)_{plate}-CRP permits the preparation of poly(2-oxazoline)s (POx) bottle-brush brushes (BBBs), which can be later on applied in the designing of biofunctional and bioinert surfaces.^{34–36} To date, 2-isopropenyl-2-oxazoline (IPOx) could only be polymerized either by free radical,³⁴ living anionic,³⁷ or group-transfer polymerization.³⁸ In contrast, the fabrication of PIPOx brushes by SI-Cu(0)_{plate}-CRP was accomplished under ambient conditions, with a δd of 40 nm h⁻¹.^{11,39}

SI-Cu(0)_{plate}-CRP also enables the rapid polymerization of various hydrophobic monomers including acrylates, methacrylates, styrene, and vinylpyridine (Table 1). Grafting of PMMA proceeds with a brush-growth rate (δd) of 83 nm h⁻¹ in dimethyl sulfoxide,^{11,15} which is significantly higher than $\delta d = 3$ nm h⁻¹, reported by Kim et al.⁴⁰ for SI-ATRP of MMA in bulk, and $\delta d = 15$ nm h⁻¹, reported by Huck et al.⁴¹ when SI-ATRP of MMA was performed in aqueous media. Relevantly, when water–methanol mixtures are used as solvent, SI-Cu(0)_{plate}-CRP of MMA shows a PMMA brush growth rate that can reach values above 100 nm h⁻¹.¹⁵ Moreover, even when less reactive, styrenic monomers such as styrene and 4-vinylpyridine (4VP; Table 1) are polymerized from surfaces by SI-Cu(0)_{plate}-CRP, significantly high δd values of ~30 and 60 nm h⁻¹,¹¹ respectively, were observed.

Structured Polymer Brushes. As mentioned above, variation of the distance (d) between the copper source and the initiating surface determines the rate of polymerization and the thickness of the subsequently obtained polymer brushes. Tilting of the metallic plate and the application of patterned copper surfaces can be thus applied to fabricate brush gradients and patterned films (Figure 5a). In particular, POEGMA, PDMAEMA, PMETAC, and PSPMA brushes featuring thickness and grafting density gradients of several centimeters in length were easily obtained (Figure 5b), without employing sophisticated setups,^{42–44} but simply by continuously varying

Table 1. Different Monomers That Could Be Polymerized by SI-Cu(0)_{plate}-CRP under Ambient Conditions

| Monomers ^[a] | | Growth rate δ (nm h ⁻¹) | Grafting density σ (chains nm ⁻²) | Ref. |
|---|--------|---|---|----------------|
|  | MA | 273 | 0.54 | 15 |
|  | EA | 462 | 0.30 | 15 |
|  | tBA | 354 | 0.10 | 15 |
|  | iBA | 405 | 0.17 | 15 |
|  | HA | 342 | 0.08 | 15 |
|  | SA | 33 | - | 3 |
|  | MMA | 80-108 | 0.42 | 11, 15, 19 |
|  | tBuMA | 112 | 0.19 | 15 |
|  | iBuMA | 146 | 0.18 | 15 |
|  | 2-EHMA | 186 | 0.08 | 15 |
|  | HEMA | 140-150 | - | 11, 13 |
|  | DMAEMA | 200-203 | - | 11, 13 |
|  | NIPAM | 190-279 | 0.94 | 11, 13 |
|  | METAC | 180-228 | - | 11, 13, 18, 19 |
|  | SPMA | 270-304 | - | 11, 13 |
|  | OEGMA | 106-124 | 0.09-0.42 | 11-13 |
|  | S | 31 | - | 11 |
|  | 4VP | 56 | - | 11 |
|  | IPOx | 40 | - | 11 |

