Fluorescent Patterns by Selective Grafting of a Telechelic Polymer

Maciej Kopeć,* Sinem Tas, Marco Cirelli, Rianne van der Pol, Ilse de Vries, G. Julius Vancso,† and Sissi de Beer

Materials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

Supporting Information

ABSTRACT: The preparation of patterned ultrathin films (sub-10 nm) composed of end-anchored fluorescently labeled poly(methyl methacrylate) (PMMA) is presented. Telechelic PMMA was synthesized utilizing activator regenerated by electron transfer atom transfer radical polymerization and consecutively end-functionalized with alkynylated fluorescein by Cu-catalyzed azide–alkyne cycloaddition (CuAAC) “click” chemistry. The polymers were grafted via the α-carboxyl groups to silica or glass substrates pretreated with (3-aminopropyl)triethoxysilane (APTES). Patterned surfaces were prepared by inkjet printing of APTES onto glass substrates and selectively grafted with fluorescently end-labeled PMMA to obtain emissive arrays on the surface.

KEYWORDS: grafting to, inkjet printing, polymer brushes, ATRP, click chemistry

Preparation of patterned functional surfaces is of paramount importance in areas such as sensing, cell adhesion, nanoelectronics, “smart textiles”, etc. Among various ways of patterning, inkjet printing of polymers provides fast, scalable deposition, which is mainly useful in fabrication of all-organic integrated circuits or optoelectronic devices.

A particularly interesting approach to patterning is employing surface-grafted polymer films (e.g., polymer brushes) as ultrathin nanocoatings. Surface-grafting of polymers has emerged as a powerful means of surface modification and preparation of hybrid materials. They can be easily obtained by various techniques, typically by reversible deactivation radical polymerizations (RDRP), which enables controlled synthesis of polymers with precisely tailored molecular weights, dispersities, chain topologies, and functionalities. Two general approaches to surface-anchored polymer layers involve attaching end-functionalized polymer chains to a surface modified with reactive groups (grafting to) or surface-initiated polymerization from a surface-immobilized initiator layer (grafting from).

Furthermore, state-of-the-art patterning techniques such as microcontact printing, can be employed at the stage of initiator deposition, followed by surface-initiated polymerization to introduce surface patterns. Similarly, inkjet printing has been used either to directly prepare initiator patterns or to selectively etch homogeneously deposited initiator layers. Utilizing this technique, Edmonson et al. described the deposition of polyelectrolyte-based macroinitiators which, due to phase separation in a printed drop, allowed submicrometer patterning of subsequently grafted brushes. Additionally, recent progress in photoinduced RDRP methods opened a straightforward route to photopatterning of polymer brushes by spatially controlled polymerization through a photomask. Prominent examples of applications of these patterned coatings include rewritable surfaces composed of fluorescent brushes prepared via microcontact printing demonstrated by du Prez et al. Recently, Hawker et al. reported the fabrication of photopatterned arrays of donor–acceptor photoactive brushes into a fully operating multicolor and white organic light emitting diode (OLED) devices.

The grafting from approach is predominantly used to obtain end-anchored polymer films, as it leads to higher grafting densities and thicknesses. However, coupling a presynthesized polymer to the surface allows more precise characterization of molecular weight, dispersity, and chain-end functionality of tethered chains before grafting. Furthermore, relatively straightforward scale-up and simplicity make grafting to promising for preparation of functional polymer nanocoatings.

In this study, we present the fabrication of patterned end-labeled fluorescent films grafted to surfaces selectively modified with (3-aminopropyl)triethoxysilane (APTES) utilizing inkjet printing. Precise localization of chromophores in polymer nanostructures can be especially useful in light harvesting applications, where aggregation of chromophores is often a serious limitation. Attaching the dye at the chain-end of a polymer chain rather than as a side group in each repeating unit may lead to lower aggregation and prevent self-quenching, thus increasing the quantum efficiency of the emitting layer. Additionally, it can ensure minimal interaction of...
the dye with the surface as well as enable further selective binding of molecules to the end-functionalized film. To the best of our knowledge, this is the first demonstration of the grafting to method as a route to patterned surfaces from end-labeled polymers.

