Self-Organizing Surface-Initiated Polymerization: Facile Access to Complex Functional Systems

SAKAI, Naomi, et al.

Abstract

Facile access to complex systems is crucial to generate the functional materials of the future. Herein, we report self-organizing surface-initiated polymerization (SOSIP) as a user-friendly method to create ordered as well as oriented functional systems on transparent oxide surfaces. In SOSIP, self-organization of monomers and ring-opening disulfide exchange polymerization are combined to ensure the controlled growth of the polymer from the surface. This approach provides rapid access to thick films with smooth, reactivatable surfaces and long-range order with few defects and high precision, including panchromatic photosystems with oriented four-component redox gradients. The activity of SOSIP architectures is clearly better than that of disordered controls.

Reference


DOI : 10.1021/ja203792n

Available at:
http://archive-ouverte.unige.ch/unige:17068

Disclaimer: layout of this document may differ from the published version.
Self-Organizing Surface-Initiated Polymerization: Facile Access to Complex Functional Systems

Naomi Sakai,†* Marco Lista,‡ Oksana Kel,§ Shin-ichiro Sakurai,†§ Daniel Emery,‡ Jiri Mareda,‡ Eric Vauthey,‡ and Stefan Matile†*

Departments of Organic and Physical Chemistry, University of Geneva, Geneva, Switzerland

†Department of Organic Chemistry. ‡Department of Physical Chemistry. §Current address: Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan.

*To whom correspondence should be addressed. E-mail: stefan.matile@unige.ch, naomi.sakai@unige.ch, www.unige.ch/sciences/chiorg/matile/

Facile access to complex systems is crucial to generate the functional materials of the future. Herein, we report self-organizing surface-initiated polymerization (SOSIP) as user-friendly method to create ordered as well as oriented functional systems on transparent oxide surfaces. In SOSIP, the self-organization of monomers and ring-opening disulfide exchange polymerization are combined to assure the controlled growth of the polymer from the surface. This approach provides rapid access to thick films with smooth, reactivatable surfaces and long-range organization on the molecular level, including panchromatic photosystems with oriented four-component redox gradients. The activity of SOSIP architectures is far better than that of disordered controls.

The construction of supramolecular functional multicomponent architectures on solid surfaces that are both oriented and ordered is a key challenge in current materials sciences and beyond.1-19 Essential processes and motifs such as lateral self-sorting or oriented antiparallel gradients are intrinsically inaccessible by solution processing and related current methods.19 We have recently introduced zipper assembly of double-gradient supramolecular n/p-heterojunction (SHJ) photosystems as powerful yet less practical solution.17 “Polymer brushes” have been around for a while as promising high-speed low-cost alternative.14-16 However, they seem to stop growing well as soon as more interesting chemistry concern- ing organization or function is addressed. Implementing lessons from nature, we here report self-organizing surface-initiated polymerization (SOSIP) as general method to create ordered and oriented functional systems on transparent oxide surfaces.

We thought that reversible surface initiated polymerization of the functional monomers equipped with functional domains embedded within self-organizing domains would afford highly ordered and oriented architectures. To test the hypothesis, initiator 1 and propagators 2-6 were designed and synthesized (Fig. 1A, see Supporting Information). As functional domain, naphthalenediimides (NDIs) were selected. Their π-stacks can be used to transport electrons efficiently, their color and redox properties can be changed without global structural changes.20 As self-organizing domain in 1 and 2, lysine-derived diamides were envisioned to organize SOSIP architectures with networks of hydrogen bonds 17-19,21,22 around the equally organizing NDI π-stacks.23-24

For ring-opening surface-initiated polymerization, several candidates were screened. Reversible disulfide exchange turned out to be best. This reaction is well known from protein folding and has been used to tackle other challenges in chemistry and biology such as lipid bilayer polymerization, dynamic molecular recognition or mechanical bonding.25-29 More classical methods such as ROMP29 or ATRP14 but also bio-inspired alternatives such as ring-opening thioester30 or hydrazone exchange11 were more problematic in our hands. To realize SOSIP with ring-opening disulfide-exchange polymerization, protected cysteine and asparagusic acid, a strained

