

Polymer Chemistry

rsc.li/polymers



ISSN 1759-9962



PAPER

Mojtaba Enayati and Alireza Abbaspourrad
Glass surface modification via Cu(0)-mediated living radical polymerization
of fluorinated and non-fluorinated acrylates



Cite this: *Polym. Chem.*, 2017, **8**, 7457

Glass surface modification *via* Cu(0)-mediated living radical polymerization of fluorinated and non-fluorinated acrylates

Mojtaba Enayati  and Alireza Abbaspourrad  *

Terminal silanol groups on the glass surface were used for the chemical bonding of α -bromo amide as the initiator for surface initiated Cu(0)-mediated living radical polymerization (LRP) to graft well-defined poly(butyl acrylate) (PBA) and poly(2,2,2-trifluoroethyl methacrylate) (PTFEM) brushes on the glass surface. A grafting to methodology was also performed by the modification of the glass surface using a thiosilane agent and performing a thio-bromo click reaction in the presence of PBA and PTFEM synthesized *via* Cu(0)-mediated LRP. Furthermore, a one-pot grafting to method was developed that proved a facile, fast, and efficient method for grafting a bromo-terminated polymer to the glass surface in one step. All glass slides were characterized using ATR-FTIR and UV-vis spectroscopy, water contact angle measurements and SEM. The surface topology and roughness of selected samples were analyzed using AFM. Results show that an ultrathin layer of a polymer with nanoscale features and high roughness was chemically grafted to the glass surface without compromising glass transparency. These methodologies can be used to graft well-defined polymers with different functionalities on the glass surface.

Received 7th September 2017,
Accepted 18th October 2017

DOI: 10.1039/c7py01530e

rsc.li/polymers

Introduction

The modification of different surfaces has been an extensively used method for the addition of functionalities to the surface including superhydrophobicity,¹ superhydrophilicity,² chemical resistance,³ UV protection,⁴ corrosion inhibition,⁵ anti-bacterial,⁶ anti-icing,^{7,8} sensing, and stimuli-response.⁹ Instead of physisorption, which relies on the secondary binding forces such as hydrogen bonding for the interaction of the surface with the coating material, chemisorption methods use chemical bonding to anchor the coating material to the surface. Therefore, it provides a more robust and durable coating that cannot be easily removed by solvents, mechanical forces, or processing conditions. Polymers are among the best materials for surface modification¹⁰ because of their ease of synthesis and their ability to be tailored for a specific application. Two methods widely used for the chemical anchoring of polymers to the surface of different materials are grafting from and grafting to. In the grafting from method the surface is functionalized with appropriate molecules that can initiate polymerization and a surface initiated polymerization (SIP) is subsequently performed in the presence of monomer(s) and solvent. In the grafting to method a chain end group of a pre-

synthesized polymer is reacted with a suitable functional group prepared on the surface of the material. While the grafting from method provides higher grafting densities (a requirement to prepare polymer brushes), the grafting density is low in the grafting to method because of steric hindrance.¹¹

Different polymerization methods were used for surface modification *via* grafting from and grafting to strategies. However, controlled/living radical polymerization (CRP/LRP) methods¹² have received the greatest attention because of their extraordinary ability to control the polymer molecular weight, dispersity, macromolecular architecture, and composition. These methods provide unprecedented polymer structures that would not be possible or would be hard to achieve by using the conventional polymerization methods, including block copolymer brushes,¹³ surface grafted comb-structured polymers,¹⁴ bimodal polymer brushes,¹⁵ molecular weight gradient polymer brushes,¹⁶ and mixed binary polymer brushes.¹⁷ Of the many CRP/LRP methods available,¹² four of them are the most frequently used for surface initiated polymerization (grafting from). These include atom transfer radical polymerization (ATRP),¹⁸ reversible addition-fragmentation chain transfer (RAFT),¹⁹ photoiniferter-mediated polymerization (PIMP),²⁰ and nitroxide-mediated polymerization (NMP).²¹ These methods owe their wide applications to the simplicity of the experimental setup, compatibility with different functional groups, mild reaction conditions, and their ability to be run in different solvents as well as water.

Department of Food Science, College of Agriculture and Life Sciences,
Cornell University, Ithaca 14853, NY, USA. E-mail: alireza@cornell.edu

Since its invention and development by Percec *et al.*²² single electron transfer living radical polymerization (SET-LRP) or Cu(0)-mediated LRP has been used extensively within the polymer community as a simple and robust LRP method to synthesize well-defined polymers with complex structures.^{23,24} Cu(0)-mediated LRP uses copper(0) in different forms (wire, powder, and *in situ* produced nascent particles) as the catalyst with the combination of a ligand such as tris(2-dimethylaminoethyl)amine (Me₆-TREN) in polar protic and aprotic solvents that facilitate the disproportionation of Cu(I)X to Cu(0) and Cu(II)X₂. Cu(0)-mediated LRP is attractive because of its high tolerance to air,^{25,26} impurities,²⁷ and even radical inhibitors.²⁸ Cu(0)-mediated LRP is also well known for its ultrafast rate of polymerization at room temperature and below^{22,29} and its ability to generate polymers with perfect and near-perfect chain end functionality.³⁰ This is crucial in terms of making block copolymers as well as functional polymers. A polymer with high chain end fidelity is a perfect macroinitiator³¹ for the polymerization of the second monomer and for the functionalization of the chain end with other desired functionalities, especially through click chemistry.³² One of the reactions of the bromo-functionalized chain end of polymers synthesized *via* Cu(0)-mediated LRP is the “thio-bromo click” reaction with the thiol group that was originally used for showing the chain end fidelity and the livingness of SET-LRP.³³

While Cu(0)-mediated LRP appears to be an ideal method for surface initiated polymerization of different surfaces for the production of surfaces with special properties such as thermoresponse^{34,35} and anti-biofouling,³⁶ there are few publications using Cu(0)-mediated LRP for surface initiated polymerization. The materials that were modified with surface initiated Cu(0)-mediated LRP include silicon wafers,^{34–39} nanoparticles,^{40,41} carbon nanotubes, graphene,^{42–45} silicon nanowire arrays,⁴⁶ cellulose nanocrystals,^{47,48} and even sweet potato starch residue.⁴⁹ These publications are a few examples showing the ability and opportunities provided by Cu(0)-mediated LRP for use in grafting different monomers to a variety of surfaces. To our knowledge, however, there is no report of a surface initiated Cu(0)-mediated LRP performed directly on the glass surface. Glass surface modifications have been studied and done for more than 7 decades after the first application of glass fibers inside polymeric resins. This has led to a huge demand for new bonding technologies.^{50,51}

Here we report a glass surface initiated Cu(0)-mediated LRP of BA and TFEM in DMSO and 2-propanol to modify the glass surface with chemically bound polymers, which are hydrophobic and UV absorbent. The glass surface was also modified *via* the grafting to method by using the thio-bromo click reaction of the bromo chain end of the well-defined PBA and PTFEM. The PBA and PTFEM were synthesized *via* conventional Cu(0)-mediated LRP and then reacted with the glass surface that was functionalized with thiosilane. A one-pot grafting to method was also developed to chemically modify the glass surfaces in a one-step reaction. In all cases, an ultrathin polymer layer with high roughness formed on the glass surface. This layer was characterized by SEM, AFM, ATR-FTIR, and UV-vis

spectroscopy and contact angle measurements. Results showed that both the grafting from and grafting to methodologies can be used to functionalize the glass surface by Cu(0)-mediated LRP.

Results and discussion

Cleaning and functionalization of glass slides

Fig. 1 shows the water contact angle of the glass slides after cleaning with an aqueous 10 wt% NaOH solution. The water contact decreased with the increase of the immersion time in the base solution. The contact angle reaches almost zero upon heating the glass slide at 400 °C for 2 h. The glass slides, however, should not be used immediately for the functionalization with silane coupling agents, since a thin layer of water is recommended for the formation of a uniform and packed organosilane monolayer.⁵²

Surface initiated Cu(0)-mediated LRP (grafting from) of BA and TFEM

α -Bromo esters and amides are the most popular initiators for Cu(0)-mediated LRP and are usually synthesized using the reaction of appropriate acid bromide with alcohols or amines.^{33,53} An amide bond, however, is substantially stronger and more stable than an ester bond.⁵³ Scheme 1a and b demonstrate a two-step method of attaching the initiator to the surface of the clean glass slides through an amide bond.