Designer telechelic poly(methyl methacrylate) (PMMA) functionalized with a surface-reactive carboxyl group and a fluorescent dye was synthesized according to Scheme 1. The familiar combination of atom transfer radical polymerization (ATRP) with Cu-catalyzed azide−alkyne cycloaddition (CuAAC) was used as a straightforward route to prepare polymers with desired chain-end functionality. First, well-defined PMMA was synthesized by activators regenerated by electron transfer (ARGET) ATRP. Importantly, α-bromophenylelactic acid (BPAA) was used as initiator to introduce carboxyl groups at the α-chain ends. The reaction was conducted at 60 °C in anisole with 50 ppm (vs monomer) of CuBr2/TPMA (tris(2-pyridiylmethyl)amine) catalyst and tin(II) 2-ethylhexanoate as a reducing agent. Gel permeation chromatography (GPC) measurements (Figure 1a) confirmed excellent control over the polymerization and formation of well-defined PMMA (Mn,theory = 17 000, Mn,GPC = 18 500, Mn/Mw = 1.15). Next, the bromine chain-ends were transformed to azides by reacting PMMA-Br with NaN3 before employing CuAAC to click azides with an alkyne-functionalized fluorescein derivative (5-FAM). 1H NMR measurements showed typical spectra of PMMA, although due to the relatively high Mn, no peaks assignable to the end groups (i.e., the initiator and the fluorescent dye) were detected (Figure S1). Interestingly, the chromatograms of PMMA-Br and PMMA-N3 essentially overlapped, while a visible shift toward higher molecular weights was observed after reaction with 5-FAM (Figure 1a). This was likely due to the high molar mass of the dye (M_m,FAM = 413 g/mol). A GPC trace of a control experiment, namely upon treating PMMA-N3 with 5-FAM without the catalyst, did not exhibit any shift (Figure S2).

In all cases, dispersities remained low (Mw/Mn < 1.15), without any visible tailing. To unequivocally confirm the chain-end functionalization, the attachment of the fluorescein was followed by spectrofluorometry in isopropanol/water mixture (4/1 v/v, Figure 1b), a good solvent for both PMMA and fluorescein. The excitation and emission spectra of the PMMA-FAM showed maxima at 488 and 524 nm, respectively, corresponding to the free 5-FAM (Figure S3). No fluorescence was observed for control samples obtained by stirring PMMA-N3 in DMF with 5-FAM without CuBr overnight, ruling out any physical contamination of the polymer with the dye.

Dye-functionalized films were prepared by surface grafting to silica substrates previously modified with APTES via chemical vapor deposition (CVD). Simple dip coating from a DMF solution of the PMMA-FAM (1 mg/mL) was used to couple α-carboxyl groups of the telechelic polymer with the amine groups of APTES. The reaction was conducted at room temperature without any additional catalyst. After 72 h, the wafers were removed from the solution and analyzed by atomic force microscopy (AFM) to reveal a uniform film on the surface (Figure 1c). The average dry thickness of the film measured by AFM after gently scratching the surface using Teflon tweezers was found to be 6 ± 2 nm. Grafting density was then determined from the equation:

\[
\sigma = \frac{N_A \rho h}{M_n}
\]

where \(N_A\) is the Avogadro number, \(\rho\) is polymer density (1.18 g/cm³), \(h\) is dry film thickness, and \(M_n\) is the molecular weight of the dye-functionalized PMMA (Mn = 19 000−20 000). The grafting density was calculated to be in the range of \(\sigma = 0.14−0.22\) nm⁻². Due to the slow diffusion of polymer chains to the surface, shorter deposition times resulted in very thin films with no uniform surface coverage, rendering AFM thickness measurements inconclusive (Figure S4).
Glass substrates were functionalized in a similar fashion to enable fluorescence measurements. Figure 1d shows a plane scan of the PMMA-FAM layer recorded by confocal microscopy. An isopropanol/water mixture (4/1 v/v) was used as solvent to ensure good solubility of the PMMA backbone as well as efficient solubilization of the hydrophilic chain-ends. Clear, uniform emission corresponding to the fluorescein-modified chain ends was observed. The dark area of the image corresponds to the region where the liquid already evaporated, leaving a dry film. As expected, fluorescence was quenched due to aggregation of the dye upon the collapse of the grafted polymer chains, and no emission was observed in this area. We very recently presented a similar behavior in an analogous system of polymer brushes synthesized by the grafting from approach.

