

## Supporting Information

### Phase Transition Characterization of Poly(oligo(ethylene glycol) methyl ether methacrylate) Brushes using the Quartz Crystal Microbalance with Dissipation

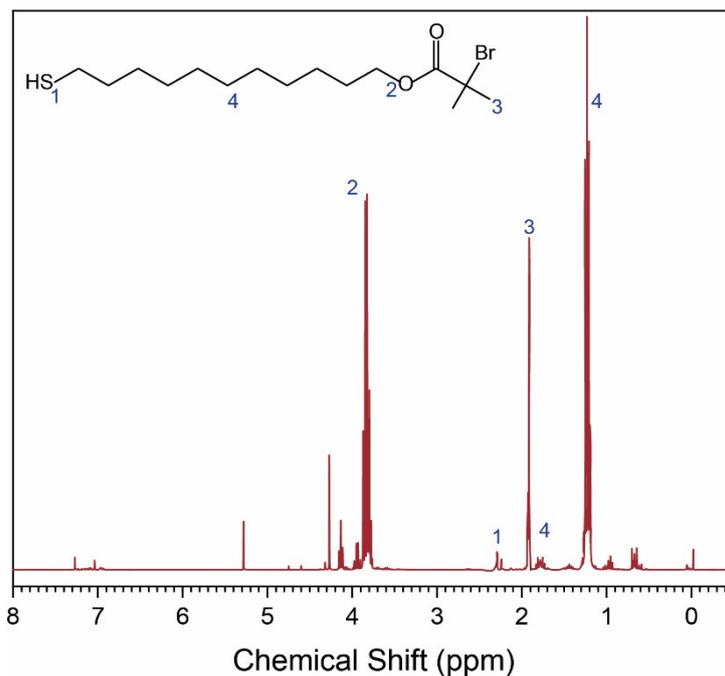
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**Supplementary Note.** Synthesis of 2-Bromo-2-methylpropionyloxy propyl triethoxysilane (BPE) initiator.

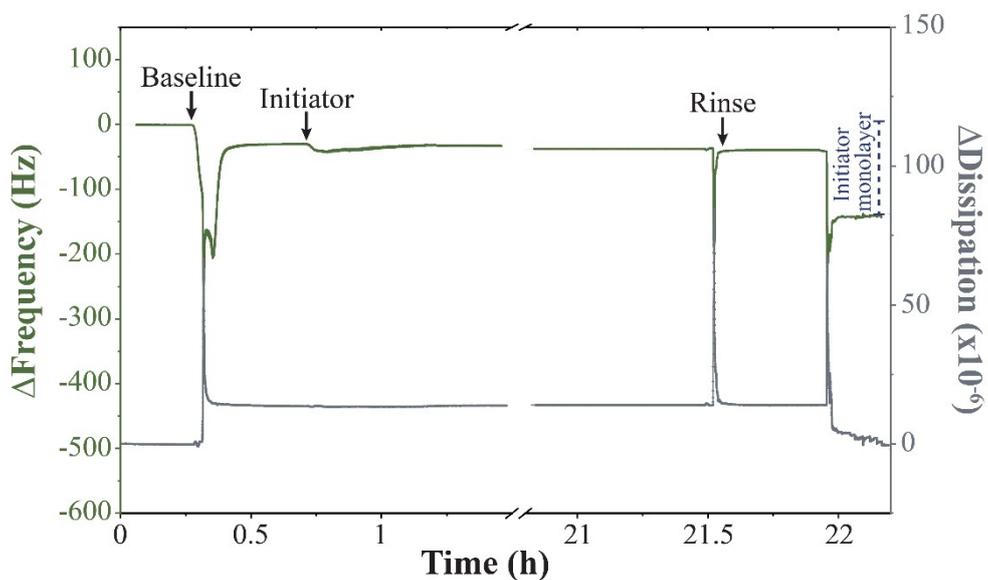
*Materials.* Ethyl alcohol, dimethylformamide (DMF), copper chloride, tetrahydrofuran (THF), 4,4'-dinonyl-2,2'-dipyridyl, allyl alcohol, triethylamine,  $\alpha$ -bromoisobutyryl bromide, sodium sulphate, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (known as Karstedt's catalyst), potassium chloride were purchased from Sigma Aldrich. Dichloromethane (DCM) was purchased from Alfa Aesar. Triethoxysilane was purchased from ACROS organics. All chemicals were used with no further purification. Millipore water from Thermo scientific barnstead SMART2PURE UV/UF water filter was used for experiments.