A Teflon vessel was used for the functionalization as well as grafting from and grafting to reactions to avoid side reactions with the glassware. Reagents were used in excess to ensure maximum functionalization. An increase in contact angle from almost zero to 84.6° was observed upon functionalization of glass slides with alpha-bromo amide (Fig. 2). These glass slides were used for the surface initiated Cu(0)-mediated LRP (grafting from) of BA in 2-propanol and TFEM in DMSO using copper powder as the catalyst (Scheme 1c). Since the initiator is immobilized on the surface of the glass, and the catalyst Cu(0) does not dissolve in the reaction mixture and is heterogeneous, a fine copper powder is necessary to help the acti-

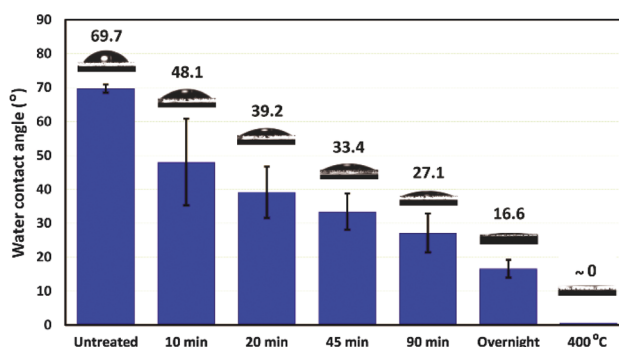
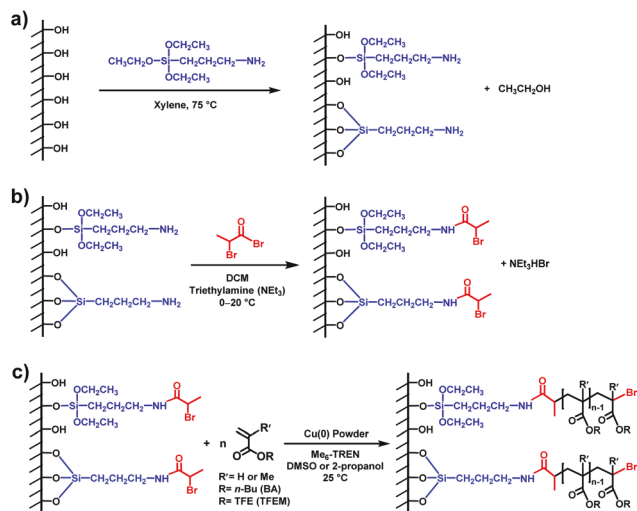


Fig. 1 Contact angles of glass slides before and after cleaning with 10% NaOH for different times compared to the slides heated at 400 °C for 2 h.



Scheme 1 "Grafting from" methodology used for the growth of the polymer chains on the glass surface.

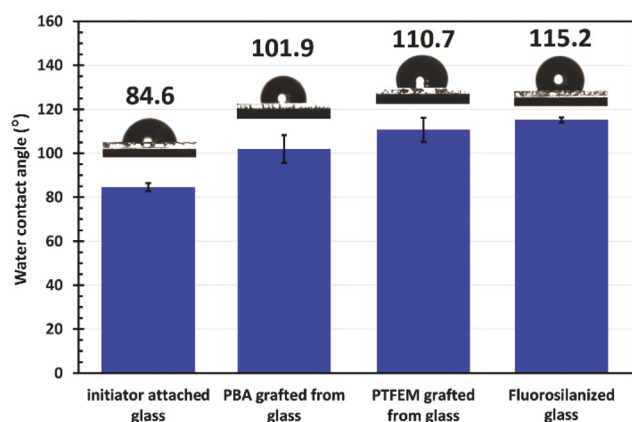


Fig. 2 Contact angles of glass slides before and after grafting of PBA and PTFEM *via* surface initiated Cu(0)-mediated LRP compared to the glass slide functionalized with perfluoro trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane.

vation process happen smoothly. It has been proved that the particle size of Cu(0) has a profound effect on the rate of the reaction,⁵⁴ because Cu(0)-mediated LRP is believed to be a surface-mediated process.²² Therefore, a moderate particle size (44 μm) was chosen here to provide a moderate polymerization rate. These moderately sized particles are also easier to remove after polymerization.

Fig. 3 shows the ATR-FTIR spectra of the glass slides after surface initiated Cu(0)-mediated LRP reaction. The peak of the carbonyl group for PBA at 1735 cm^{-1} and for PTFEM at 1750 cm^{-1} and also the peak for the C-H bond at 2840 to 3000 cm^{-1} can be easily observed in this figure showing the grafting of PBA and PTFEM on the glass surface. For the PTFEM, peaks at 1120 , 1160 and 1280 cm^{-1} which are characteristic of this polymer⁵⁵ can be observed. However, the characteristic absorptions for the $-\text{CF}_3$ band at 630 cm^{-1} ,⁵⁵ and other

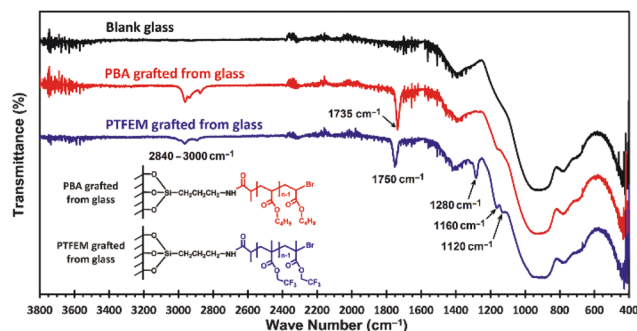


Fig. 3 ATR-FTIR spectra of the blank glass slide compared to the glass surface grafted by PBA and PTFEM *via* the "grafting from" methodology.

characteristic bands of these two polymers in the range of 600 to 1000 cm^{-1} , are covered by the dominant Si-O-Si and Si-OH bands of the glass.

As mentioned in the introduction, one application of grafting polymers on the surface is to provide a UV absorbing layer. Glass has a strong UV absorption profile but mostly in the UV-C range (280 to 200 nm); these wavelengths are almost completely removed by ozone and other atmospheric gases from sunlight. For the 400 to 280 nm range, however, the atmospheric absorption of UV light is not complete and for this range of UV, protection is necessary. Fig. 4 shows the UV-vis spectra of the PBA and PTFEM grafted glass by surface initiated Cu(0)-mediated LRP in the 800 to 200 nm range. As can be seen in this figure, the absorbance in the visible range (800 to 400 nm) is almost the same as blank glass (Fig. 4a), showing the transparency of these samples. There is a relatively large difference observed in the range of 400 to 200 nm (Fig. 4b), showing superior UV absorption compared to glass alone. The UV absorption, however, is more efficient in the range of 320 to 280 nm (UV-B) and less efficient in the range of 400 to 320 nm (UV-A). This is in agreement with the UV absorption of PTFEM, which has the maximum at around 305 nm (ref. 56) and the PBA that has several strong UV peaks at 275 , 328 and 345 nm in solution⁵⁷ and at 300 nm as a film.⁵⁸ It is important to mention that the PBA provides slightly better UV protection compared to PTFEM in our samples.