^aMA: methyl acrylate, EA: ethyl acrylate, tBA: *tert*-butyl acrylate, iBA: isobutyl acrylate, HA: hexyl acrylate, SA: sodium acrylate, MMA: methyl methacrylate, tBuMA: *tert*-butyl methacrylate, iBuMA: isobutyl methacrylate, 2-EHMA: 2-ethylhexyl methacrylate, HEMA: 2-hydroxyethyl methacrylate, DMAEMA: 2-(dimethylamino)ethyl methacrylate, NIPAM: *N*-isopropylacrylamide, METAC: (methacryloyloxy)ethyl trimethylammonium chloride, SPMA: 3-sulfopropyl methacrylate potassium salt, OEGMA: oligo(ethylene glycol) methyl ether methacrylate, S: styrene, 4VP: 4-vinylpyridine, IPOx: 2-isopropenyl-2-oxazoline.

the distance between the metallic surface and the initiating substrates.^{11,12}

Alternatively, when microstructured copper surfaces are applied, a local variation of catalyst concentration is obtained across the substrate, resulting in a polymer brush with a morphology that reproduces the texture characteristic of the metallic surface (Figure 5a, second panel). As an example, a negative image of the structured surface of a copper coin (2 Euro cent) could be obtained by SI-Cu(0)_{plate}-CRP of METAC, yielding a patterned PMETAC brush film that

precisely followed the micromorphology of the metallic substrate used as catalyst source (Figure 5c).¹³

The unique experimental setup of SI-Cu(0)_{plate}-CRP, comprising two facing surfaces separated by a very small reaction volume, further offers the possibility to spatially confine the grafting of chemically diverse brushes from a single substrate, by employing a polydimethylsiloxane (PDMS) spacer featuring microchannels that can be filled with different polymerization mixtures (Figure 5a, third panel). By this technique, polymer brush arrays of different compositions were obtained by SI-Cu(0)_{plate}-CRP in one reaction step, and using

