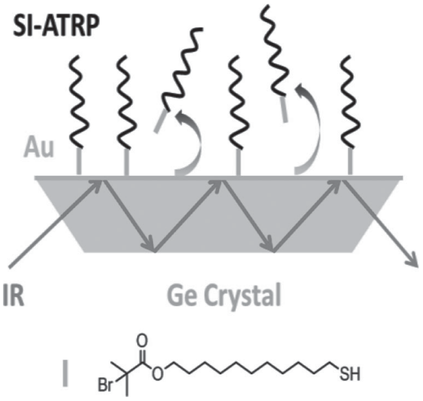
Impact of Catalyst on the Stability of Initiators on Au Substrate in Atom Transfer Radical Polymerization

Yongming Tang, Richard O. Osibanjo, Jessica Moore, Elyse N. Towns, Tonya L. Kuhl, Donald P. Land*

Desorption of thiol-based self-assembled monolayers on gold surfaces makes surface-initiated atom transfer radical polymerization (SI-ATRP) challenging and results in reduced density "grafted from" polymer film. In this work, in situ attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy shows that copper-based catalysts typically used in SI-ATRP cause substantial desorption of bound thiol-based initiator films from gold surfaces. Other reaction conditions factors such as low temperature, presence of radicals, and solvents selection have relatively minor effects in comparison. Indeed, the desorption of initiator films is reduced from more than 80% to about 45% when CuCl catalyst is used for the ATRP of styrene instead of CuBr catalyst. However, the polymerization rate is significantly slower in this case.



1. Introduction

Surface initiation atom transfer radical polymerization (SI-ATRP) is actively studied as a means to modify surfaces by directly growing chains from surface-grafted initiator layers.[1–3] SI-ATRP on gold is especially desirable because gold surfaces are homogeneous, easy to clean, free of contamination, and compatible with a diverse range of analytical techniques.[1,4–6] Unfortunately, thiol-based initiators tethered to gold surface by self-assembled monolayers (SAMs) are relatively unstable due to the lability of the Au—S bond.[1,4,7] At elevated temperature such as above 60 °C, which is used in most radical polymerization, SAM-based initiators can desorb from the gold surface.[4,5,7,8] The loss of initiator results in a reduced density and thickness of the SI-ATRP polymer film. To get around the desorption problem, SI-ATRP carried out at a lower temperature has been proposed.[7,9] However, a recent study showed that even at 60 °C, desorption of the initiators from gold surface was still significant.[10] In addition to temperature-induced desorption, studies by Baker and co-workers and Bruening et al. showed that solution or surface radicals can accelerate desorption of surface bound thiols and further decrease the grafting

Dr. Y. Tang, Dr. R. O. Osibanjo, J. Moore, E. N. Towns,
Prof. D. P. Land
Department of Chemistry, University of California,
Davis, CA 95616, USA
E-mail: dpland@ucdavis.edu
Dr. Y. Tang
School of Science, Nanjing University of Technology,
Nanjing 211816, P. R. China
Prof. T. L. Kuhl
Department of Chemical Engineering and Material Science,
University of California, Davis, CA 95616, USA

DOI: 10.1002/macp.201400230

Table 1. Loss of thiols under various conditions.

Solution	Temp. [°C]	Catalyst	Loss of thiols [%]
Styrene + toluene	50	None	18.7 ± 5.6
	Room temp.	CuBr	>95.0
Toluene	Room temp.	CuBr	>95.0
	Room temp.	CuCl	60.5 ± 4.9
SI-ATRP	50	CuCl	45.7[a)]

[a)] The value was obtained from the absorbance of C=O.

density.[4,7,11] Bruening et al. showed a 40–80% loss in the initiator SAM from gold surfaces resulting in no significant polymerization (less than 5 nm).[4] They argued that the chain-transfer reactions caused by the desorbed thiols with high chain-transfer constants on a surface result in a termination of polymer growth from the surface and hence inhibit surface radical polymerization. In addition, Schlenoff et al. observed up to 40% loss in the initiator layer when the gold surfaces with SAMs were immersed into a solvent without initiators.[8] The effect of ATRP catalysts on the stability of alkanethiol initiators on Au surfaces has, until now, received little attention.[7]