The contact angles of the glass slides before and after grafting *via* Cu(0)-mediated LRP are shown in Fig. 2. A glass slide functionalized with trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane was also prepared for comparison. It is remarkable that samples with PTFEM brushes show almost the same contact angle as the fluorosilanized sample having 13 fluorine atoms per chain. This indicates that the chemical structure of the coating itself is not enough for achieving higher contact angles, but an appropriate degree of roughness is also needed for that, as explained by the Cassie-Baxter model.⁵⁹ As shown by the morphology of these glass slides (Fig. 12 and 14), a rather ordered roughness generated on the surface of the glass, together with the chemical structure of the polymers, is responsible for the increase in contact angle. The contact angle of PTFEM (110.7°)

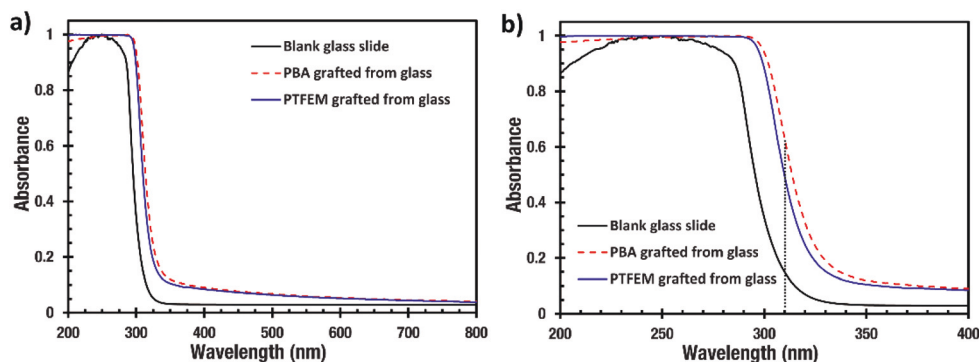
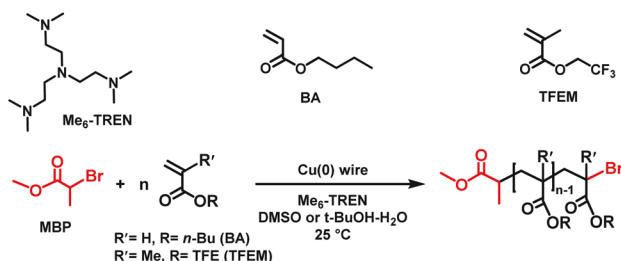


Fig. 4 UV-vis spectra of the blank glass slide (black solid line) compared to PBA (red broken line) and PTFEM (blue solid line) grafted from the glass surface.

is remarkably higher than the numbers reported for a surface coated with this polymer (99.9%).⁶⁰ This further highlights the importance of the presence of an appropriate roughness of the grafted surface compared to the physically coated glasses.⁶¹



Scheme 2 Cu(0)-mediated LRP of BA and TFEM using a copper wire as the catalyst and methyl 2-bromopropanoate (MBP) as the initiator.

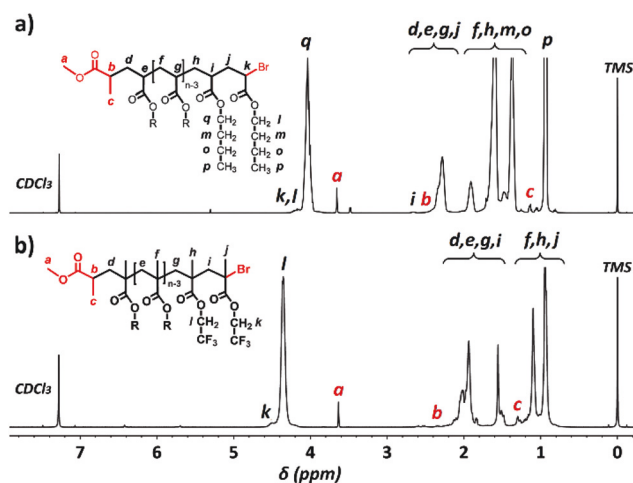


Fig. 5 (a) 500 MHz ^1H -NMR of PBA synthesized *via* Cu(0)-mediated LRP of BA in *t*-BuOH–water catalyzed by an activated Cu(0) wire of 12.5 cm at 25 °C, isolated at 97% conversion. Reaction conditions: BA = 2.0 mL, *t*-BuOH = 1.9 mL, water = 0.1 mL, $[\text{BA}]_0/[\text{MBP}]_0/[\text{Me}_6\text{-TREN}]_0 = 80/1/0.1$, (b) 500 MHz ^1H -NMR of PTFEM synthesized *via* Cu(0)-mediated LRP of TFEM in DMSO catalyzed by an activated Cu(0) wire of 12.5 cm at 25 °C, isolated at 96% conversion. Reaction conditions: TFEM = 2.0 mL, DMSO = 2.0 mL, $[\text{TFEM}]_0/[\text{MBP}]_0/[\text{Me}_6\text{-TREN}]_0 = 60/1/0.1$.

Grafting BPA and PTFEM synthesized by Cu(0)-mediated LRP to the glass surface *via* a thio-bromo click reaction

Thio-bromo click chemistry was used for grafting well-defined PBA and PTFEM synthesized by Cu(0)-mediated LRP using a copper wire as the catalyst (Scheme 2). BA was poly-

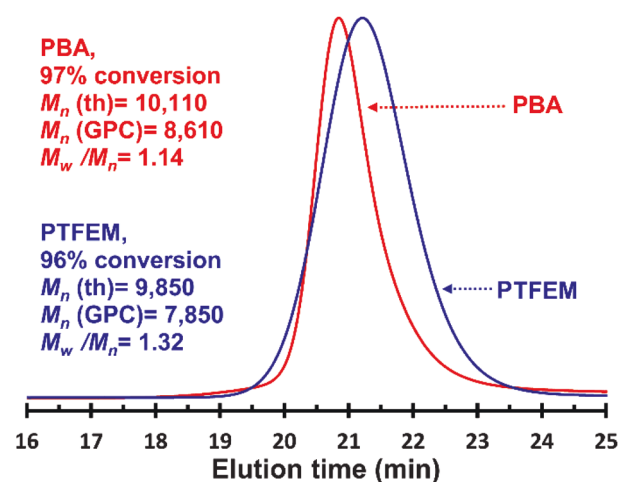
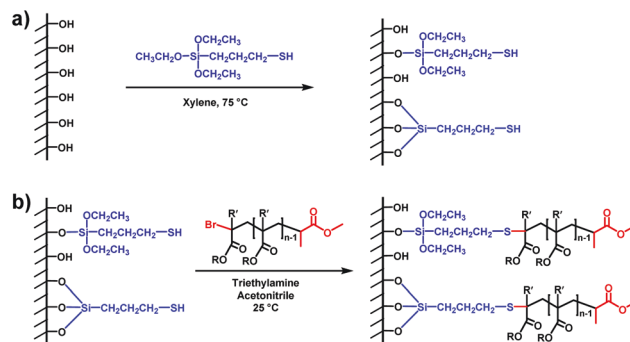


Fig. 6 GPC of the PBA and PTFEM synthesized *via* Cu(0)-mediated LRP using a 12.5 cm Cu(0) wire in *t*-BuOH–water (95/5, v/v) and DMSO, respectively.



Scheme 3 "Grafting to" methodology *via* "thio-bromo click" used for the growth of the polymer on the surface of the glass.

merized in *t*-BuOH–water (95/5, v/v)²⁶ with a targeted molecular weight of 10 000 g mol^{−1} and TFEM was polymerized in DMSO also with a targeted molecular weight of 10 000 g mol^{−1}. Fig. 5 shows the ¹H-NMR spectra of PBA and PTFEM after purification and Fig. 6 shows the GPC graphs for the two polymers. Dispersity values were as low as 1.14 for PBA and 1.32 for PTFEM.

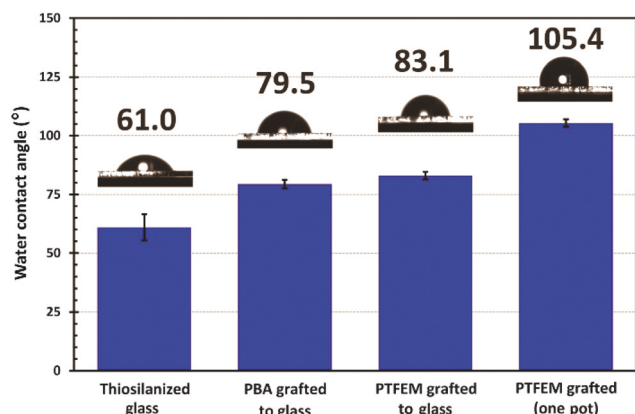


Fig. 7 Contact angles of glass slides before and after grafting to using PBA and PTFEM *via* thio-bromo click compared to glass slide functionalized with (3-mercaptopropyl)triethoxysilane.