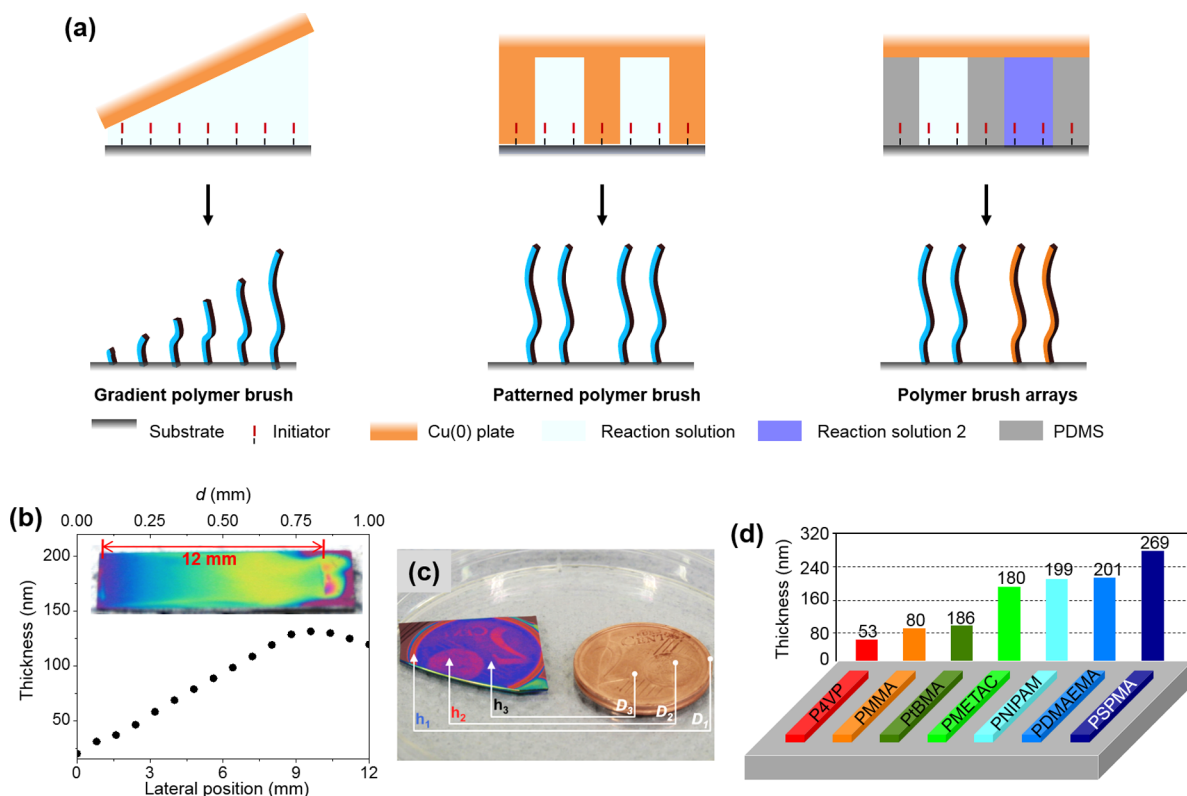


Figure 5. (a) Strategies to fabricate structured polymer brushes by SI-Cu(0)_{plate}-CRP, including brush gradients (first panel), structured brushes (second panel) and arrays of brushes featuring different compositions (third panel). (b) A PMETAC brush gradient extending on a 15 mm long substrate could be prepared by tilting the copper plate used as catalytic source. A nearly linear variation of PMETAC brush thickness (measured by VASE) was obtained across the substrate. (c) PMETAC brushes presenting a morphology that reproduces the negative image of the structured surface of a copper coin (2 Euro cent). D_1 , D_2 , and D_3 refer to three typical distances (0, 0.21, and 0.28 mm, respectively) between Cu(0) surface and initiator substrate. h_1 , h_2 , and h_3 refer to three distinct brush thicknesses of 17, 50, and 80 nm, respectively. (d) Arrays of compositionally different polymer brushes can be synthesized on a single substrate by applying a PDMS spacer presenting microchannels that spatially confine different reaction volumes. Panels (b) and (c) are adapted with permission from ref 13 and panel (d) from ref 11. Copyright 2015 The Royal Society of Chemistry.

just $\sim 20 \mu\text{L}$ of monomer mixture for each microchannel (Figure 5d).¹¹

Besides the ambient conditions required for polymerization and its tolerability to oxygen, SI-Cu(0)_{plate}-CRP demonstrates a surface-confined process (no polymer is formed in solution) and features a high retention of polymer end groups, since chain-transfer and termination reactions can be easily suppressed.⁴⁵ These unique features enable the accessible synthesis of multiblock copolymer brushes. For example, P(OEGMA-*b*-HEMA-*b*-OEGMA-*b*-HEMA) tetrablock copolymer brushes featuring a thickness of nearly 300 nm could be prepared over an area of $\sim 50 \text{ cm}^2$ by four sequential SI-Cu(0)_{plate}-CRP steps, obtaining homogeneous multifunctional films.¹³ The application of aqueous SI-Cu(0)_{plate}-CRP further permitted the synthesis of decablock (homo)polymer brushes from MA, *t*BA, and EA during 10 consecutive polymerization steps.¹⁵

The defined and reproducible quasi-3D variation of brush composition and morphology granted by SI-Cu(0)_{plate}-CRP further enabled the precise control over technologically relevant interfacial properties, including surface wetting, lubrication, and biopassivity,^{43,44} demonstrating the applicability of this surface-confined polymerization technique for the fabrication of advanced polymeric materials.

Challenges and Outlook. SI-Cu(0)_{plate}-CRP is emerging as an attractive surface-confined polymerization technique,

providing extremely fast brush growths for a variety of vinyl monomers, enabling the fabrication of brushes with high grafting densities, and assuring high retention of active polymer end groups. SI-Cu(0)_{plate}-CRP is performed at ambient temperature, thus, suppressing chain transfer reactions,⁴⁵ while the low concentration of catalyst typical of this grafting process reduces radical termination reactions between growing chains.²⁸

Besides its fast kinetics and monomer compatibility, the reaction setup applied for SI-Cu(0)_{plate}-CRP enables the facile fabrication of gradient, patterned and arrayed polymer brushes without the need of complex procedures or multiple surface modification steps.

