SUPPORTING INFORMATION

In situ Monitoring of SI-ATRP Throughout Multiple Reinitiations under Flow by Means of the Quartz Crystal Microbalance

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The transient but sharp change in frequency (ΔF) at the onset of polymerization is mainly due to a change of viscosity because of the replacement of IRM (water + monomer + ligand) by CRM (water + monomer + ligand + CuCl + $CuBr_2$). But at the washing step, a higher degree of solvation of the polymer brush in IRM compared to the solvation in CRM counteracts the effect of viscosity and a decrease in frequency (ΔF) is observed upon replacement of CRM by IRM (S2-S7). Such differential solvation could be caused by an interaction of -OH groups of poly(HEMA) brushes with Cu(II) as it is observed with polyvinyl alcohol.[1] Notably, an opposite trend is observed in the washing step when SI-ATRP was performed in 7:3 HEMA/water mixture at 25 °C (S1) due to very low polymer-brush thickness (3 nm dry thickness) where again the change in the viscosity dominates the effect of solvation of the polymer brush in IRM.

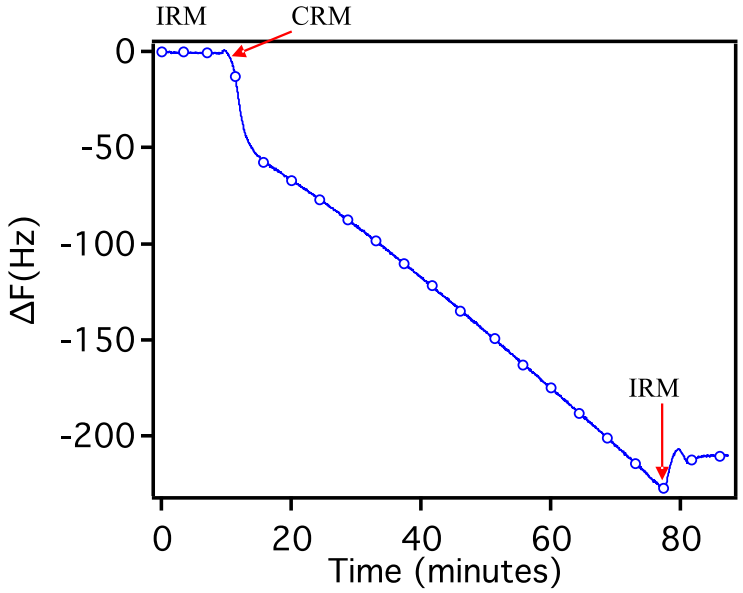

Figure S1. Frequency (ΔF) changes measured *in situ* by QCM during SI-ATRP of 7:3 HEMA/water mixture, carried out under continuous flow of CRM with a relative 100 % catalyst concentration at 25 °C.

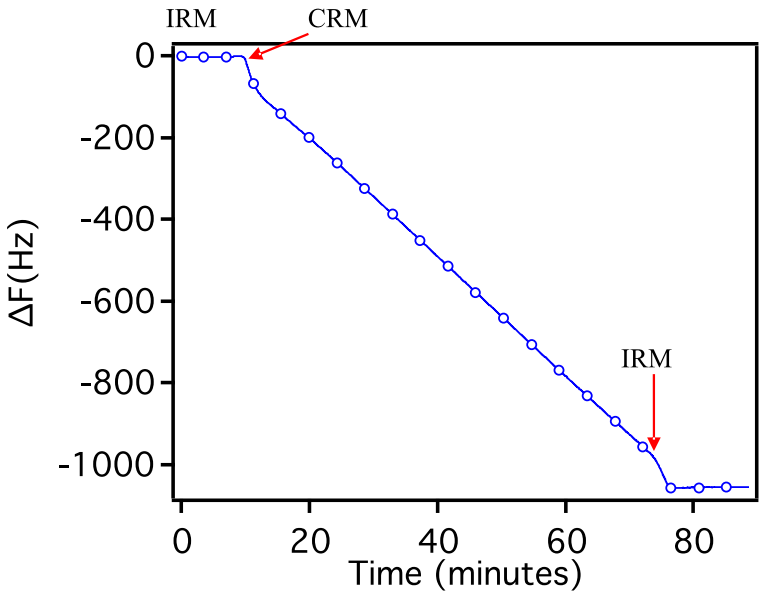

Figure S2. Frequency (ΔF) changes measured *in situ* by QCM during SI-ATRP of 1:1 HEMA/water mixture, carried out under continuous flow of CRM with a relative 100 % catalyst concentration at 25 °C.