Understanding the factors that influence SAM stability and desorption at low temperature provides a deeper insight into ATRP mechanism and kinetics. This paper aims to clarify the role of SI-ATRP catalysts — copper (I) bromide and copper (I) chloride — on the stability and desorption of thiol-based SAM on gold. Fourier transform infrared spectra with attenuated total reflection (ATR-FTIR), a powerful in situ technique of surface analysis, were used to quantify the desorption of thiols and thiol-based initiators from gold. In this study, a Ge crystal was used as the internal ATR reflection element. Considering the refraction indexes of both Ge and polystyrene, we estimated that the effective penetration depth of IR radiation is not less than 250 nm in the wavenumber range from 3000 to 1000 cm^{-1}.[12] The penetration depth is more than the thickness of polymer layers formed in similar cases.[7,13] Accordingly, ATR-FTIR is highly sensitive to both SAM layer and polymer film on gold.

2. Results and Discussion

Since more than 80% loss of initiators has been observed after SI-ATRP of styrene,[10] we first examined the effect of catalysts on desorption of initiators under polymerization conditions in which styrene, toluene, 1,1,4,7,7-pentamethyl-diethylene-triamine (PMDETA), and mixture of CuBr and CuBr_2 (15:1 in mole) were serially added to SAMs of the initiator on gold surfaces. Less than 20% desorption of initiators from the surface was observed in the absence of catalysts, and more than 95% desorption in the presence of catalysts (Table 1 and Figure S1, Supporting Information). It should be noted that the position and full width at half maximum (FWHM) of a chemical group band may be altered by changes in molecular orientation of the chemical group on the surface. As a result, the change in the integrated absorbance of the bands was used to evaluate the loss of thiols in Table 1. The above-mentioned results indicate that catalyst — rather than thermal contributions — plays a major role in desorption of the initiators in the relatively modest temperatures, <60 °C. In the presence of catalysts, radicals generated from both initializing and polymerizing stages may induce desorption of thiol SAMs from gold surfaces.[4,7] To test this hypothesis, a catalyst solution containing ethanol and a mixture of CuBr and CuBr_2 catalysts was introduced to an initiator-immobilized and 11-mercaptoundecanol (MUA)-immobilized gold surfaces, respectively. In comparison with the initiator SAMs, the MUA SAMs do not have a halide end group so no radicals are generated. It was found that over 95% of both the initiator and MUA desorbed from gold surfaces after the introduction of catalysts (Figure S2, Supporting Information). The almost complete removal of the MUA SAM clearly demonstrates that radicals do not contribute significantly to breaking the Au—S bonds.

Solvents may also influence the stability of Au—S bonds. It has been reported that the solvents with different dielectric constant have an great effect on both adsorption and desorption of thiols on gold surfaces.[14,15] In the previous studies, ATRP was carried out in toluene while the thiol SAMs were prepared in ethanol. So it is necessary to ascertain whether there is a solvent effect in the desorption of thiols from the gold surfaces in the presence of catalysts. We deposited MUA SAMs on the gold surfaces in toluene and then introduced mixture of CuBr and CuBr_2 in toluene to the surfaces at room temperature. Over 95% of the thiols have desorbed from the surface after 17 min (Table 1 and Figure 1a), which is similar to what was obtained when ethanol was used. This shows the loss of the thiols from the surface is not solvent