*BPE initiator synthesis.* The alkyl halide 2-Bromo-2-methylpropionyloxy propyl triethoxysilane (BPE) was used as ATRP initiator for the AFM samples in this study. A two-step BPE synthesis was adapted from previously reported protocols<sup>1</sup>. First, 1-[(2-bromo-2-methylpropionyl) oxy]-2-propene (BPP) was synthesized by adding  $\alpha$ -bromoisobutyryl bromide (97.89 mmol) dropwise into a cold solution (0 °C) made of allyl alcohol (146.3 mmol), DCM (1.56 mol), and triethylamine (117.6 mmol) and magnetically stirred for 3 hours at 0 °C. Stirring was continued for another 10 hours at room temperature. Following, the solvent was evaporated using a rotavapor. The residue was diluted in 50 mL of DCM and washed twice with 50 mL of 1N HCl, 1N NaHCO<sub>3</sub>, and millipore water sequentially. Washed product was dried over Na<sub>2</sub>SO<sub>4</sub> for 12 hours. After, the solution was filtered and dried under vacuum yielding BPP.

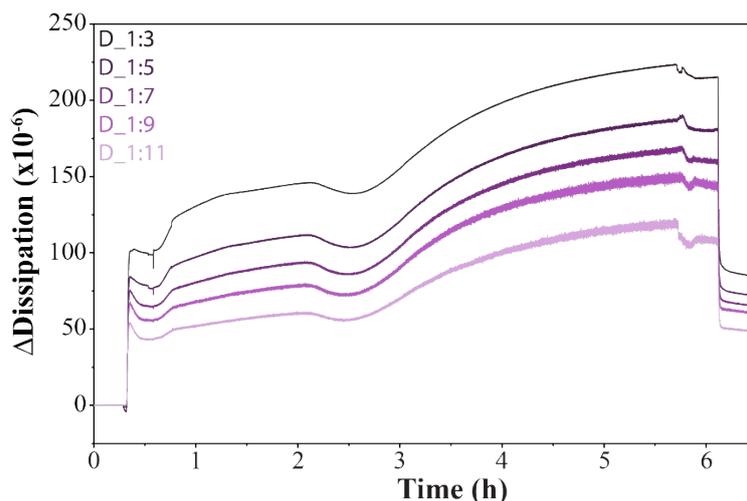
Second, BPP was modified to obtain BPE. BPP (86.2 mmol) was added into a two-neck round bottomed flask and purged with N<sub>2</sub> gas for 5 minutes. Triethoxysilane (136.27 mmol) and Karstedt's catalyst (0.106 mmol) were injected into the reaction and stirred for 24 hours under N<sub>2</sub> gas. At last, the reaction product was dried under vacuum yielding BPE. BPE was characterized by <sup>1</sup>H NMR in Chloroform-D. The software ACD/Spectrus by ACD Labs was used to analyse NMR spectra and to determine the purity of the synthesized BPE. Only BPE with more than 80% purity was utilized for ATRP. A Bruker 300 MHz Avance III HD Nano NMR machine was used to analyse both BPP and BPE.



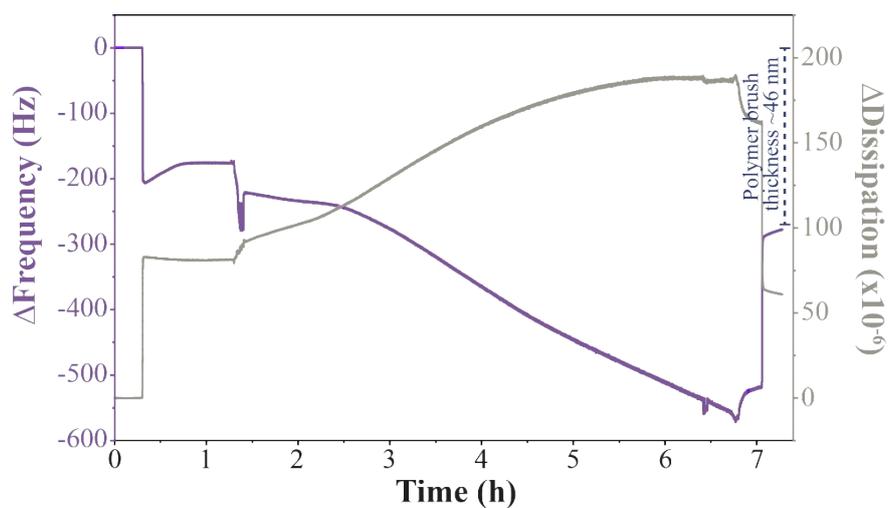
**Figure S1.**  $^1\text{H}$  NMR in deuterated chloroform of synthesized BBU initiator.