Patterned surfaces were then fabricated to demonstrate the versatility of the developed approach and to prove the selective binding between the PMMA-FAM polymer and the APTES-based patterns. Hydrophilic glass substrates were modified by inkjet printing of APTES ink prepared in a mixture of ethanol and glycol (3/2 v/v), followed by annealing in vacuum at 110 °C for 1 h. Surface wettability is a critical parameter, which has an effect on the final sizes and shape of printed droplets. Therefore, ethylene glycol was used as a cosolvent due to its high boiling point and low surface tension. The contact angle between the APTES ink and glass substrate was measured to be 20°. Thus, the diameter of the printed droplets (around 100–120 μm, Figure 2 top row) was larger than the diameter of the droplet generated by the nozzle (60 μm).

As-prepared printed surfaces were immersed in a DMF solution of PMMA-FAM under the same conditions as described above for the silicon wafers. AFM imaging of the dry printed droplets revealed few-micrometer-thick features of polymerized/cross-linked APTES (Figure S5). The surface roughness values of the annealed drops were on the order of R_a = 100–150 nm. Confocal fluorescent microscopy was used to visualize printed patterns functionalized with PMMA-FAM films in isopropanol/water or acetone (Figure S6). Fluorescent patterns were obtained selectively at the printed spots of ~120 μm in diameter and with various spacing between the droplets. Most importantly, no signs of fluorescence were detected outside of the printed areas, confirming that nonspecific deposition on the nonfunctionalized surface did not occur via, e.g., physisorption. Even though high surface roughness of the drops prevented direct measurements of grafting density of PMMA-FAM films, observed uniform emission from the printed spots indicated
they were successfully decorated with a thin film of PMMA-FAM.

In summary, we demonstrated a straightforward procedure to fabricate end-functionalized polymer films by the grafting to method using a designer well-defined telechelic polymer synthesized by combination of ARGET ATRP and click chemistry. By employing CVD or inkjet printing of APTES to pretreat the surface, the following attachment of a fluorescent PMMA-FAM was realized by dip-coating from DMF solution. Selective functionalization of the APTES-modified surfaces or printed spots was confirmed by AFM and fluorescence microscopy. Given the versatility of both ATRP and click chemistry, this approach can be viewed as a general strategy for fabrication of polymer-grafted surfaces with various functionalities readily available by simple chain-end substitution. Such functional patterned surfaces can find applications in sensing, light harvesting, or organic electronics. Further experiments are underway to extend this approach to different polymer systems as well as to elucidate the effect of grafting density on the photophysical properties of end-labeled surface-anchored chains.

**ASSOCIATED CONTENT**

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsapm.8b00180.

Experimental procedures, 1H NMR spectrum of PMMA-FAM, GPC traces of control experiments, excitation and emission spectra of 5-FAM, AFM images of printed drops, and fluorescence images recorded in acetone (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: m.m.kopec@utwente.nl.

ORCID ®

Maciej Kopec: 0000-0003-0852-1612
G. Julius Vancso: 0000-0003-4718-0507

Present Address

†G.J.V.: School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

M.K. and G.J.V. thank the 4TU.High-Tech Materials research program “New Horizons in designer materials” (www.4tu.nl/htm) 32 for financial support. M.C. and G.J.V. thank the Marie Curie Initial Training Network “Complex Wetting Phenomena” (CoWet), grant agreement 607861. S.T. thanks the University of Twente and the MESA+ Institute for Nanotechnology for financial support. Mr. Clemens Padberg is acknowledged for his support with polymer characterization.