With respect to other SI-CRP methods, the only observed limitation of SI-Cu(0)_{plate}-CRP is that it cannot be applied to prepare uniform brush coatings on high-aspect ratio substrates, such as micro and nanofibers⁴⁶ or particles.⁴⁷ This is due to the planar geometry of the copper plate, which does not permit a uniform diffusion of catalytic species to take place when curved or highly structured initiating substrates are intended to be modified.

SI-Cu(0)_{plate}-CRP is envisioned to be extended to less activated monomers, such as vinylpyrrolidone, vinyl acetate, or vinyl chloride,^{2,48} which will significantly broaden the application of this technique for the designing of functional polymeric surfaces.

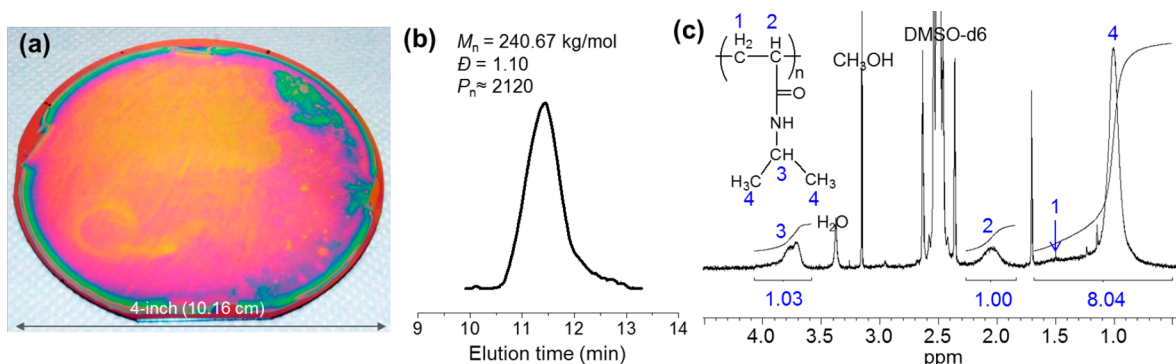


Figure 6. (a) PNIPAM brush with uniform thickness synthesized on an entire silicon oxide wafer by SI-Cu(0)_{plate}-CRP. The thickness (T_{dry}) of PNIPAM brush was determined by VASE and atomic force microscopy (AFM): $T_{\text{ellipsometry}} = 280$ nm and $T_{\text{AFM}} = 300$ nm. (b) Size-exclusion chromatography (SEC) trace of detached PNIPAM brush using *N,N*-dimethylacetamide (DMAc) as eluent (5 g L^{-1} LiBr, 70°C , 1 mL min^{-1}). The molecular weight (M_n), polydispersity (\bar{D}), and degree of polymerization (P_n) of the PNIPAM sample are also indicated. (c) ^1H -nuclear magnetic resonance (^1H NMR) spectrum of the detached PNIPAM brush. Adapted with permission from ref 13. Copyright 2015 The Royal Society of Chemistry.

More efforts are required to comprehensively dissect the mechanism of SI-Cu(0)_{plate}-CRP, which appears to be more complex than “classical” SI-CRP or others Cu(0)-mediated CRP, as the involvement of dissolved Cu salts in the polymerization process is strictly correlated to the distance from the copper plate.^{17,49} The relative contributions by the different Cu species involved in polymerization process have still to be clearly identified,^{5,24,27,50} while the roles played by the type of solvent, and the nature of the ligand for each class of monomers also have to be unambiguously defined.

In addition to the already mentioned advantages with respect to SI-CRP methods involving homogeneous catalytic systems, SI-Cu(0)_{plate}-CRP allows one to easily fabricate brushes over large areas by employing extremely small reaction volumes (e.g., approximately 4 mL of monomer mixture are enough for functionalizing a silicon wafer of 4 in. in diameter), giving direct access to high amounts of polymer samples, from which standard analytical parameters can be determined (Figure 6). Such a comprehensive polymer-brush characterization would provide a complete understanding of the surface-initiated polymerization kinetics, the accessible determination of polymer-brush grafting density, and it would lead to a better definition of structure–property relationships for different brush structures and compositions.

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Notes

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