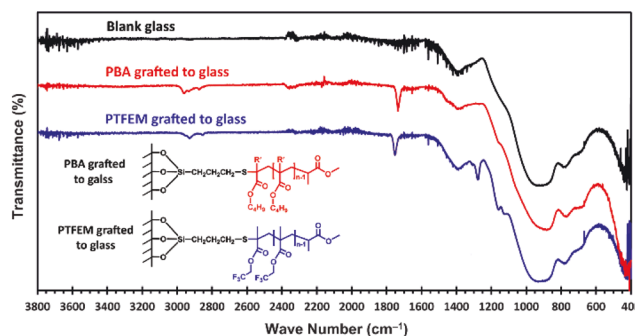


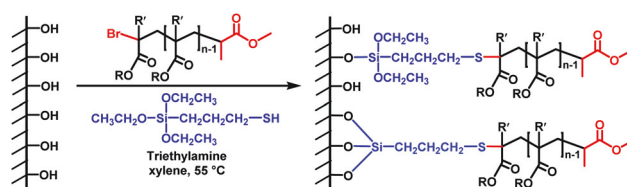
Fig. 8 ATR-FTIR spectra of the blank glass slide compared to the glass surface grafted by PBA and PTFEM *via* the “grafting to” methodology.

For performing a grafting to reaction by a thio-bromo click reaction of the bromo chain end of PBA and PTFEM, a thiol functionality would be needed on the surface of the glass. To do this, (3-mercaptopropyl)triethoxysilane was used to insert thiol groups on the surface of glass slides (Scheme 3a) and then they were subjected to grafting to using PBA and PTFEM in the presence of triethylamine (NEt₃).

Fig. 7 shows the contact angle of the thiosilane functionalized (Scheme 3) glass slide compared to glass slides that are functionalized by PBA and PTFEM *via* the grafting to methodology. An increase in contact angle was observed for the grafting on functionalized slides, which is lower compared to slides that were modified *via* the grafting from methodology (Fig. 2). This was not unexpected, since as per the literature, grafting to generates less grafting density compared to grafting from.¹¹

ATR-FTIR spectra as well as UV-vis spectra of the glass slides modified by the grafting to method are shown in Fig. 8 and 9. These spectra are almost the same as the slides modified with the grafting from method presented in Fig. 4 and 5. However, the UV absorbance in the range of 400 to 320 nm is almost the same as glass itself.

Besides the two-step grafting to methodology that was used (Scheme 3), a one-step (one-pot) methodology was also performed where glass slides, the thiosilane coupling agent, triethylamine, and the PTFEM were put together into the Teflon vessel using xylene as the solvent and heated at 55 °C for 3 hours (Scheme 4). The glass slides functionalized using this one-pot grafting method showed an even higher contact angle compared to those functionalized using the common two-step grafting to method (Fig. 7). As shown in the morphology sub-



Scheme 4 One-pot “grafting to” methodology *via* “thio-bromo click” used for the growth of the polymer on the surface of glass.

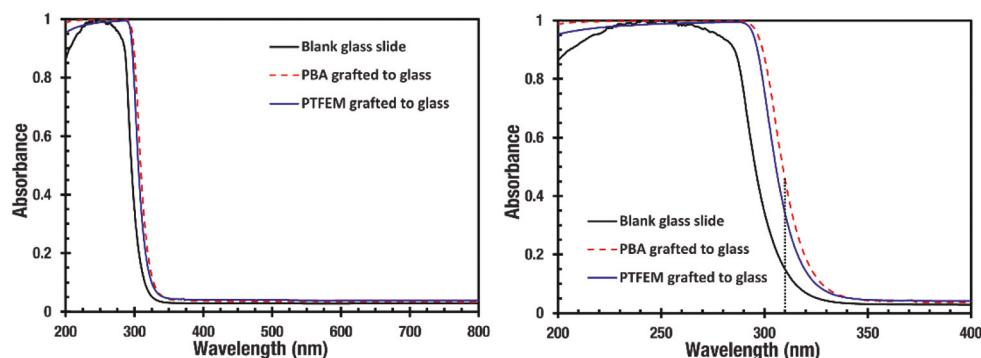
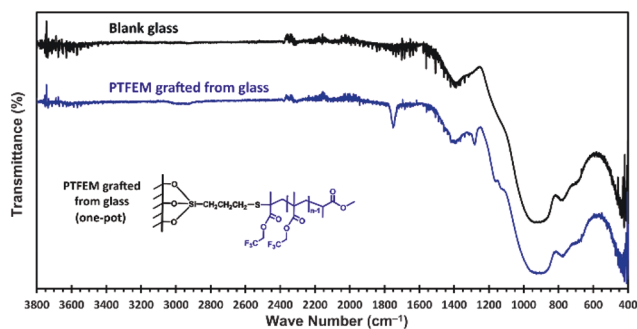


Fig. 9 UV-vis spectra of the blank glass slide (black solid line) compared to PBA (red broken line) and PTFEM (blue solid line) grafted to the glass surface.

Table 1 The roughness of selected samples compared to a blank glass slide

Entry	Sample name	Average roughness (R_a) (nm)	Root mean square roughness (R_q) (nm)
1	Blank slide	0.18	0.26
2	PTFEM grafted from glass	5.63	8.68
3	PTFEM grafted on glass	2.42	4.72
4	PTFEM grafted on glass (one-pot)	8.46	10.58

**Fig. 10** ATR-FTIR spectrum of the blank glass slide compared to the glass surface grafted by PTFEM *via* thio-bromo click in one pot.

chapter and Table 1, the one-pot methodology provides higher roughness compared to the other two methods, which is responsible for the high contact angle. ATR-FTIR and UV-vis spectra of the glass slide modified by the one-pot grafting to method (Fig. 10 and 11) confirm the attachment of PTFEM on the surface of the glass slides. This one-pot grafting to method using thio-bromo click provides a facile, fast, and effective route for the modification of glass and silica surfaces with different polymers.

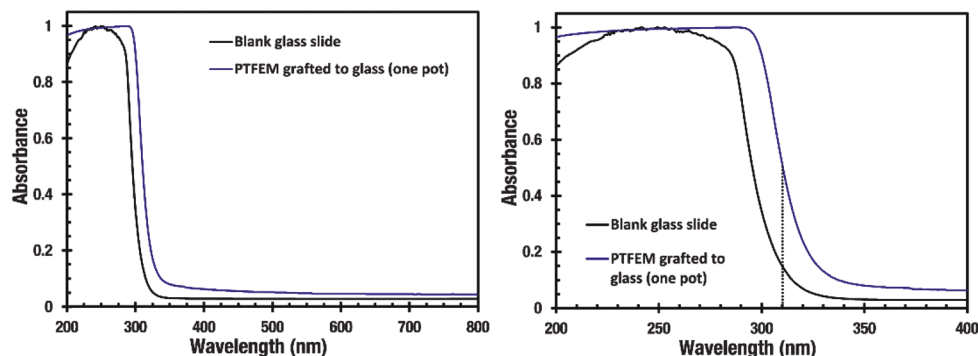
Morphology and roughness of the glass slides modified *via* the grafting from and grafting to methodologies by SEM

In order to observe the surface morphology of the glass slides modified through surface initiated Cu(0)-mediated LRP (graft-

ing from) and thio-bromo click (grafting to), the glass slides were analyzed by SEM. Fig. 12 shows SEM images of the glass slides modified by using the grafting from and grafting to methodologies. In all cases, a well-distributed surface roughness with nanometer size features in the range of 100 to 200 nm width was generated by the modification method. However, in the case of the glass slides modified with PTFEM *via* the grafting to method (Fig. 12j–l), a different roughness was observed with a microstructure that is similar to shark skin.⁶² It is remarkable that the thickness of the polymer layer is less than 100 nm (Fig. 12c), which indicates the formation of an ultrathin coating on the glass surface (this is further confirmed by AFM topographic images in Fig. 14). When trying to measure the weight percentage of this coating by TGA analysis, the weight loss was negligible (from 0.20 wt% to 0.27 wt%) – this value lies almost within the instrumental error of the TGA (Fig. 13). Due to this extremely low weight loss, further interpretation of the TGA is not provided. SEM and TGA results, also confirmed by the UV-vis spectra shown in Fig. 4, 9 and 11, indicate almost equal absorption of the coated glass and blank glass in the visible region.

