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Electronic Supplementary Information

Swelling Induced Au-S Bond Breakage is Determined by the Molecular Composition of Surface Tethered Copolymers-carboxylated poly(OEGMA-*r*-HEMA)

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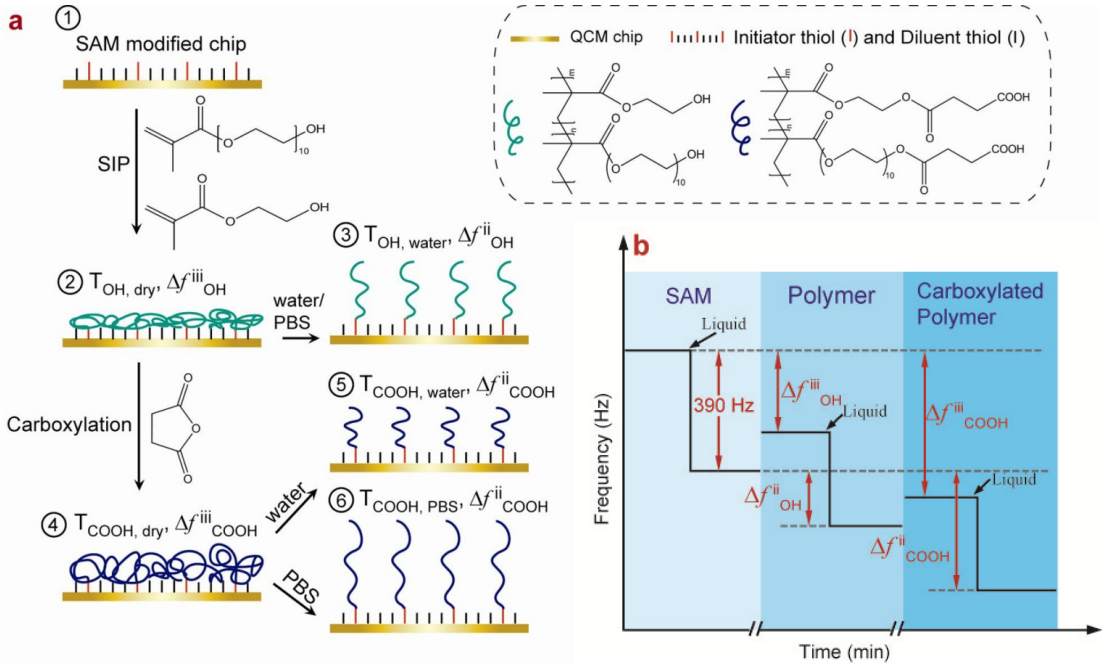
1. Experimental design



Scheme S1 Illustration of the experimental design and parameters used in this work. (a) States of QCM chip we proceeded with: an initiator SAM functionalized QCM chip vibrating in air (①), poly(OEGMA-*r*-HEMA) coated chip in air (②) and water (③), carboxylated poly(OEGMA-*r*-HEMA) coated chip in air (④) and in water (⑤) and PBS (⑥). The subscripts in the parameters indicated the corresponding states. Each state had its corresponding frequency measurement by QCM indicated in (b), where liquid refers to water or PBS.

We designed the experiments as following (Scheme S1). First, a bare QCM chip was measured for its absolute frequency as a reference. QCM chips with or without SAM modification showed no measurable frequency difference. After the QCM chip was coated with polymers by SIP, the dry thickness ($T_{OH,\ dry}$) and frequency change (Δf^{iii}_{OH}) were measured by ellipsometry and QCM respectively (subscript "OH" is used to indicate states before carboxylation). Δf^{iii}_{OH} was linearly related to the mass of the grafted polymer and $T_{OH,\ dry}$ (Fig. S3), which was in agreement with our previous work.[1] After the polymer-grafted QCM chip was carboxylated and tested again, one got $T_{COOH,}$

$_{dry}$ and Δf^{iii}_{COOH} (subscript "COOH" is used to indicate states after carboxylation). The polymer coated QCM chips before and after carboxylation were exposed to liquids as shown in Scheme S1. From the frequency shifts Δf^{ii}_{OH} and Δf^{ii}_{COOH}, as described in Scheme S1 and calculated according to our previous work[1], the wet thicknesses T_{wet} of the swelling polymer films were calculated based on the *solidified liquid layer* Model.[2]

