

A novel way to prepare ultra-thin polymer films through surface radical chain-transfer reaction

Feng Zhou,^a Weimin Liu,^{*a} Miao Chen^a and D. C. Sun^b

^a Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou, China 730000.

E-mail: wmlu@ns.lzb.ac.cn; Fax: +86-931-8277088

^b State University of New York at Binghamton, Binghamton, N. Y, USA 13902-6000

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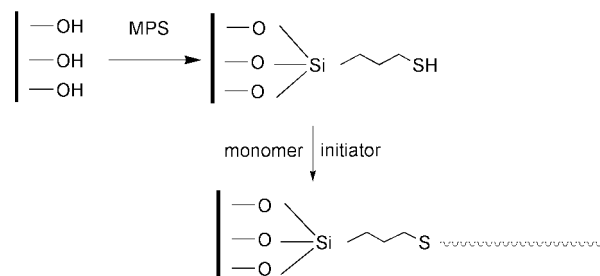
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Radical chain transfer to bonded thiol groups and surface re-initiated polymerization resulted in ultra-thin polymer films.

In-situ grafting polymer films through surface initiated polymerization (SIP) from inorganic substrates are gaining increasing interest in recent years.¹ The key step is to introduce initiating points on substrates surfaces, which can be carried out through the assembly of self-assembly-initiators or the *in-situ* modification of end group functionalized surfaces by using self-assembling techniques.² Therefore, most polymerization techniques including conventional free radical polymerization,³ 'living' radical polymerization based on 'iniferter',⁴ 'TEMPO',⁵ and 'ATRP',⁶ ionic polymerization,⁷ ROMP,⁸ *etc.* have been realized on surfaces. However, most of these SIPs require the synthesis of self-assembly-initiator molecules with complex structures. Thus, the formation of initiating points on surfaces often involves many reaction steps. Radical chain-transfer reaction is widely used in molecular weight control, synthesis of end group functionalized polymers and macromonomers, *etc.*⁹ and has once been used for the modification of solid substrates via the so-called radical transfer addition of olefin derivatives.¹⁰ Here we report that it may also serve as the intermediate reaction for surface induced polymerization to fabricate covalently attached polymer films with the emphasis on planar substrates.

Surface bonded thiol groups were used as the radical chain transfer agents because of their relative high chain transfer constant. A widely used silane coupling reagent, mercaptopropyltrimethoxysilane (MPS), was used to prepare thiol-terminated silica or silicon wafer (denoted as HS-silica and HS-silicon) according to the corresponding published procedures¹¹ using toluene as the solvent. The grafting amount of MPS on silica surface (S_{BET} , 250 m² g⁻¹) was about 0.9 mmol g⁻¹ from elemental analysis. HS-silicon had a water contact angle of 70°, which indicated a complete coverage of thiol-terminated monolayer. *In-situ* polymerization was carried out in a 20 ml mixture of methyl methacrylate (MMA), azodiisobutylnitrile (AIBN) as the initiator and toluene at 60 °C for a certain time in the presence of HS-silica or HS-silicon. The molar ratio of MMA:AIBN (100:1) and the volume ratio of MMA:toluene (1:2) were kept constant. The thiol terminated silica or silicon wafers and the polymer film modified silica/silicon (denoted as polymer-silica or polymer-silicon) were extracted with CH₂Cl₂ to ensure the removal of all unbonded species. The basic strategy of this novel process is depicted in Scheme 1.

The obvious Raman shift at 2577 cm⁻¹ for HS-silica was attributed to the stretching vibration of S-H (Fig. 1a). After polymerization, its intensity decreased dramatically but still could be detected, indicating that radical chain transfer to (a part of, but not all) thiol groups occurred. The other absorbance bands characteristic of PMMA proved that MMA was grafted onto silica surface. The normalized transmittance FTIR of HS-silicon, PMMA-silicon and spin-cast PMMA film as a control for the selected region between 3200 and 1500cm⁻¹ also



Scheme 1 Reaction procedures of *in-situ* grafting polymer film through radical chain transfer reaction.

indicated that a layer of PMMA was formed on silicon wafer (Fig. 1b).

The role of silica-carried thiol groups as the potential chain-transfer agents was verified by measuring the molecular weight of the free polymers formed simultaneously in the bulk solution. As is shown in Fig. 2, increasing the amount of HS-silica

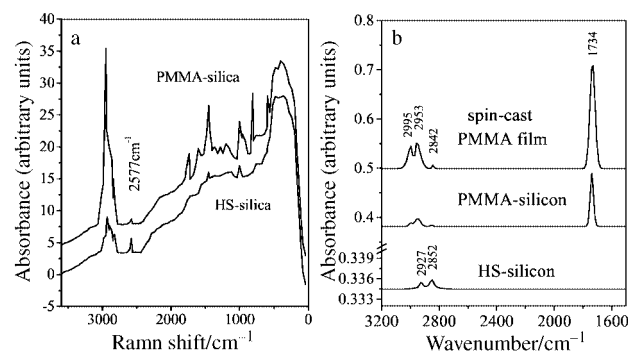


Fig. 1 (a) Raman spectra of HS-silica, PMMA-silica and (b) normalized transmittance FTIR of HS-silicon, PMMA-silicon as well as spin-cast PMMA film.