Figure 1. Design and model of SOSIP architectures with structures of initiator 1 and propagators 2-6. (A) Synthesis of 10 by (i) deposition of initiator 1 on ITO, (ii) activation with DTT, self-organizing recognition of propagator 2 and ring-opening disulfide exchange (iii) for continuing SOSIP (iv). For full chemical structures, please see Fig. S2. Polymerization mechanisms and polymer structures are shown with the only intention to explain design strategies. They can be considered as mostly speculative but consistent with all reported experimental data and (B) General Amber Force Field (GAFF) models of 10 (NDIs, yellow; H-bond donors, red; H-bond acceptors, blue; polymer backbone, silver).
cyclic disulfides,27,28 were added next to the self-organizing domains in initiator 1 and propagators such as 2. To bind to indium tin oxide (ITO) surfaces in a well-defined orientation, initiator 1 was finally equipped with two diphosphonate “feet”.29 From here, SOSIP was designed to occur as follows: Reduction of the disulfides in 7 with dithiothreitol (DTT) liberates reactive thiolates on the surface of 8. Recognition of propagators such as 2 on the surface of 8 by the topologically matching self-organizing and functional domains was expected,23,24 to position the terminal disulfides of 2 on top of two thiolates on the surface of 8. This self-organization was thus conceived to facilitate intramolecular ring-opening disulfide exchange at both termini of 2 to freeze the desired surface architecture in a covalent macrocycle.25 At the same time, active thiolates are reproduced on the surface of intermediate 9 to react with the next propagator 2 to continue with reversible disulfide exchange to ultimately yield the desired ladder- 

architecture in a covalent macrocycle.25 

Microcontact printing (µCP) was used to prove the occurrence of SOSIP.26 An ITO surface was patterned with initiator 1 (Fig. 2A), activated with DTT and incubated with 2 and rPr2NET as a base catalyst under optimized conditions (see below). AFM images demonstrated that polymerization occurred exclusively on activated surfaces (Fig. 2B).

![AFM images of SOSIP architectures](image)

**Figure 2.** Comparing SOSIP architectures 10 with disorganized controls 10' obtained by polymerization in solution. Both were made with propagator 2. (A) AFM height image after µCP of 1 on ITO; the printed areas are not visible at the AFM detection limits. (B) µCP becomes visible by AFM after treatment with DTT and then propagator 2 (c: 0 (black) - 100 nm (white)). (C) AFM height images of 10; (D) same for 10' (c: 0 (black) - 50 nm (white)). (E) AFM phase-contrast image of 10 (corresponding to C). (F) Zoom of E. (G) Transient absorption at 550 nm of 10 (green) and 10' (blue) after excitation at 400 nm with a 100-fs laser pulse. (H) Transmittance-normalized photocurrent generated by 10 (solid) and 10' (dashed).

SOSIP was strongly dependent on nature and concentration of propagators 2-6, and the base catalyst (Figs. S5-S6). The dependence on propagator concentration was characterized by $c_{\text{SOSIP}}$, the critical propagator concentration needed to achieve significant SOSIP. Above $c_{\text{SOSIP}}$, SOSIP showed a steep non-linear increase with propagator concentration (Fig. S5). This behavior, characteristic for polymerizations, hampered quantitative reproducibility, whereas the qualitative reproducibility of SOSIP was perfect. The onset of competing polymerization in solution occurred at higher concentration $c_{\text{SOL}}$. Whereas absolute values for $c_{\text{SOSIP}}$ and $c_{\text{SOL}}$ varied from case to case, a significant SOSIP window $c_{\text{SOSIP}} < c < c_{\text{SOL}}$ was reproducibly found for all bis-asparagusyl propagators. Very weak polymerization found with mono-asparagusyl propagator 6 supported the importance of surface-bound and preorganized dithiophanes to template the polymerization (Fig. S5D).

SOSIP with propagator 2, performed in the window between $c_{\text{SOSIP}} = 7$ mM and $c_{\text{SOL}} = 11$ mM, exhibited saturation behavior with $t_{50}$ = 6 h and a maximal NDI absorption of ~0.15 at 470 nm (Fig. S4). This inactive surface could be reactivated with DTT to continue with polymerization for $\geq$ 23 times (Figs. S7-S9). The resulting $A_{\text{ETN}}$ 0.9 corresponds to a thickness of ~250 nm or, in an ideal SOSIP architecture, a stack of ~750 NDIs. Successful reactivation of smooth, ordered surfaces (Fig. 2C, 2E) with DTT supported the expected vertical growth of the polymer from the surface and confirmed reversibility of the polymerization. The latter should be important for self-organization driven self-repair23-29,36 to minimize crosslinking and produce low-defect ladder- 

phane23,33 polymer brushes.

The polymeric precipitate formed at $c > c_{\text{SOL}}$ was insoluble in all common solvents. Only small oligomers could be detected by MALDI-MS (Fig. S19). Polymers could adsorb randomly on initiator-free ITO surfaces when precipitating during their synthesis at $c > c_{\text{SOL}}$ in solution. Comparison of the obtained architectures 10 with SOSIP architectures 10 was of use to characterize the latter, using propagator 2 in both cases (Fig. 2). According to AFM images, the surface of SOSIP architectures 10 (Fig. 2C, roughness $R_{a} = 5.1$ nm) was clearly smoother than that of solution polymerized 10' (Fig. 2D, $R_{a} = 87$ nm) and not much rougher than the bare ITO surfaces used. Phase-contrast images revealed long-range low-defect organization of SOSIP architectures 10 on the molecular level (Figs. 2E and F).