The difference in surface morphology of these samples can be related to different parameters such as differences in the molecular weight and dispersity of the brushes by different methods. The chemical bonds that attach these polymers to the surface are different, including a rigid amide bond for the grafting from method and a flexible thioether bond for the grafting to method. Also, the grafting density is different based on the method that is used (Fig. 13).

In order to investigate the surface topology and roughness of the glasses modified by polymer brushes, atomic force microscopy (AFM) analysis of the selected samples from each category was performed, using a blank glass slide for comparison. Fig. 14 shows the topology of the blank glass slide (Fig. 14a) compared to the topology of the PTFEM grafted from glass (Fig. 14b), the PTFEM grafted on glass (Fig. 14c) and the PTFEM grafted on glass in one pot (Fig. 14d). Table 1 summarizes the roughness data of these samples obtained by AFM. It is obvious from the data in Table 1, as well as the surface topologies in Fig. 14, that the grafting methods

**Fig. 11** UV-vis spectra of the blank glass slide (black) compared to PTFEM (blue) grafted to the glass surface *via* thio-bromo click in one pot.

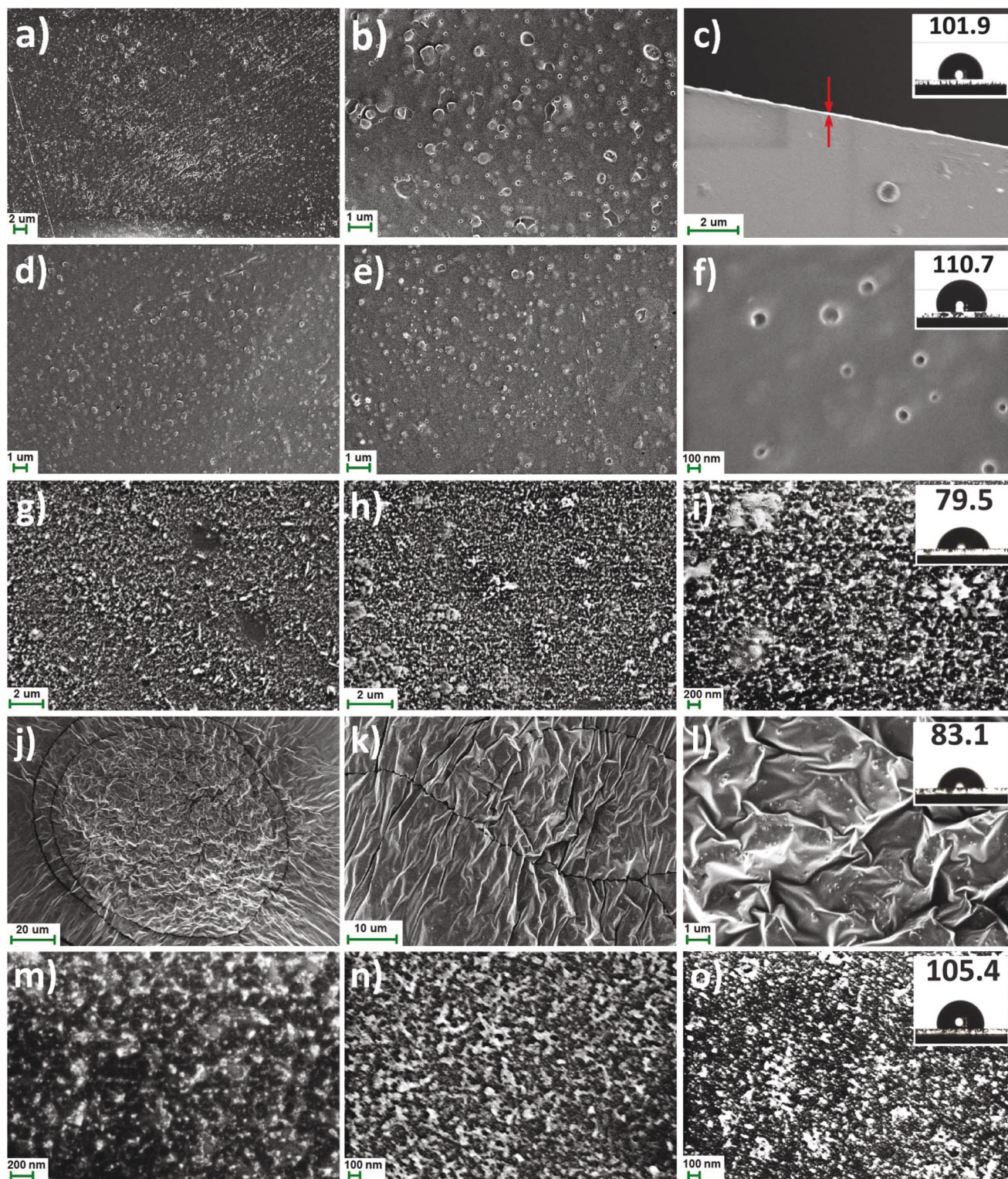


Fig. 12 SEM photographs of glass slides grafted with polymers on the surface. (a, b, c) PBA grafting from and (d, e, f) PTFEM grafting from via surface initiated Cu(0)-mediated LRP; (g, h, i) PBA grafting to and (j, k, l) PTFEM grafting to via thio-bromo click and (m, n, o) PTFEM grafting to via a one-pot thio-bromo click reaction.

indeed increase the roughness of the glass surface. This roughness as well as the chemical structure of the polymer brushes are responsible for the water contact angle on the

modified glass slides (Fig. 12). For the blank glass slides that show low roughness, with exposed silanol groups, most probably a Wenzel mode⁶³ of interaction between the water

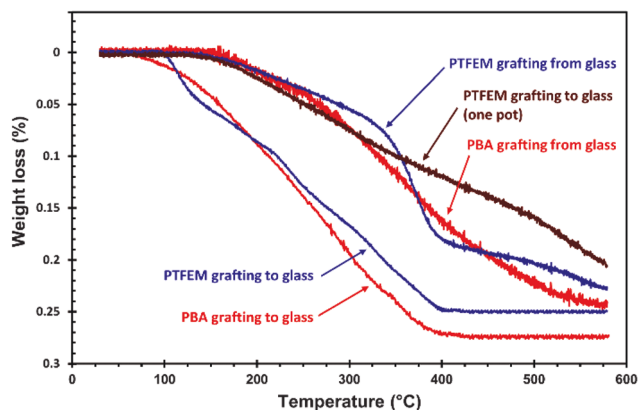


Fig. 13 TGA thermograms of the glass slides grafted with PBA and PTFEM via grafting from and grafting to. The thermograms were prepared at $10\text{ }^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere.

droplet and the surface exists. However, for the glass slides grafted with polymers, the increased roughness (Table 1) and hydrophobicity of the polymer brushes are responsible for providing a Cassie–Baxter mode⁵⁹ of interaction with the water droplet. From the surface topologies in Fig. 14, and the data in Table 1, it can be concluded that the one-pot grafting on methodology provides the highest roughness and a fair uniformity of grafting.