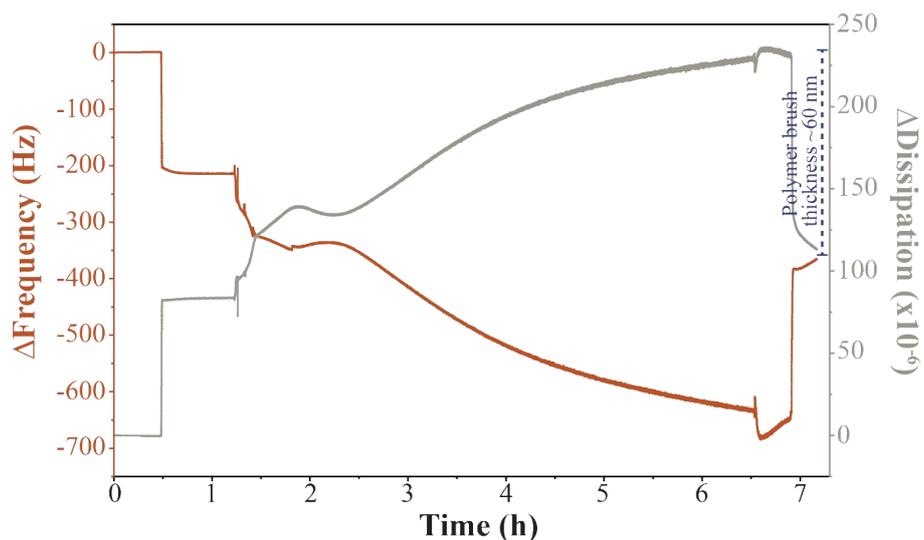
**Figure S2.** Immobilization of initiator over then QCM-D crystal. A solution of ATRP initiator in ethanol was incubated in the QCM-D chamber overnight and the initiator attachment the crystal was monitored. Monitoring of  $\Delta$ Frequency is indicated in green,  $\Delta$ Dissipation in grey and the difference in  $\Delta$ Frequency used to calculate the initiator monolayer thickness in blue.



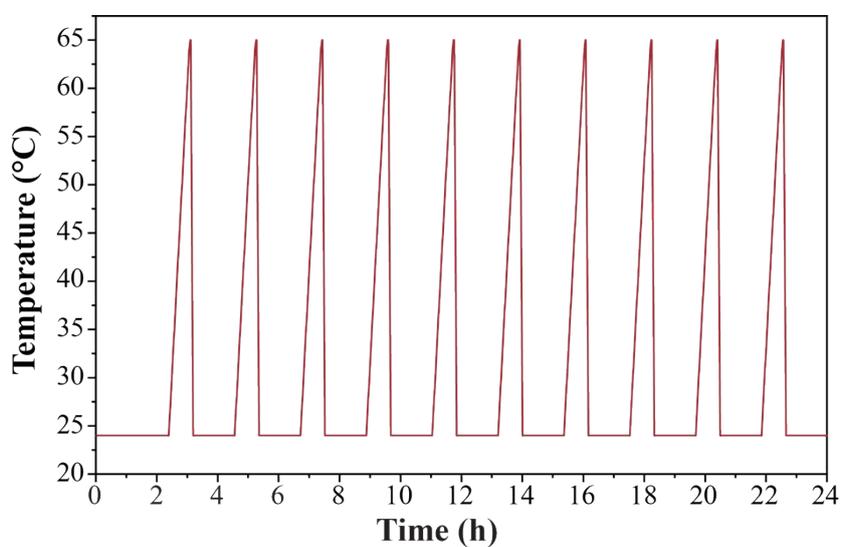
**Figure S3.** Dissipation changes during ATRP reaction. The spread of harmonics during the ATRP indicates the viscoelasticity changes due to polymer brush synthesis from the surface of a QCM-D sensor.