**REFERENCES**

(1) Rim, Y. S.; Bae, S.-H.; Chen, H.; De Marco, N.; Yang, Y. Recent Progress in Materials and Devices toward Printable and Flexible Sensors. Adv. Mater. 2016, 28, 4415–4440.
(2) Nie, Z.; Kumacheva, E. Patterning Surfaces with Functional Polymers. Nat. Mater. 2008, 7, 277.
(3) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. High-Resolution Inkjet Printing of All-Polymer Transistor Circuits. Science 2000, 290, 2123.
(4) de Gans, B.-J.; Duineveld, P. C.; Schubert, U. S. Inkjet Printing of Polymers: State of the Art and Future Developments. *Adv. Mater.* 2004, 16, 203−213.

(5) Tekin, E.; Smith, P. J.; Schubert, U. S. Inkjet Printing as a Deposition and Patternning Tool for Polymers and Inorganic Particles. *Soft Matter* 2008, 4, 703−713.

(6) Currie, E. P. K.; Norde, W.; Cohen Stuart, M. A. Tethered polymer chains: surface chemistry and their impact on colloidal and surface properties. *Adv. Colloid Interface Sci.* 2003, 100−102, 205−265.

(7) Zoppo, J. O.; Ataman, N. C.; Mocny, P.; Wang, J.; Moraes, J.; Klok, H.-A. Surface-Initiated Controlled Radical Polymerization: State-of-the-Art, Opportunities, and Challenges in Surface and Interface Engineering with Polymer Brushes. *Chem. Rev.* 2017, 117, 1105−1131.

(8) Feng, X.; Sui, X.; Hempenius, M. A.; Vancso, G. J. Electrografting of Stimuli-Responsive, Redox Active Organometallic Polymers to Gold from Ionic Liquids. *J. Am. Chem. Soc.* 2014, 136, 7865−7868.

(9) Matyjaszewski, K.; Tsarevsky, N. V. Nanostructured Functional Materials Prepared by Atom Transfer Radical Polymerization. *Nat. Chem.* 2009, 1, 276−288.

(10) Matyjaszewski, K.; Tsarevsky, N. V. Macromolecular Engineering by Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* 2014, 136, 6513−6533.

(11) Zdyrko, B.; Luzinov, I. Polymer Brushes by the “Grafting to” Method. *Macromol. Rapid Commun.* 2011, 32, 859−69.

(12) Minxuan, K.; Libin, W.; Yanlin, S. Controllable Printing of PMMA in Alcohol-Water Solvent Mixtures. *Adv. Mater.* 2008, 20, 719−727.

(13) Jhaiver, S. B.; Beinhoff, M.; Hawker, C. J.; Carter, K. R.; Sogah, D. Y. Chain-End Functionalized Nanopatterned Polymer Brushes Grown via in Situ Nitroxide Free Radical Exchange. *Adv. Mater.* 2008, 20, 1178−1183.

(14) Zoppo, J. O.; Ataman, N. C.; Duineveld, P. C.; Schubert, U. S. An Unexpected Discovery from Inkjet Printing of Polyelectrolyte Macrominitiators. *J. Am. Chem. Soc.* 2016, 138, 9009−9012.

(15) Poelma, J. E.; Fors, B. P.; Meyers, G. F.; Kramer, J. W.; Hawker, C. J. Fabrication of Complex Three-Dimensional Polymer Brush Nanostructures through Light-Mediated Living Radical Polymerization. *Angew. Chem., Int. Ed.* 2013, 125, 6982−6986.

(16) Discekici, E. H.; Pester, D. Y.; Stricker, L.; Körsgen, M.; Ailinghaus, H. F.; Ravoo, B. J.; Prez, F. E. Reversible Polymer Brush Micropatterns Grafted by Triazolinedione Click Chemistry. *Angew. Chem.* 2015, 140, 13126−13129.