In ultrafast spectroscopy measurements, SOSIP architectures 10 and the disorganized control 10', made both with propagator 2, had identical properties except for the important background noise produced by the rough surface of 10' (Figs. 2G, S12, S18). This finding confirmed that it is the long-range organization as well as the orientation with respect to the oxide surface that account for the superior performance of SOSIP photosystem 10 compared to solution-polymerized 10', whereas their local structure is indistinguishable. Transient absorption spectra with SOSIP architectures (Fig. S14) compared to those of photochemically generated NDI10 and NDI10' (Fig. S15) demonstrated that the yellow NDIs in architectures 10 and 10' can function as both donors and acceptors to undergo symmetry-breaking photoinduced charge separation (PCS) (Fig. S16).6,15 Ultrafast non-radioactive deactivation in fluorescence kinetics confirmed that PCS occurs with an average time constant of about 6 ps (Fig. S12). The decay of the transient absorption of the charge-separated state was found to be biphasic with 80 ps and >2 ns lifetimes (Fig. 2G, S18).

Photocurrent generation was determined with a wet set-up analog to dye-sensitized solar cells,8,36 using SOSIP photosystems 10 as working electrode, a Pt wire counter electrode, a Ag/AgCl reference electrode, and TEOA as mobile electron carrier (Fig. 2H, solid).17,19 Compared to disorganized photosystems 10', SOSIP photosystems produced about 5-times more photocurrent (Fig. 2H, dashed). Photocurrent generation by SOSIP 10 compared to control 10' was also much faster, a finding that was consistent with decreasing resistivity with increasing organization (Fig. S10).
To build panchromatic SOSIP photosystems 11 with oriented four-component redox gradients, red and blue propagators 4 and 5 were designed and synthesized (Fig. 3). Increasing bandgap with decreasing LUMO energies produces gradients for directional electron (e) transport from blue toward red, yellow and colorless NDIs (i.e. 5 → 4 → 2 → 1), whereas holes (h) could move in the other direction (i.e. 1 → 2 → 4 → 5, Fig. 3A).

With SOSIP, the construction of multicomponent photosystems 11 was very straightforward. Deposition of initiator 1 was followed by activation with DTT and incubation with yellow, red and blue propagators 2, 4 and 5 for one hour each (Fig. 3B). The absorption spectrum of the panchromatic photosystem 11 demonstrated that all chromophores are incorporated at roughly equal amounts (Fig. 3C). The action spectrum (Fig. 3B). The absorption spectrum of the panchromatic photosystem 11 demonstrated that all chromophores are incorporated at roughly equal amounts (Fig. 3C). The action spectrum of multicomponent SOSIP photosystem 11 compared to that of the uniform 10 revealed that already the presence of one redox gradient suffices to increase photocurrent generation by yellow NDIs significantly (Fig. 3D, • and O). Much poorer photocurrent generation by the red and particularly the blue NDIs in the same system indicated that these electron-rich stacks transport holes better than electrons.

**Figure 3.** Panchromatic photosystems with four-component redox gradients. (A) HOMO and LUMO energies of 1, 2, 4 and 5 with possible electron and hole transfer cascades. (B) SOSIP of 11 by deposition (i) and activation (ii) of 1 on ITO followed by incubation with propagators 2 (iii), 4 (iv) and 5 (v). (C) Transmission spectrum of 11. (D) Action spectra of multicolor photosystem 11 (●) compared to unicolor photosystem 10 (O), in transmittance-normalized IPCE (%).

Taken together, these results identify SOSIP as a user-friendly and attractive approach to oriented surface architecture with organization on the molecular level. Now we are moving on to expand the approach with the introduction of more ambitious structuring units (i.e., R^1 \neq H, Chs, Fig. 1) to build the oriented multicolored antiparallel redox gradient (OMARG) SHJ architectures needed for long-distance PCS and high efficiencies.23–30

**Acknowledgments.** We thank D. Jeannerat, A. Pinto and S. Grass for NMR measurements, the Sciences Mass Spectrometry (SMS) platform for mass spectrometry services, P. Maroni and M. Borkovec for access to and assistance with surface analytics equipment, D.-H. Tran for contributions to synthesis, and the University of Geneva, the European Research Council (ERC Advanced Investigator, S.M.), the National Centre of Competence in Research (NCCR) Chemical Biology (S.M.), the NCCR MUST (E.V.) and the Swiss NSF for financial support (S.M., E.V.).

**Supporting Information Available.** Details on experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

(35) Preliminary results on surface-templated self-sorting during co-SOSIP corroborate the crucial importance of preorganized initiators for SOSIP.
(36) Preliminary results obtained for barrier removal during self-sorting co-SOSIP of double-channel photosystems are in support of the existence of self-repair during SOSIP.