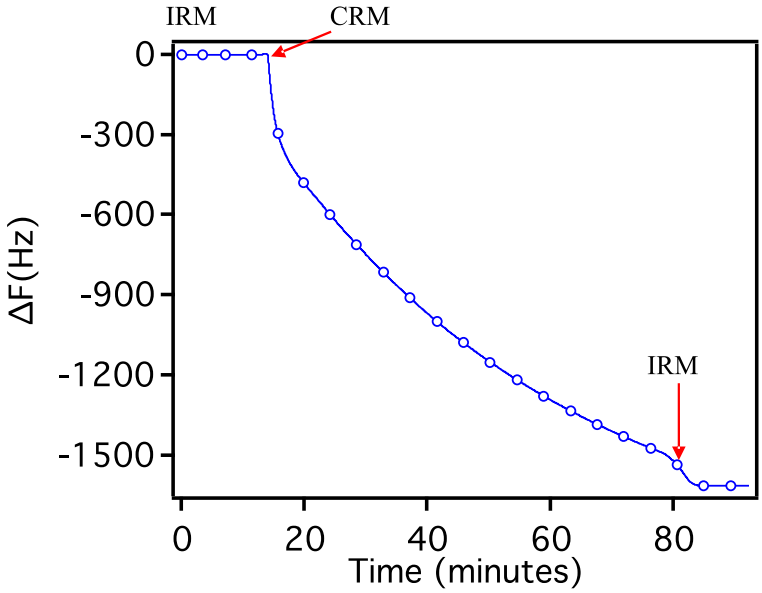

Figure S3. Frequency (ΔF) changes measured *in situ* by QCM during SI-ATRP of 3:7 HEMA/water mixture, carried out under continuous flow of CRM with a relative 100 % catalyst concentration at 25 °C.

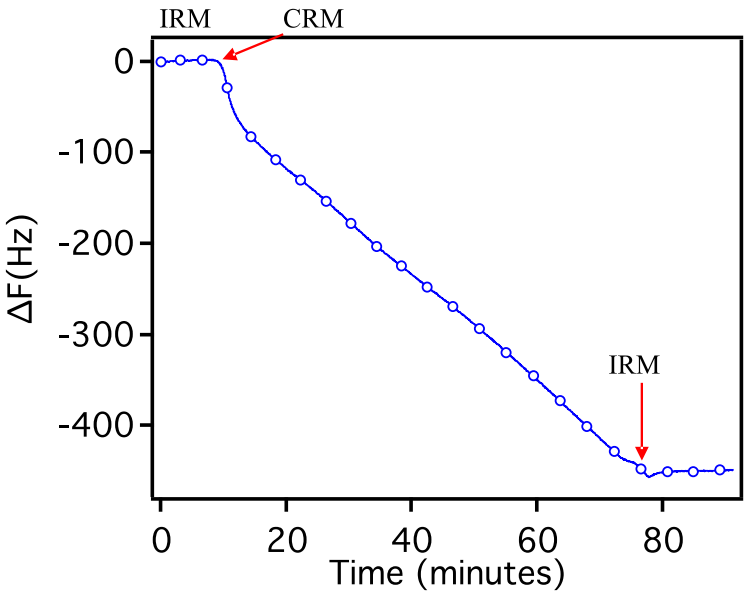

Figure S4. Frequency (ΔF) changes measured *in situ* by QCM during SI-ATRP of 7:3 HEMA/water mixture, carried out under continuous flow of CRM with a relative 100 % catalyst concentration at 35 °C.