Conclusions

The glass surfaces were cleaned to expose most of the terminal silanol groups for use in chemically attaching an α -bromo amide as the initiator for Cu(0)-LRP of BA and TFEM from the surface of glass. This grafting from methodology through surface initiated Cu(0)-mediated LRP provides an ultrathin polymer layer that chemically bonds to the surface of the glass. The thickness of the polymer layer can be easily controlled by the time of the reaction and the mole ratio of the monomer to the surface initiator. Also in a grafting to methodology, the glass surfaces were functionalized by a thiosilane reagent to put thiol groups on the surface and use them in the subsequent thio-bromo click reaction with bromo-terminated PBA and PTFEM. The ATR-FTIR spectra show the formation of a polymer layer on the surface of the glass. This was confirmed by the UV-vis spectra of the functionalized glass compared to blank glass slides, showing superior UV protection of these polymeric layers. The contact angle measurements also showed a dramatic increase in water contact angle compared to blank glass slides with higher angles for the grafting from methodology, as is expected from the ability to produce higher grafting density in this method. A one-pot grafting to methodology was also developed by the reaction of blank glass slides with the thiosilane, the bromo-terminated polymer, the solvent and a base all together in a Teflon vessel, which

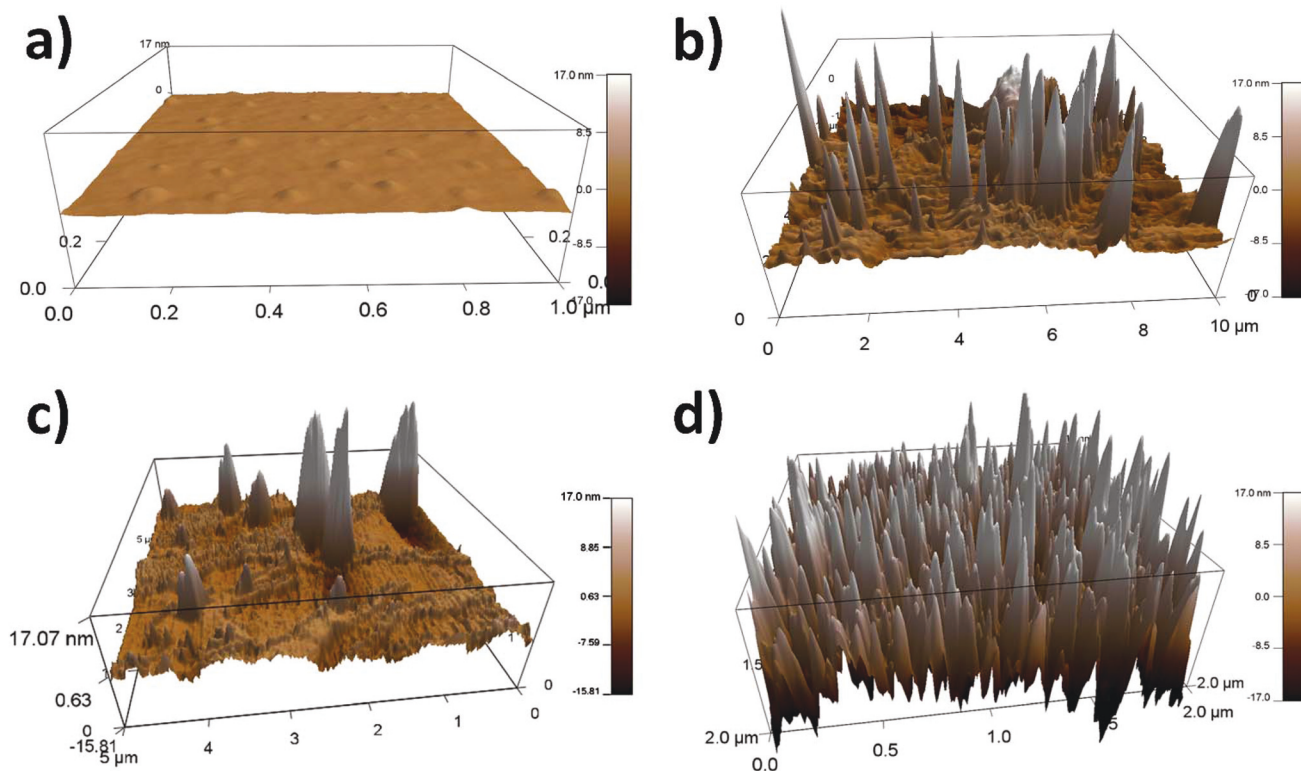


Fig. 14 AFM topographic images of a blank glass slide (a), the PTFEM grafted from glass (b), the PTFEM grafted on glass (c), and the PTFEM grafted on glass in one pot (d). Analysis of roughness is available in Table 1.

showed the superfast and efficient one-step grafting of polymer chains to the glass surface at relatively low temperature (55 °C). SEM photographs of all samples and AFM topographic images of selected samples showed the formation of a uniform ultrathin polymer layer with nanoscale roughness.

The one-pot grafting to methodology provides a robust and fast method for the functionalization of glass surfaces in any form without the need for complicated and tedious processes. These methodologies open up new avenues that have the potential to simplify and expand the modification of any kind of glass and silica surface with a large variety of polymers accessible *via* Cu(0)-mediated LRP.²³ Any kind of functionality and application such as impact modification, UV absorption, stimuli-response, *etc.* can be imparted to these surfaces by choosing the appropriate monomers and polymers. Results along these lines will be reported by our laboratory in the near future.

Experimental section

Materials

BA (99+%, Acros) and TFEM (99%, Oakwood Chemical) were passed over a short column of basic Al₂O₃ to remove the radical inhibitors just before being used. Methyl 2-bromopropanoate (MBP) (98%, TCI America), copper powder 325 mesh (44 µm) (99.9%, Oak wood chemical), 2-bromopropionyl bromide (97%, Alfa Aesar), NEt₃ (99.91%, Chem-Impex), DMSO (≥99.9%, certified ACS, Fisher), *t*-butanol (99.5%, certified, Fisher), 2-propanol (99.5%, certified, Fisher), xylene (mixture of isomers, ACS, Electron Microscopy Sciences), acetonitrile (99.5+%, EMD Chemicals Inc.), methanol (99.9%, Certified ACS, Fisher), acetone (99.8% Certified ACS, Fisher), (3-aminopropyl)triethoxysilane (≥98%, Sigma-Aldrich), (3-mercaptopropyl)triethoxysilane (94%, Alfa Aesar), and trichloro (1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (97%, Sigma-Aldrich) were used as received. Methylene chloride, also called DCM (99.9%, Certified ACS, Fisher), was dried over CaH₂ and freshly distilled before use. Milli-Q water was used in all experiments. Me₆-TREN was synthesized following a procedure found in the literature.⁶⁴ Square cover glass (18 × 18 mm, 0.17 to 0.25 mm thickness, Fisher) was used, after cleaning, for surface modification by the grafting from and grafting to methodologies.

Techniques

500 MHz ¹H-NMR spectra were recorded on a Bruker INOVA 500 NMR instrument at 28 °C in CDCl₃ using tetramethylsilane as an internal standard. Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were recorded on a Shimadzu IRAffinity-1S spectrophotometer. 128 scans with a resolution of 1 cm⁻¹ were performed on all samples. UV-vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer. A Waters Breeze GPC system with THF as the eluent, operated at 40 °C with a flow rate of 1.00 mL min⁻¹, was used for molecular weight and dispersity measurements. Three columns from Polymer Standards Service, USA

(Amherst, MA), PSS SDV (3000 Å, 1000 Å, and Linear M) calibrated with 19 narrow PS standards (PSS USA; Amherst, MA) with a MW range of 1000 to 1 000 000 g mol⁻¹, were used with an RI detector. Samples were dissolved in THF and passed through a small basic alumina column followed by filtering (0.2 micron, a nylon membrane) before injection. TGA thermograms were prepared using a TA Q100 instrument in the temperature range of 30 to 600 °C at a rate of 10 °C min⁻¹ under N₂ flow. Small pieces of grafted glass were taken carefully, weighed and put into the pan for measurement. The contact angles of water on different glass surfaces were recorded using a ramé-hart model 500. Around 2 µL of Milli-Q water was put on the surface and the contact angle was measured. SEM photographs were taken using a Zeiss 1550 Field Emission SEM machine. Samples were coated with an ultrathin Au/Pd coating before analysis. AFM analysis was done using an Asylum-MFP3D-Bio-AFM-SPM.