2. Detailed derivation of Equation (1) – (3)

2.1. Calculation of $\chi_{HEMA,final}$.

According to the definition of q, we have:

$$q = \frac{\Delta m}{m} = \frac{\Delta M \cdot N \cdot e}{Mn_{OH} \cdot N} = \frac{100e}{Mn_{OH}} \qquad \text{(S1)}$$

where m and Δm are the mass and the mass increment, Mn_{OH} is the number-average molecular weight of poly(OEGMA-r-HEMA) before carboxylation process, e is the carboxylation efficiency, which is defined as the proportion of the carboxylated units to all units, ΔM = 100 is the molecular weight's increment of a carboxylated unit (ΔM = 100 for both OEGMA and HEMA units) and N is the degree of polymerization. From equation (S1), carboxylation efficiency e can be expressed as:

$$e = \frac{qMn_{OH}}{100} \qquad \text{(S2)}$$

As for homopolymers poly(OEGMA) and poly(HEMA), their carboxylation efficiencies e_{OEGMA} and e_{HEMA} were:

$$e_{OEGMA} = \frac{526q_{OEGMA}}{100} = 5.26q_{OEGMA}$$

$$e_{HEMA} = \frac{130q_{HEMA}}{100} = 1.3q_{HEMA}$$

where the numbers of 526 and 130 are the molecular weights of the OEGMA and HEMA monomers, respectively.

As for poly(OEGMA-r-HEMA), its carboxylation efficiency e is:

$$e = \frac{qMn_{OH}}{100} = \frac{q[130\chi_{HEMA,final} + 526(1-\chi_{HEMA,final})]}{100} \quad \text{(S3)}$$

where $\chi_{HEMA,final}$ is defined as the molar fraction of HEMA units in the copolymer; the subscript "final" is used to distinguish it from the molar fraction of HEMA monomers in the reaction solutions, $\chi_{HEMA,feed}$.

We assumed that the carboxylation efficiencies of OEGMA and HEMA remained unchanged in copolymer, which is true as proved in the following comparison experiment. Thus, the carboxylation efficiency of copolymer can also be expressed as:

$$e = e_{HEMA}\chi_{HEMA,final} + e_{OEGMA}(1-\chi_{HEMA,final}) = 1.3q_{HEMA}\chi_{HEMA,final} + 5.26q_{OEGMA}(1-\chi_{HEMA,final}) \quad \text{(S4)}$$

Combining (S3) and (S4), one got Equation (2):

$$\chi_{HEMA,final} = \frac{526(q-q_{OEGMA})}{130q_{HEMA} + 396q - 526q_{OEGMA}} \quad (2)$$

Based on eq. (2), one can now calculate the final copolymer composition $\chi_{HEMA,final}$ from q_{OEGMA}, q_{HEMA} and q.

The value of q could be calculated by eq. (1):

$$q = \frac{\Delta m}{m} = \frac{\Delta f^{iii}_{COOH} - \Delta f^{iii}_{OH}}{\Delta f^{iii}_{OH}} \quad (1)$$

Each value of q was determined by plotting Δf^{iii}_{COOH} against Δf^{iii}_{OH} of a range of samples with various thickness and linearly fitting the curves (Fig. S1). With the values of q, the values of $\chi_{HEMA,final}$

and e can be obtained from eq. (2) and (S4) in succession and results were presented in Table 1 (data of e not shown).