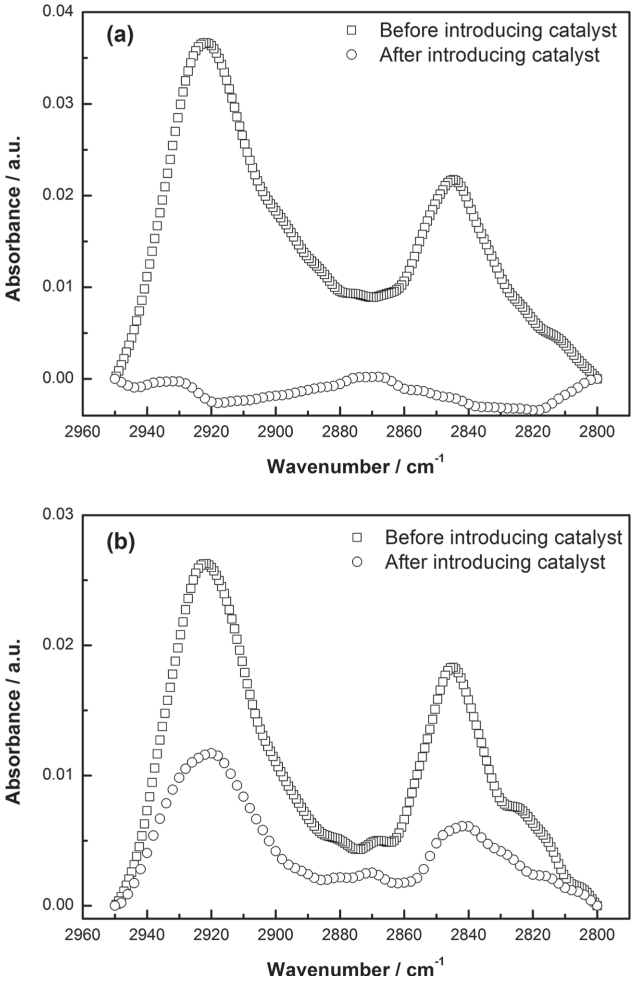


Figure 1. Absorbance spectrum of CH_2 asymmetric and symmetric stretches in MUA (dry surface) before and after introduction of Cu(I) and Cu(II) in toluene at room temperature: a) CuBr and b) CuCl.

dependent. And the results further show the impact that the Cu (I) and Cu (II) catalyst have on the thiol-Au stability.

CuCl has also been widely used as ATRP catalyst. As a contrast to CuBr, we tested the impact of CuCl on desorption of thiols by introducing a mixed solution of CuCl and $CuBr_2$ (15:1 in mole) to gold surfaces with MUA SAMs deposited in toluene. About 60% of the thiols desorbed from the surface after 17 min in the presence of CuCl (Table 1 and Figure 1b) in contrast to more than 95% loss in the case of CuBr. Successive scanning over 2 h confirmed that CuCl results in less damage of thiol SAMs than CuBr (Figure S3, Supporting Information). However, the reason for less influence of CuCl on thiol SAMs than CuBr remains unknown. Venkataramanan et al. proposed that free metal ions may reach the Au–thiol interface and participate in bonding, which weakens the Au–thiol binding resulting in monolayer desorption at a low temperature.[16] In this study, since Cu—Cl binding is stronger than Cu—Br, fewer copper ions are released in the case of CuCl reducing the desorption of thiols from the surface due to metal cation bond competition.

Since the loss of thiols can be reduced by substituting CuCl for CuBr, ATRP of syrene with CuCl/$CuBr_2$ catalyst was carried out at 50 °C for 10 h for the purpose of comparison. In this study, the polymerization of styrene was monitored by the increase in integrated absorbance of CH_2, and the loss of initiators was monitored by the decrease in integrated absorbance of C=O. As shown in Figure 2, the CH_2 signal is enhanced after polymerization, indicating the formation of polystyrene on the gold surfaces. At the same time, the strength of C=O signal shows desorption of the initiators from the gold surfaces. The integrated absorbance of C=O shows two apparent desorption stages: fast desorption within 60 min after the beginning of polymerization and subsequently slow desorption in the rest of time. After 10 h of polymerization, the loss of initiators was about 45% (Table 1), much smaller than that in the case of CuBr (over 80%). Moreover, compared with the studies in Figure 1 where the loss of initiator SAM is more than 95% without ATRP at room temperature in the presence of CuBr, the loss of initiator SAM is greatly reduced with ATRP at 50 °C in the case of CuCl. The improvement in the initiator retention during SI-ATRP is attributed to the growth of the polymer film, which may partly protect the initiators from desorbing from the gold surfaces. Figure 2 also shows the fast increase of integrated absorbance of CH_2 in the first 1 h, which is similar to that in the case of CuBr.[10] After 2 h, however, the integrated absorbance remains relatively unchanged, suggesting that an approximate equilibrium is established between the increase in amount of CH_2 on the gold surface (resulting from surface polymerization) and the decrease (resulting from desorption of the initiators). This is greatly different from the case of CuBr. In the presence of CuBr, the integrated absorbance of CH_2 sustained growth at a certain rate after the initial fast stage. This can be attributed to the higher polymerization rate in the presence of CuBr. In fact, it has been confirmed that the polymerization rate decreased with the catalyst in the order of CuBr > CuCl.[17] However, the reason for the higher polymerization rate in the case of CuBr remains unknown. Some researchers proposed that for transfer of halogen atoms between catalysts to polymer moieties, the higher free energy of dissociation of the C—Cl bond compared to the C—Br bond may shift the equilibrium between dormant and propagating radical species on the side of dormant species,[18,19] resulting in the lower polymerization rate in the case of CuCl.