Cleaning of glass slide surfaces

Before performing any reaction on the surface of the glass slides, a cleaning process was needed to remove any surface contamination and to expose the terminal silanol groups on the surface. While different methods are available for cleaning the glass surface before functionalization, base wash⁶⁵ and basic and acidic piranha^{46,66} are the most common methods used. Fig. 1 shows the contact angle of the slides after the cleaning process in a 10% aqueous NaOH bath for different times. For the samples heated at 400 °C and washed subsequently in a NaOH bath for 10 min, the water droplet spread out totally on the glass surface, so the contact angle was too small to be measured by the tensiometer. Therefore, these slides were used for the functionalization process.

Functionalization of the glass surface

After the cleaning process, glass slides were mounted on a Teflon rod and inserted into a Teflon vessel for the reaction. A certain quantity of xylene was added to submerge the slides and a silane coupling agent ((3-aminopropyl)triethoxysilane, Scheme 1a or (3-mercaptopropyl)triethoxysilane, Scheme 3a) was added to prepare a 10% (v/v) solution. Reactions were run at 75 °C for 15 h (overnight) under N₂. Glass slides were washed with excess xylene and with acetone in a sonication bath, and dried under vacuum for the next reaction. For attaching the initiator moiety to the aminosilane (Scheme 1b), the same Teflon vessel methodology was used with a 10% (v/v) solution of 2-bromopropionyl bromide in DCM containing the equimolar triethylamine (NEt₃). The acid bromide was added slowly to the solution containing the glass slides and NEt₃ at 0 °C under N₂ and the reaction mixture was allowed to reach room temperature over 1 h after which it was maintained for another 12 h.

Surface initiated Cu(0)-mediated LRP of BA and TFEM (grafting from)

For surface initiated Cu(0)-mediated LRP (Scheme 1c), three glass slides with initiator functionality as well as three blank

slides were mounted on a Teflon rod and inserted into the Teflon vessel and copper powder was added. The Teflon vessel was closed and purged with N_2 . In a glass vial, monomer (BA or TFEM), solvent (2-propanol or DMSO) and Me_6 -TREN were mixed (total volume 20 mL, containing 10 wt% monomer) and bubbled with N_2 for 60 min at 20 °C, to remove oxygen. This solution was added to the Teflon vessel containing the slides under N_2 using a gas-tight syringe purged with N_2 at 25 °C. A high stirring rate is necessary especially at the beginning because of the heterogeneity of the reaction including initiator and catalyst. For the BA the reaction conditions are: $[BA]_0/[Cu(0)]_0/[Me_6-TREN]_0 = 80/1/0.5$ and for the TFEM the reaction conditions are: $[TFEM]_0/[Cu(0)]_0/[Me_6-TREN]_0 = 60/1/0.5$. Based on the integral of the vinyl hydrogens at 5.75–6.45 ppm compared to the methyl group of the BA and PBA at 0.94 ppm in 1H -NMR, a conversion of 81% was measured after 24 h according to eqn (1).

$$\begin{aligned} \text{Conversion (\%)} &= (1 - [(\text{peak area of double bond})/(\text{peak area of methyl group})]) \\ &\times 100 \end{aligned} \quad (1)$$

Glass slides were rinsed with excess solvent and washed with acetone in an ultrasonic bath to remove any physisorbed chemicals and then dried under vacuum.

Cu(0)-Mediated LRP of BA and TFEM to be used for grafting to on thiosilanized glass slides

A copper wire (12.5 cm, 20 gauge) was washed with acetone and scratched,⁶⁷ wrapped around a stir bar, dried under vacuum and inserted inside a glass vial under N_2 . In another glass vial, monomer (BA or TFEM), solvent (DMSO or *t*-BuOH), Me_6 -TREN, and methyl 2-bromopropanoate (MBP) were added (total volume 4 mL). For the BA reaction the conditions are as follows: BA = 2.0 mL, *t*-BuOH = 1.9 mL, water = 0.1 mL, $[BA]_0/[MBP]_0/[Me_6-TREN]_0 = 80/1/0.1$ and for the TFEM reaction the conditions are: TFEM = 2.0 mL, DMSO = 2.0 mL, $[TFEM]_0/[MBP]_0/[Me_6-TREN]_0 = 60/1/0.1$. The reaction mixture was purged with N_2 for 30 min at 20 °C and then transferred into the glass vial containing the copper wire using a gas-tight syringe purged with N_2 . This was considered time zero for the polymerization. A stirring rate of 300 rpm was used for the polymerization. Reactions were stopped after ~95% conversion and polymers were purified by precipitation in cold methanol for PBA and cold water for PTFEM and then dried at 50 °C under vacuum. For running a grafting to methodology by using a thio-bromo click reaction,³³ three glass slides functionalized with (3-mercaptopropyl)triethoxysilane (Scheme 3b) as well as three blank slides were mounted on a Teflon rod and inserted in the Teflon vessel. An appropriate amount of BPA and PTFEM was dissolved in acetonitrile to prepare a 2 wt% solution. Excess NEt_3 (two equimolar with regard to the polymer) was added to the solution and the solution was transferred to the Teflon vessel containing the glass slides. Reactions were run for 3 h at 25 °C at a stirring rate of 500

rpm. Glass slides were washed with excess acetonitrile after the reaction followed by washing with acetone in an ultrasonic bath to remove the physisorbed polymer and then dried under vacuum.

One-pot grafting on methodology using thio-bromo click

A one-pot grafting on methodology using PTFEM synthesized via Cu(0)-mediated LRP was performed (Scheme 4). The previous method was a two-step reaction needing a separate thio-silane functionalization of the glass followed by a thio-bromo click reaction. For performing a one-pot grafting on reaction, cleaned glass slides were mounted on a Teflon rod and inserted into the Teflon vessel. A solution of 3 wt% PTFEM in xylene was prepared and two equimolar of NEt_3 (with respect to polymer) was added. The mixture was then transferred to the Teflon vessel and an equimolar amount of (3-mercaptopropyl)triethoxysilane was slowly added to the mixture while stirring. The reaction was run for 3 h at 55 °C. After that, the glass slides were rinsed with excess xylene and then washed with acetone in an ultrasonic bath to remove the physisorbed polymer.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

Authors acknowledge Cornell's Department of Food Science. This work made use of the Cornell Center for Materials Research's Shared Facilities, which are supported through the NSF MRSEC programme (DMR-1719875), as well as the Cornell NMR Facility, which is supported in part by NSF-MRI grant no. CHE-1531632.

Notes and references

- 1 Y. Y. Yan, N. Gao and W. Barthlott, *Adv. Colloid Interface Sci.*, 2011, **169**, 80–105.
- 2 X. Liu and J. He, *J. Colloid Interface Sci.*, 2007, **314**, 341–345.
- 3 T. K. Pavlushkina and O. A. Gladushko, *Glass Ceram.*, 2000, **57**, 310–313.
- 4 N. Abidi, E. Hequet, S. Tarimala and L. L. Dai, *J. Appl. Polym. Sci.*, 2007, **104**, 111–117.
- 5 M. L. Zheludkevich, D. G. Shchukin, K. A. Yasakau, H. Möhwald and M. G. Ferreira, *Chem. Mater.*, 2007, **19**, 402–411.
- 6 M. Cloutier, D. Mantovani and F. Rosei, *Trends Biotechnol.*, 2015, **33**, 637–652.
- 7 S. Chernyy, M. Jarn, K. Shimizu, A. Swerin, S. U. Pedersen, K. Daasbjerg, L. Makkonen, P. Claesson and J. Iruthayaraj, *ACS Appl. Mater. Interfaces*, 2014, **6**, 6487–6496.