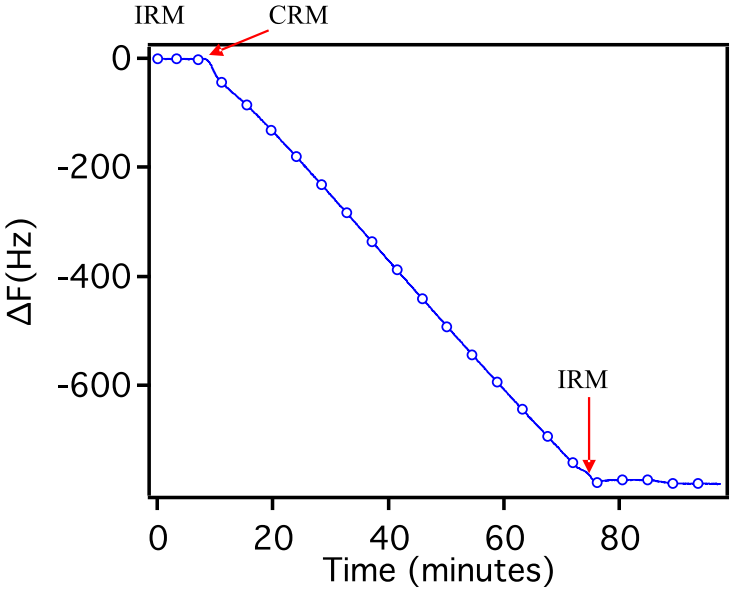

Figure S5. Frequency (ΔF) changes measured *in situ* by QCM during SI-ATRP of 7:3 HEMA/water mixture, carried out under continuous flow of CRM with a relative 100 % catalyst concentration at 45 °C.

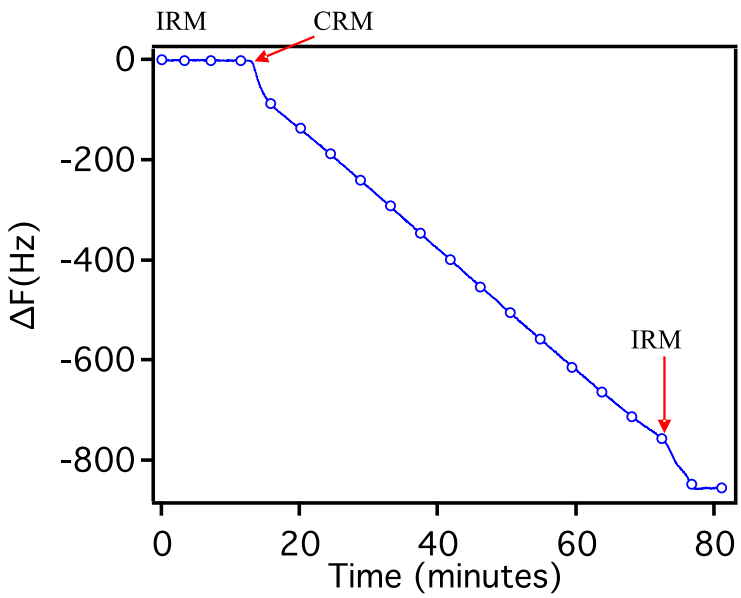

Figure S6. Frequency (ΔF) changes measured *in situ* by QCM during SI-ATRP of 1:1 HEMA/water mixture, carried out under continuous flow of CRM with a relative 70 % catalyst concentration at 25 °C.