3. Conclusion

Cu(I)/Cu(II) catalysts dominate the desorption of thiol initiators from the gold surfaces for SI-ATRP at a relatively

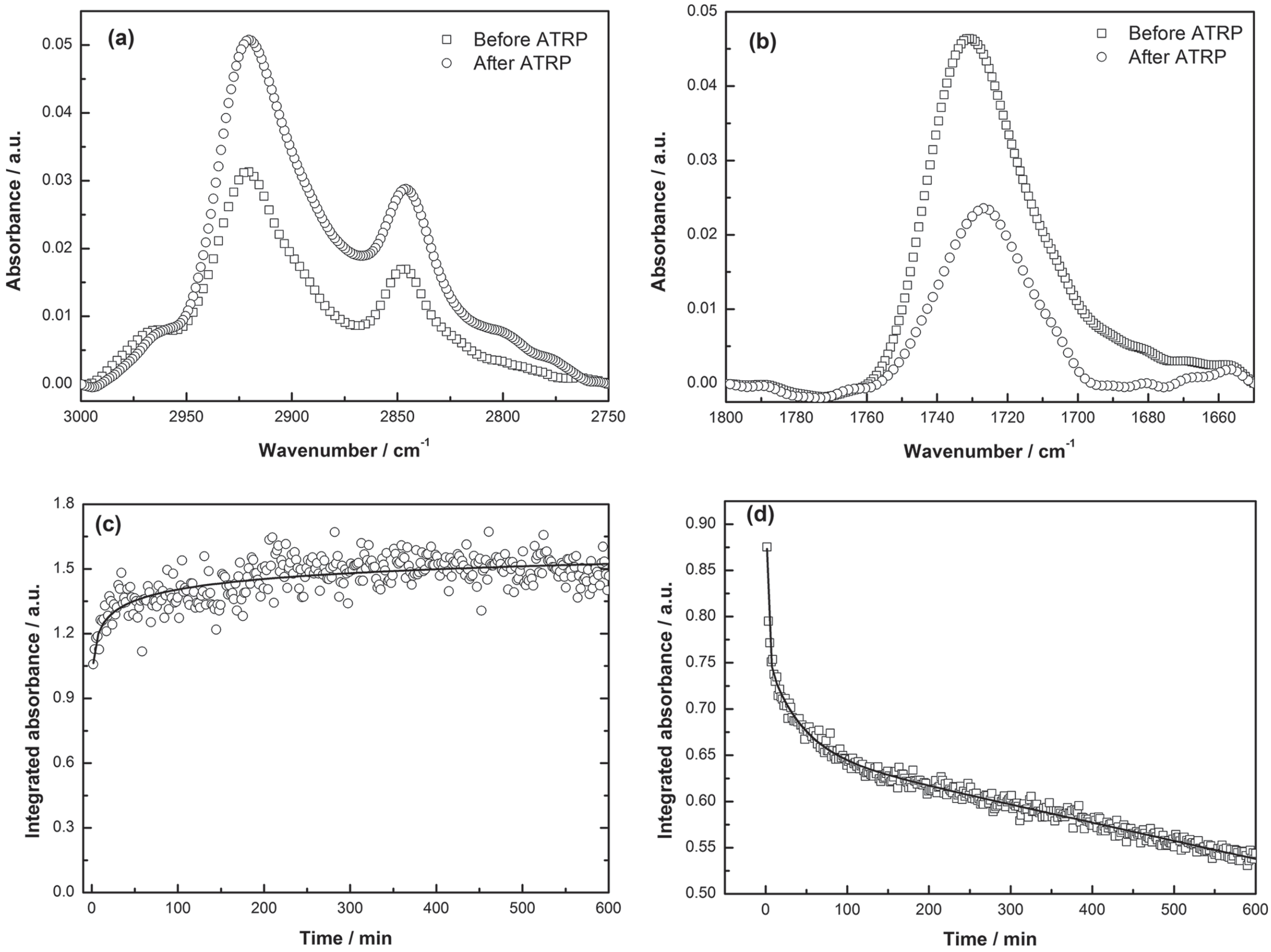


Figure 2. Absorbance spectrum of CH_2 (a) and C=O (b) on dry surfaces before and after ATRP. (c) and (d) are the integrated absorbance of CH_2 and C=O during ATRP, respectively.

low temperature. The loss of thiols on the gold surfaces in the presence of CuCl is less than in the presence of CuBr. Under SI-ATRP conditions of styrene, the loss of initiators is greatly reduced when CuCl was used as the catalysts. As a result, CuCl is much more effective in the SI-ATRP of polymer films from gold surfaces than the more widely used CuBr, however, the polymerization rate of styrene with the catalyst of CuCl is lower.

4. Experimental Section

4.1. Materials

11-Mercaptoundecanol (97%; Aldrich), 1,1,4,7,7-pentamethyl-diethylene-triamine (98%; Alfa Aesar), $HAuCl_4·3H_2O$, CuCl (99.999%; Aldrich), CuBr (99.999%; Aldrich), and $CuBr_2$ (99.999%; Aldrich) were used as received. Styrene was distilled under reduced pressure to remove the inhibitor and stored at 4 °C under nitrogen. Initiator, mercaptoundecyl-2-bromoisobutyrate, was synthesized following an established protocol.[10] 18 MΩ Millipore water was used in all experiments.

4.2. Self-Assembled Monolayer on the Gold Surface