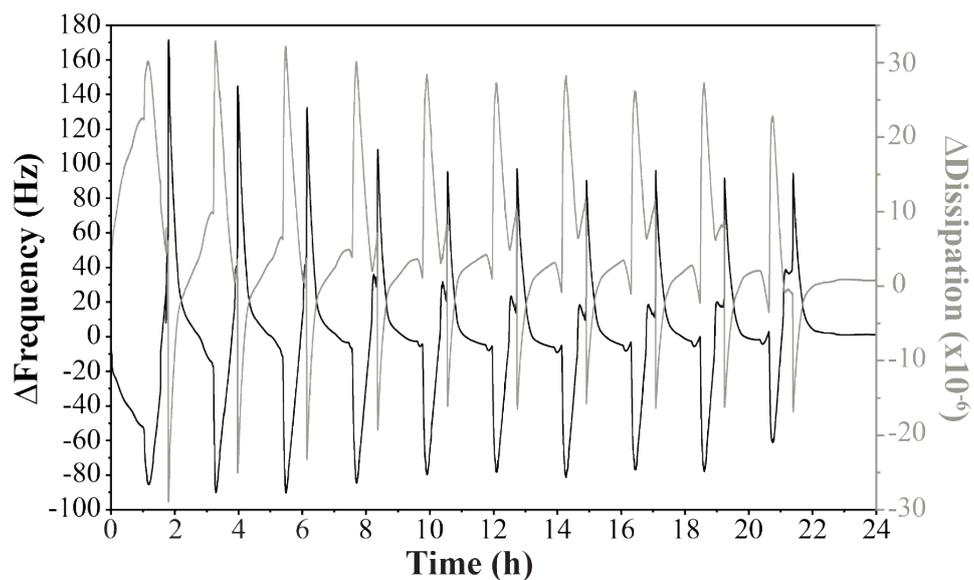
**Figure S4.** POEGMA-188 brushes ATRP synthesis followed by QCM-D. Monitoring of  $\Delta$ Frequency is indicated in purple,  $\Delta$ Dissipation in grey and the difference in  $\Delta$ Frequency used to calculate polymer brush thickness in blue.



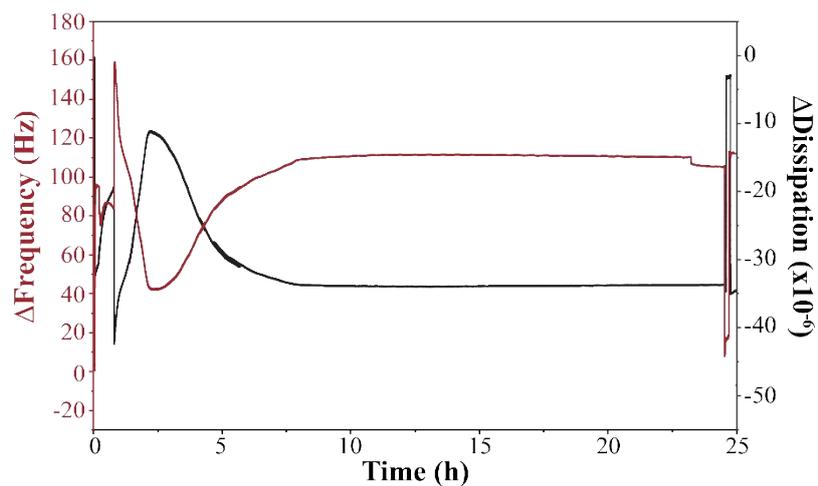
**Figure S5.** POEGMA-300 brushes ATRP synthesis followed by QCM-D. Monitoring of  $\Delta$ Frequency is indicated in orange,  $\Delta$ Dissipation in grey and the difference in  $\Delta$ Frequency used to calculate polymer brush thickness in blue.



**Figure S6.** Programed temperature cycles used for testing the phase transitions of POEGMA brushes grafted from the surface of a QCM-D sensor.



**Figure S7.** Behavior of an empty QCM-D sensor subjected to ten consecutive temperature cycles from 24 °C to 65 °C.



**Figure S8.** Phase transition of PNIPAM brushes followed by QCM-D. Polymer brushes were subjected to 10 consecutive temperature cycles.

## References

1. K. Ohno, T. Akashi, Y. Huang and Y. Tsujii, *Macromolecules*, 2010, **43**, 8805-8812.