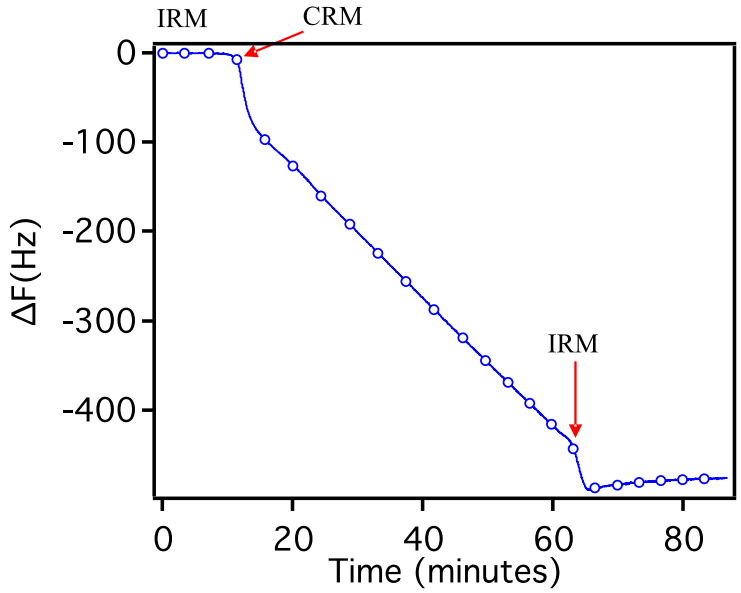

Figure S7. Frequency (ΔF) changes measured *in situ* by QCM during SI-ATRP of 1:1 HEMA/water mixture, carried out under continuous flow of CRM with a relative 40 % catalyst concentration at 25 °C.

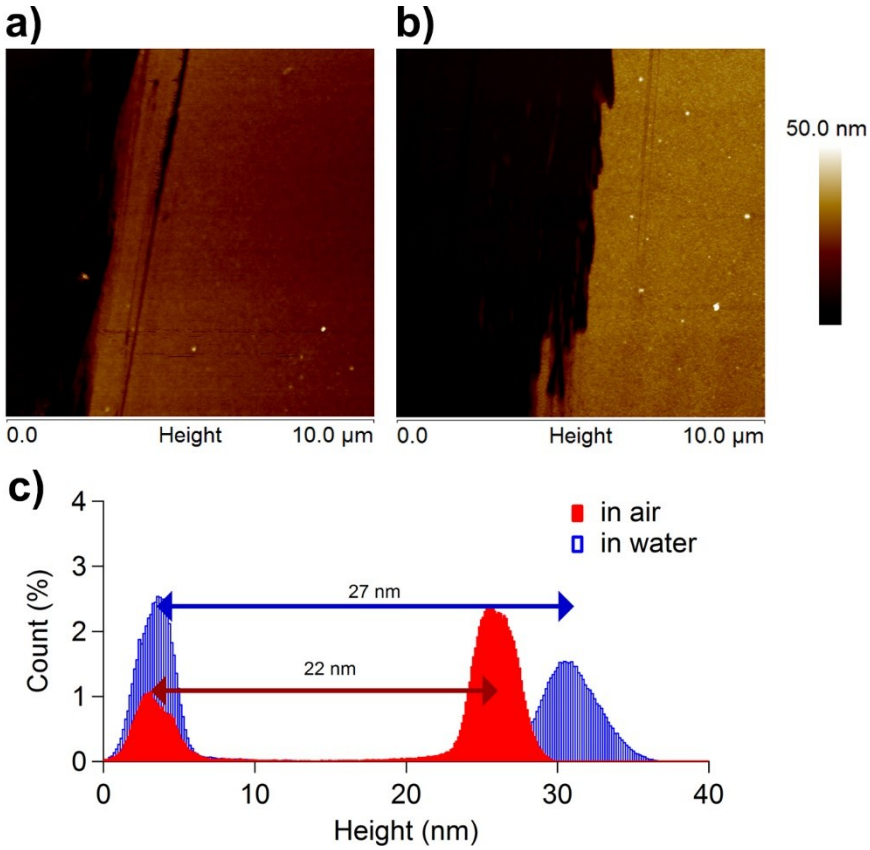

Figure S8. Step-height AFM images of a PHEMA film synthesized using 40 % catalyst. a) AFM height image acquired using TappingMode® in air, b) AFM height image acquired using PeakForce® tapping in water and c) height image histograms of (a) and (b) showing distribution film thickness.