A multiple internal reflection element, 56 mm × 10 mm × 4 mm Ge crystal (PIKE) was used as the substrate. The Ge crystal was serially polished using Al_2O_3 powders of 0.3 and 0.05 μm and silicon colloid solution prior to use. After rinsing with water, isopropyl alcohol, and acetone, the crystal was cleaned for 10 min in a UV–O_3 oven. Gold was electrolessly deposited onto the Ge substrate from a solution of 1.00×10^{-3} M $HAuCl_4·3H_2O$ with the deposition time of 5 min. Afterwards, the Au-coated Ge crystal was rinsed with copious amounts of ethanol and dried under nitrogen. To deposit the thiol SAMs, the Au-coated crystal surface was immersed into a 1.00×10^{-3} M in either ethanol or toluene solutions for about 12 h. The SAMs were then rinsed with either ethanol or toluene and dried with N_2.

4.3. Effect of Catalyst on Stability of SAMs on Gold Surfaces

Catalyst solutions comprising CuBr or CuCl (0.125 mmol) and $CuBr_2$ (0.007 mmol) in 1 mL ethanol or toluene were introduced to the SAM-coated surfaces at room temperature. After 17 min, the catalyst solution was removed and the surfaces were rinsed with either ethanol or toluene and dried with N_2. The dry surfaces before and after introduction of catalysts were compared and the amount of SAM on the surfaces quantified by infrared spectra. Infrared spectra were obtained using a Mattson Infinity FTIR spectrometer with a Pike Technology ATR accessory at 45° of incidence. The detector was a cooled mercury cadmium telluride (HgCdTe, MCT) conductivity element. Each spectrum consisted of 512 scans with 4 cm^{-1} resolution. Additionally, in case of CuCl, FTIR was used to successively monitor desorption of the thiols from the gold surfaces for 2 h.