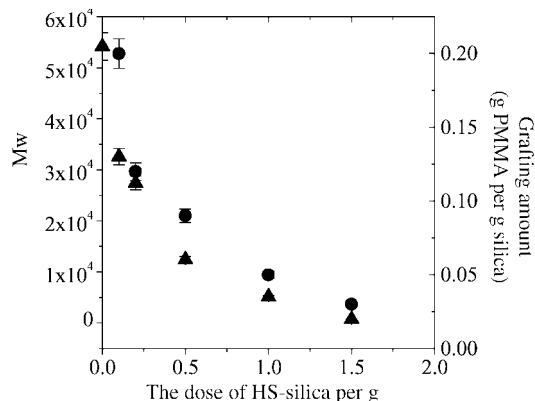


Fig. 2 Weight average molecular weight (▲) of free PMMA and the grafting amount (●) of PMMA versus the dose of HS-silica.

reduced the weight-average molecular weight of the free polymer. The results confirmed that silica-carried thiol groups played a similar role as the other thiol compounds, of being effective chain-transfer agents in polymerization. The grafting amount¹² of polymer also decreased with increasing the dose of HS-silica, closely resembling the variation of the molecular weight of the free polymer.

Our hypothesized reaction procedures were also confirmed by XPS. After polymerization of MMA for 24 h on silicon wafers, no peaks characteristic of Si_{2p} and S_{2p} were detected. This indicated that the substrate was completely covered by a polymer layer of at least 5 nm. (In fact, the film thickness was about 27 nm.) But this is not the case with the silica surface. The evaluation¹³ of the film thickness from the attenuation of Si_{2p} of PMMA-silica (even the sample having the maximum grafting amount in Fig. 2) showed a very thin polymer film of less than 2 nm. We attributed the ineffectiveness of the method on silica surfaces, against that on silicon wafers, to the different rate of termination. Propagating chains on silica surfaces were easily formed and simultaneously terminated by the chain transfer reaction because of the relatively high contents of thiol groups in polymerization systems and also the mobility of silica-carried thiol groups. But on planar substrates, the possibility of radical chain transfer could be reduced because of the two-dimension restriction of thiol groups and also the absence of effective chain transfer agents in bulk solution, which made the propagating chains on planar substrates less likely to be terminated.

Grafting polymerization on silicon wafers was found to occur during the first two hours, resulting in more than 90% of the thickness obtained with 24 h of polymerization time. The contact mode AFM topography of a 27 nm thick PMMA film revealed a homogeneous and smooth polymer film with an rms roughness of 0.207 nm.

The advantage of this method was its capability to realize polymerization of a wide range of monomers in both non-aqueous and aqueous solutions. Table 1 lists several examples of the obtained polymer films and the corresponding contact angles and film thicknesses. We aimed to fabricate surfaces with different lyphohydrophilic characters by co-polymerization of monomer pairs using different molar ratios. Fig. 3 shows that the method was effective. By simply varying the composition of the monomer pairs, the wetting behavior of the resulting copolymer films could be changed in a highly controlled fashion. Therefore, radical chain transfer reaction and surface re-initiated polymerization provides a means to control the physical properties of polymer films.

In conclusion, we have demonstrated for the first time that (1) radical chain transfer to thiol-terminated self-assembled mono-

Table 1 The static contact angles of water and thicknesses of the obtained polymer films

Film	Solvent	Contact angle	Thickness (Å)
PMMA	Toluene	70	274
PSt	Toluene	90	225
PTDMA	Toluene	94	62
PBuA	Toluene	96	134
PAN	THF	40	1356
PAA	THF	27	135
	Water	16	295
PAn	Water	46	125
	DMF	47	145

Time: 24 h; Temperature: 60 °C. For the polymerization in water (NH₄)₂S₂O₈ was used as the initiator. PMMA: poly(methyl methacrylate); PSt: polystyrene; PTDMA: poly(tetradecanyl methacrylate); PAN: polyacrylonitrile; PAA: poly(acrylic acid); PBuA: poly(butyl acrylate); PAn: polyacrylanitrile; THF: tetrahydrofuran; DMF: *N,N'*-dimethylformamide.

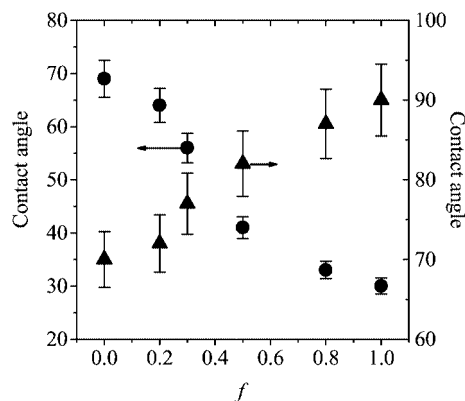


Fig. 3 The contact angle of copolymer film as a function of the molar percentage (*f*) of AA in AA-MMA pair (●) and of St in St-MMA pair (▲).

layer and (2) surface re-initiated radical polymerization on both silica surface and silicon wafers truly occurred and ultra-thin polymer films with nanometer dimensions resulted. The method is a new addition to SIP, applicable to the polymerization of a wide range of monomers (especially functionalized monomers) and workable in situations where other SIPs are inconvenient to use. The method has potential applications in tailoring the chromatographic properties of solid supports, enhancing the biocompatibility of substrate surfaces, lubricating microelectromechanical systems (MEMS), the chemical modification of electrodes, etc.

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