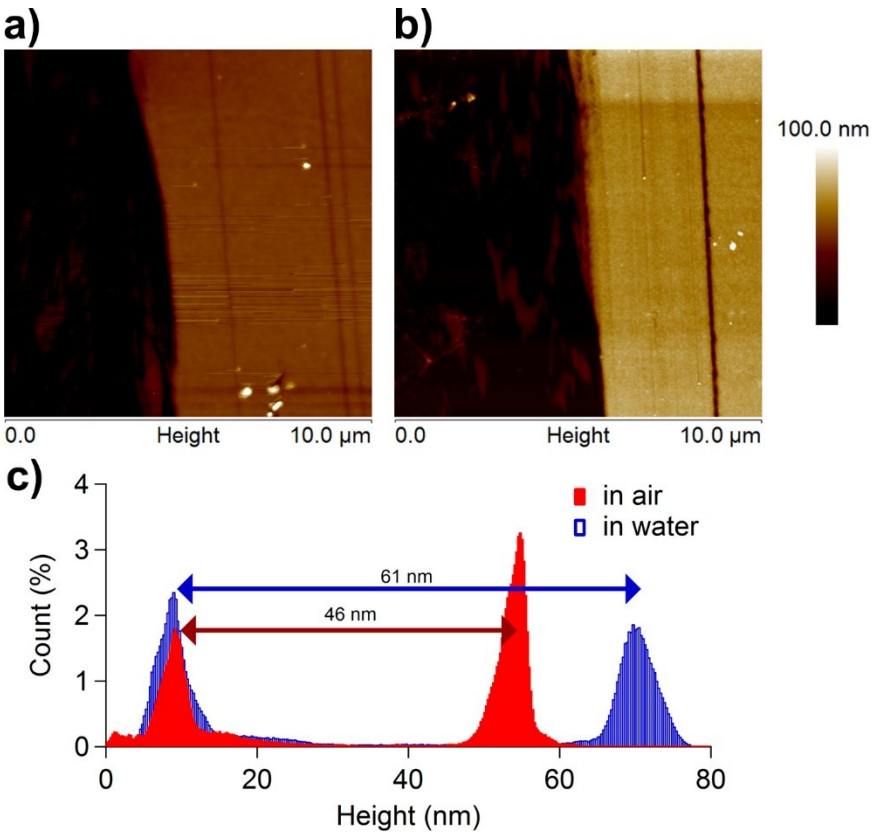

Figure S9. Step height AFM images of PHEMA film synthesized using 70 % catalyst. a) AFM height image acquired using TappingMode® in air, b) AFM height image acquired using PeakForce® tapping in water and c) height image histograms of (a) and (b) showing distribution film thickness.

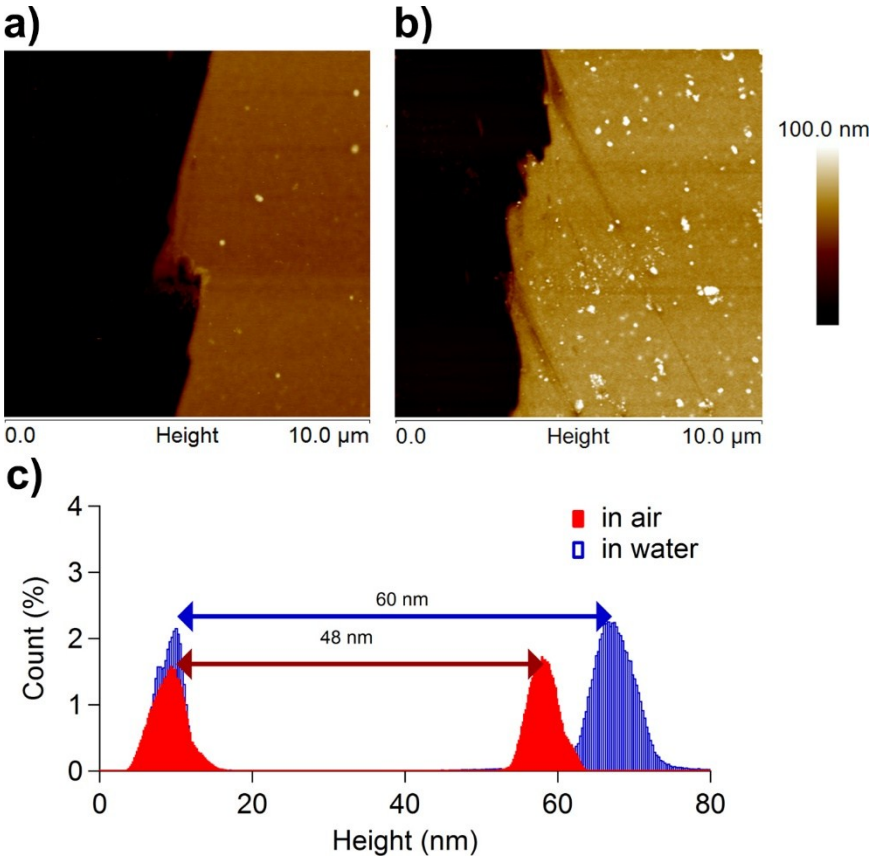

Figure S10. Step height AFM images of PHEMA film synthesized using 100 % catalyst. a) AFM height image acquired using TappingMode® in air, b) AFM height image acquired using PeakForce® tapping in water and c) height image histograms of (a) and (b) showing distribution film thickness.