- 8 X. Zhan, Y. Yan, Q. Zhang and F. Chen, *J. Mater. Chem. A*, 2014, **2**, 9390–9399.
- 9 M. A. C. Stuart, W. T. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban and F. Winnik, *Nat. Mater.*, 2010, **9**, 101–113.
- 10 P. Liu, *Appl. Clay Sci.*, 2007, **38**, 64–76.
- 11 B. Radhakrishnan, R. Ranjan and W. J. Brittain, *Soft Matter*, 2006, **2**, 386–396.
- 12 *Controlled and living polymerizations: from mechanisms to applications*, ed. K. Matyjaszewski and A. H. Müller, John Wiley & Sons, 2009.
- 13 F. J. Xu, Q. J. Cai, E. T. Kang and K. G. Neoh, *Langmuir*, 2005, **21**, 3221–3225.
- 14 Q. Yang, L. Wang, J. Huo, J. Ding and W. Xiang, *J. Appl. Polym. Sci.*, 2010, **117**, 824–827.
- 15 A. Rungta, B. Natarajan, T. Neely, D. Dukes, L. S. Schadler and B. C. Benicewicz, *Macromolecules*, 2012, **45**, 9303–9311.
- 16 Y. Mei, T. Wu, C. Xu, K. J. Langenbach, J. T. Elliott, B. D. Vogt, K. L. Beers, E. J. Amis and N. R. Washburn, *Langmuir*, 2005, **21**, 12309–12314.
- 17 N. C. Estillore and R. C. Advincula, *Langmuir*, 2011, **27**, 5997–6008.
- 18 J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614–5615.
- 19 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad and E. Rizzardo, *Macromolecules*, 1998, **31**, 5559–5562.
- 20 T. Otsu, M. Yoshida and T. Tazaki, *Makromol. Chem., Rapid Commun.*, 1982, **3**, 133–140.
- 21 M. K. Georges, R. P. N. Veregin, P. M. Kazmaier and G. K. Hamer, *Macromolecules*, 1993, **26**, 2987–2988.
- 22 V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjern Dahl, M. J. Sienkowska, M. J. Monteiro and S. Sahoo, *J. Am. Chem. Soc.*, 2006, **128**, 14156–14165.
- 23 A. Anastasaki, V. Nikolaou, G. Nurumbetov, P. Wilson, K. Kempe, J. F. Quinn, T. P. Davis, M. R. Whittaker and D. M. Haddleton, *Chem. Rev.*, 2015, **116**, 835–877.
- 24 G. Lligadas, S. Grama and V. Percec, *Biomacromolecules*, 2017, **18**, 1039–1063.
- 25 S. Fleischmann, B. M. Rosen and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1190–1196.
- 26 M. Enayati, R. L. Jezorek, M. J. Monteiro and V. Percec, *Polym. Chem.*, 2016, **7**, 3608–3621.
- 27 C. Waldron, Q. Zhang, Z. Li, V. Nikolaou, G. Nurumbetov, J. Godfrey, R. McHale, G. Yilmaz, R. K. Randev, M. Girault, *et al.*, *Polym. Chem.*, 2014, **5**, 57–61.
- 28 G. Lligadas and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 3174–3181.
- 29 S. R. Samanta, V. Nikolaou, S. Keller, M. J. Monteiro, D. A. Wilson, D. Haddleton and V. Percec, *Polym. Chem.*, 2015, **6**, 2084–2097.
- 30 N. H. Nguyen, M. E. Levere and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 860–873.
- 31 N. H. Nguyen, M. E. Levere, J. Kulis, M. J. Monteiro and V. Percec, *Macromolecules*, 2012, **45**, 4606–4622.
- 32 N. Akeroyd and B. Klumperman, *Eur. Polym. J.*, 2011, **47**, 1207–1231.
- 33 G. Lligadas and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4684–4695.
- 34 E. Turan and T. Caykara, *React. Funct. Polym.*, 2011, **71**, 1089–1095.
- 35 L. Xue, Z. Lyu, X. Shi, Z. Tang, G. Chen and H. Chen, *Macromol. Chem. Phys.*, 2014, **215**, 1491–1497.
- 36 M. Vorobii, A. de los Santos Pereira, O. Pop-Georgievski, N. Y. Kostina, C. Rodriguez-Emmenegger and V. Percec, *Polym. Chem.*, 2015, **6**, 4210–4220.
- 37 X.-J. Shi, G.-J. Chen, Y.-W. Wang, L. Yuan, Q. Zhang, D. M. Haddleton and H. Chen, *Langmuir*, 2013, **29**, 14188–14195.
- 38 E. Turan and T. Caykara, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5842–5847.
- 39 Y. Shi, D. J. Menzies, K. M. Tsang, M. P. Del Borgo, C. D. Easton, M. I. Aguilar, P. Perlmutter, V. X. Truong and J. S. Forsythe, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 2527–2536.
- 40 Y. Yang, J. Wang, F. Wu, G. Ye, R. Yi, Y. Lu and J. Chen, *Polym. Chem.*, 2016, **7**, 2427–2435.
- 41 J. Tom, K. Ohno and S. Perrier, *Polym. Chem.*, 2016, **7**, 6075–6083.
- 42 J. Tian, D. Xu, M. Liu, F. Deng, Q. Wan, Z. Li, K. Wang, X. He, X. Zhang and Y. Wei, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 1872–1879.
- 43 X. Chen, L. Yuan, P. Yang, J. Hu and D. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 4977–4986.
- 44 Y. Deng, Y. Li, J. Dai, M. Lang and X. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 4747–4755.
- 45 Z. Liu, S. Zhu, Y. Li, Y. Li, P. Shi, Z. Huang and X. Huang, *Polym. Chem.*, 2015, **6**, 311–321.
- 46 L. Xue, Z. Lyu, Y. Luan, X. Xiong, J. Pan, G. Chen and H. Chen, *Polym. Chem.*, 2015, **6**, 3708–3715.
- 47 J. O. Zoppe, Y. Habibi, O. J. Rojas, R. A. Venditti, L.-S. Johansson, K. Efimenko, M. Osterberg and J. Laine, *Biomacromolecules*, 2010, **11**, 2683–2691.
- 48 W. B. Wu, Z. Y. Xu, Z. L. Zhuang and L. Zhu, *Acta Polym. Sin.*, 2015, **3**, 338–345.
- 49 Z. Hao, D. Wang, H. Chen, J. Sun and Y. Xu, *J. Agric. Food Chem.*, 2014, **62**, 1765–1770.
- 50 S. Stermann and J. G. Marsden, *Ind. Eng. Chem.*, 1966, **58**, 33–37.
- 51 E. P. Plueddemann, in *Silane coupling agents*, Springer, USA, 1991, p. 31.
- 52 S. Onclin, B. J. Ravoo and D. N. Reinhoudt, *Angew. Chem., Int. Ed.*, 2005, **44**, 6282–6304.
- 53 G. Lligadas, M. Enayati, S. Grama, R. Smail, S. E. Sherman and V. Percec, *Biomacromolecules*, 2017, **18**, 2610–2622.
- 54 G. Lligadas, B. M. Rosen, C. A. Bell, M. J. Monteiro and V. Percec, *Macromolecules*, 2008, **41**, 8365–8371.
- 55 Y. Inoue, J. Watanabe and K. Ishihara, *J. Colloid Interface Sci.*, 2004, **274**, 465–471.

- 56 M. Semsarilar, E. R. Jones and S. P. Armes, *Polym. Chem.*, 2014, **5**, 195–203.
- 57 R. Husmann, S. Wertz, C. G. Daniliuc, S. W. Schäfer, C. B. McArdle and A. Studer, *Macromolecules*, 2014, **47**, 993–1000.
- 58 C. Qianbao, S. Tiejun and M. Xiaojun, *China Synth. Rubber Ind.*, 2011, **34**, 120–124.
- 59 A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546–551.
- 60 A. H. Xu, L. Q. Zhang, J. C. Ma, Y. M. Ma, B. Geng and S. X. Zhang, *J. Coat. Technol. Res.*, 2016, **13**, 795–804.
- 61 G. Wen, Z. Guo and W. Liu, *Nanoscale*, 2017, **9**, 3338–3366.
- 62 P. Ball, *Nature*, 1999, **400**, 507–509.
- 63 R. N. Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988–994.
- 64 M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41–44.
- 65 J. J. Cras, C. A. Rowe-Taitt, D. A. Nivens and F. S. Ligler, *Biosens. Bioelectron.*, 1999, **14**, 683–688.
- 66 R. Advincula, Q. Zhou, M. Park, S. Wang, J. Mays, G. Sakellariou, S. Pispas and N. Hadjichristidis, *Langmuir*, 2002, **18**, 8672–8684.
- 67 M. Enayati, R. L. Jezorek and V. Percec, *Polym. Chem.*, 2016, **7**, 4549–4558.