4.4. ATRP of Styrene

Prior to ATRP experiments, all reaction reagents and styrene monomer were degassed by three freeze–pump–thaw cycles. A solution containing styrene (12.2 mmol) and catalyst solution comprising CuCl (0.125 mmol), $CuBr_2$ (0.007 mmol), and PMDETA (0.12 mmol) in toluene (0.7 mL) was transferred to the initiator-coated Au/Ge substrate. The polymerization was carried out in an oxygen-free ATR chamber maintained at 50 °C using a temperature controlled water bath (Fisher Scientific). The initial system initiator/Au/Ge was allowed to equilibrate for 30 min at 50 °C prior to introduction of the reaction solutions. Infrared spectra were collected every 103 s for up to 10 h during polymerization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: Y.T. is thankful to his Jiangsu Government Scholarship for Overseas Studies and State Key Laboratory of Material-Oriented Chemical Engineering (KL12-10).

Received: May 2, 2014; Revised: July 10, 2014; Published online: August 25, 2014; DOI: 10.1002/macp.201400230

Keywords: ATR-FTIR; catalysts; desorption; polymer thin-films; surface-initiated ATRP

[1] J.-B. Kim, M. L. Bruening, G. L. Baker, *J. Am. Chem. Soc.* **2000**, *122*, 7616.
[2] A. Ramakrishnan, R. Dhamodharan, J. Rühe, *Macromol. Rapid Commun.* **2002**, *23*, 612.
[3] O. Prucker, J. Rühe, *Langmuir* **1998**, *14*, 6893.
[4] W. Huang, G. Skanth, G. L. Baker, M. L. Bruening, *Langmuir* **2001**, *17*, 1731.
[5] C. D. Bain, E. B. Troughton, Y. T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* **1989**, *111*, 321.
[6] G. Gunkel, W. T. S. Huck, *J. Am. Chem. Soc.* **2013**, *135*, 7047.
[7] S. Saha, M. L. Bruening, G. L. Baker, *ACS Appl. Mater. Interface* **2011**, *3*, 3042.
[8] J. B. Schlenoff, M. Li, H. Ly, *J. Am. Chem. Soc.* **1995**, *117*, 12528.
[9] A. Samadi, S. M. Husson, Y. Liu, I. Luzinov, S. M. Kilbey, *Macromol. Rapid Commun.* **2005**, *26*, 1829.
[10] R. O. Osibanjo, A. Yasovolian, I. G. Elliott, T. Brickey, R. Marks, T. L. Kuhl, D. P. Land, unpublished.
[11] J.-B. Kim, W. Huang, M. D. Miller, G. L. Baker, M. L. Bruening, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 386.
[12] D. A. Skoog, F. J. Holler, S. R. Crouch, *Principles of Instrumental Analysis*, 6th ed., Thomson Brooks/Cole, USA **2007**, 472.
[13] J. D. Jeyaprakash, S. Samuel, R. Dhamodharan, J. Rühe, *Macromol. Rapid Commun.* **2002**, *23*, 277.
[14] J. F. Kang, S. Liaos, R. Jordan, A. Ulman, *J. Am. Chem. Soc.* **1998**, *120*, 9662.
[15] H. Choo, E. Cutler, Y.-S Shon, *Langmuir* **2003**, *19*, 8555.
[16] V. Mahalingam, K. V. G. K. Murty, T. Pradeep, W. Deepali, K. Vijayamohanan, *Langmuir* **2000**, *16*, 7673.
[17] K. Matyjaszewski, S. Qin, *Macromolecules* **2003**, *36*, 1843.
[18] K. Matyjaszewski, D. A. Shipp, J.-L. Wang, T. Grimaud, T. E. Patten, *Macromolecules* **1998**, *31*, 6836.
[19] R. Barbey, L. Lavanant, D. Paripovic, N. Schüwer, C. Sugnaux, S. Tugulu, H. Klok, *Chem. Rev.* **2009**, *109*, 5437.