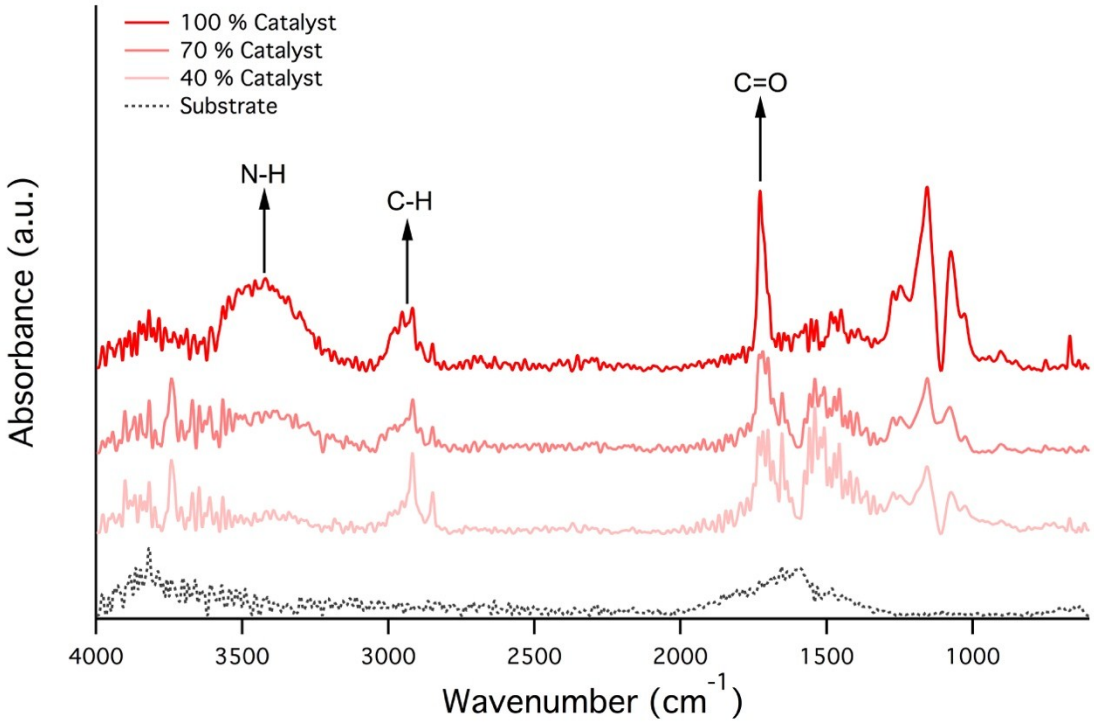

Figure S11. FT-IR transmission spectra of the poly(HEMA) modified silicon wafers grafted using various relative catalyst concentrations. Substrate only shows peaks characteristic of water.

Table 1: Catalyst composition of the reaction mixtures with different relative catalyst concentration

Catalyst Concentration (%)	(Water + HEMA) (mL)	Cu(I)Cl (mmol)	2,2′-bipyridyl (mmol)	$Cu(II)Br_2$ (mmol)
100	15	1.0	3.0	0.3
70	15	0.7	2.1	0.21
30	15	0.3	0.9	0.09

The catalyst concentration was varied with respect to the total volume of water and HEMA mixture. So, the concentration of catalyst in this manuscript is mmol mL^{-1} of reaction mixture.

Reference

1. Hojo, N.; Shirai, H.; Hayashi, S. In *Complex formation between poly (vinyl alcohol) and metallic ions in aqueous solution*, Journal of Polymer Science: Polymer Symposia, Wiley Online Library: 1974; pp 299-307.