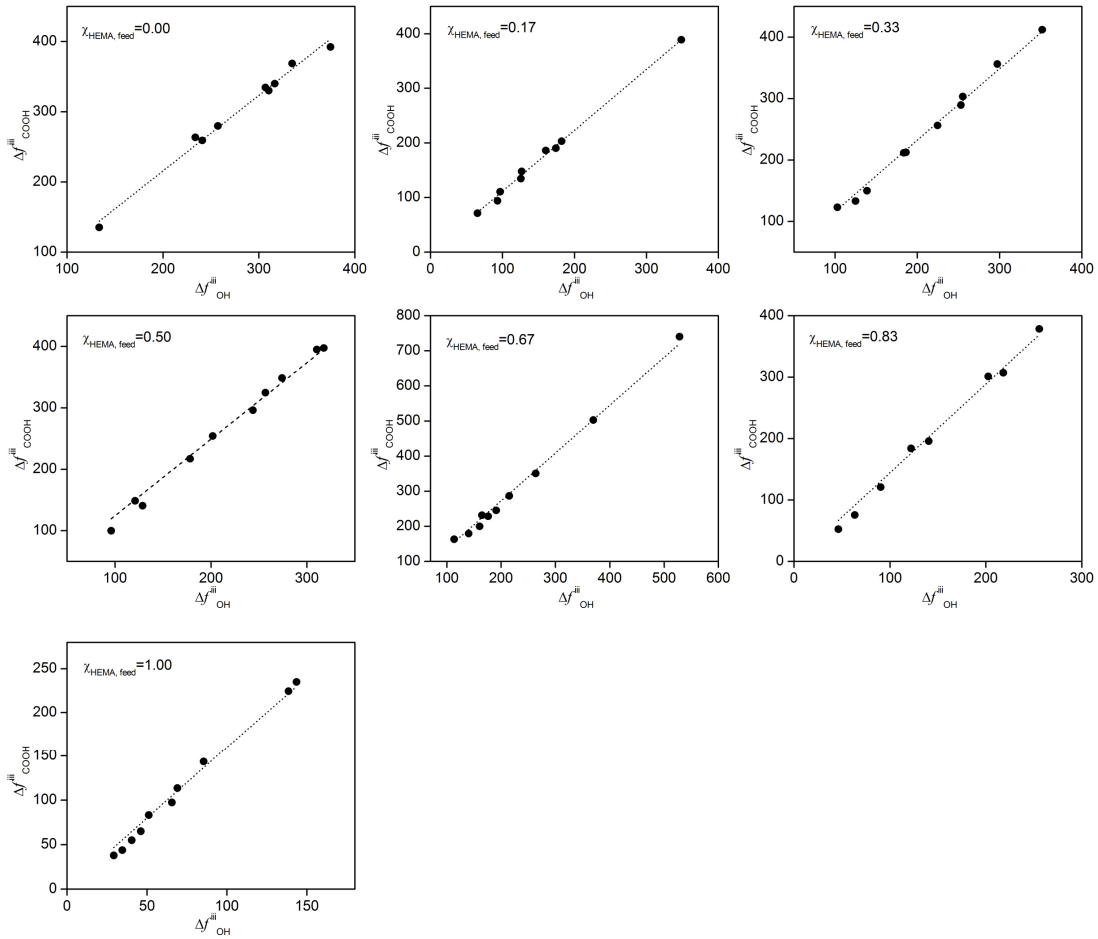


Fig. S1 The relations between Δf^{iii}_{COOH} and Δf^{iii}_{OH} for each $\chi_{HEMA,feed}$. For each $\chi_{HEMA,feed}$, the values of Δf^{iii}_{COOH} and Δf^{iii}_{OH} were measured for films of various thickness. The slopes (q+1) was linearly fitted from the curves and all R^2>0.98.

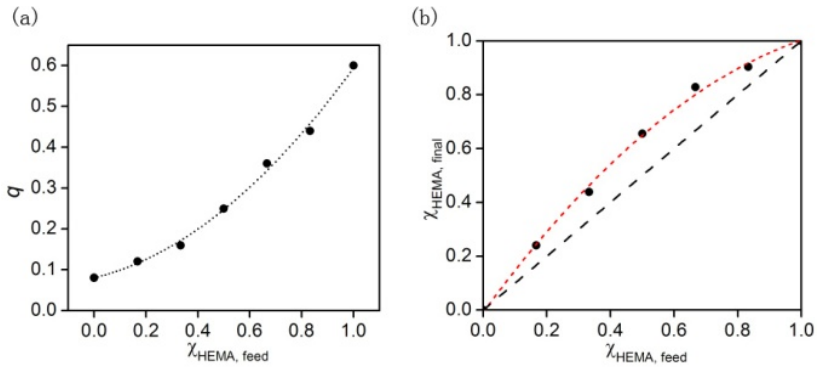


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Fig. S2 (a) The relation between feed ratio $\chi_{HEMA,feed}$ and mass increase ratio q. Higher value of q corresponds to larger fraction of HEMA in the copolymer; (b) is the copolymer composition curve of poly(OEGMA-r-HEMA), from which we obtained the reactivity ratios: $r_{HEMA} = 2.47 \pm 0.27 > 1 > r_{OEGMA} = 0.83 \pm 0.1$ (Section 5 of ESI).

2.2. Calculation of n.

From our previous work extended from the Sauerbrey Equation[3], we have:

$$N = \frac{C\Delta f_{OH}^{iii} N_A}{3\sigma Mn_{OH}} \qquad \text{(S5)}$$

where constant C is 17.7 ng cm^{-2} Hz^{-1} for the QCM chips we used, $\sigma = 0.116$ chains nm^{-2} is the polymer chain density (see section 4 of ESI for the detailed calculation), N_A is the Avogadro's constant. As for the thickness-normalized degree of polymerization n, from its definition we have:

$$n = \frac{C\Delta f_{OH}^{iii} N_A}{3\sigma Mn_{OH} T_{OH,dry}} = \frac{CN_A}{\sigma Mn_{OH}} k_{2,dry} \qquad \text{(S6)}$$

in which

$$k_{2,dry} = \frac{\Delta f_{OH}^{iii}}{3T_{OH,dry}}$$

$$Mn_{OH} = 130\chi_{HEMA,final} + 526(1 - \chi_{HEMA,final})$$

For every feed ratio $\chi_{HEMA,feed}$, we obtained the values of $k_{2,dry}$ by plotting Δf^{iii}_{OH} against $T_{OH,dry}$ and linearly fitting the curves (Fig. S3). With the values of $k_{2,dry}$, the values of n can be obtained from eq. (S6). The results were presented in Table 1.

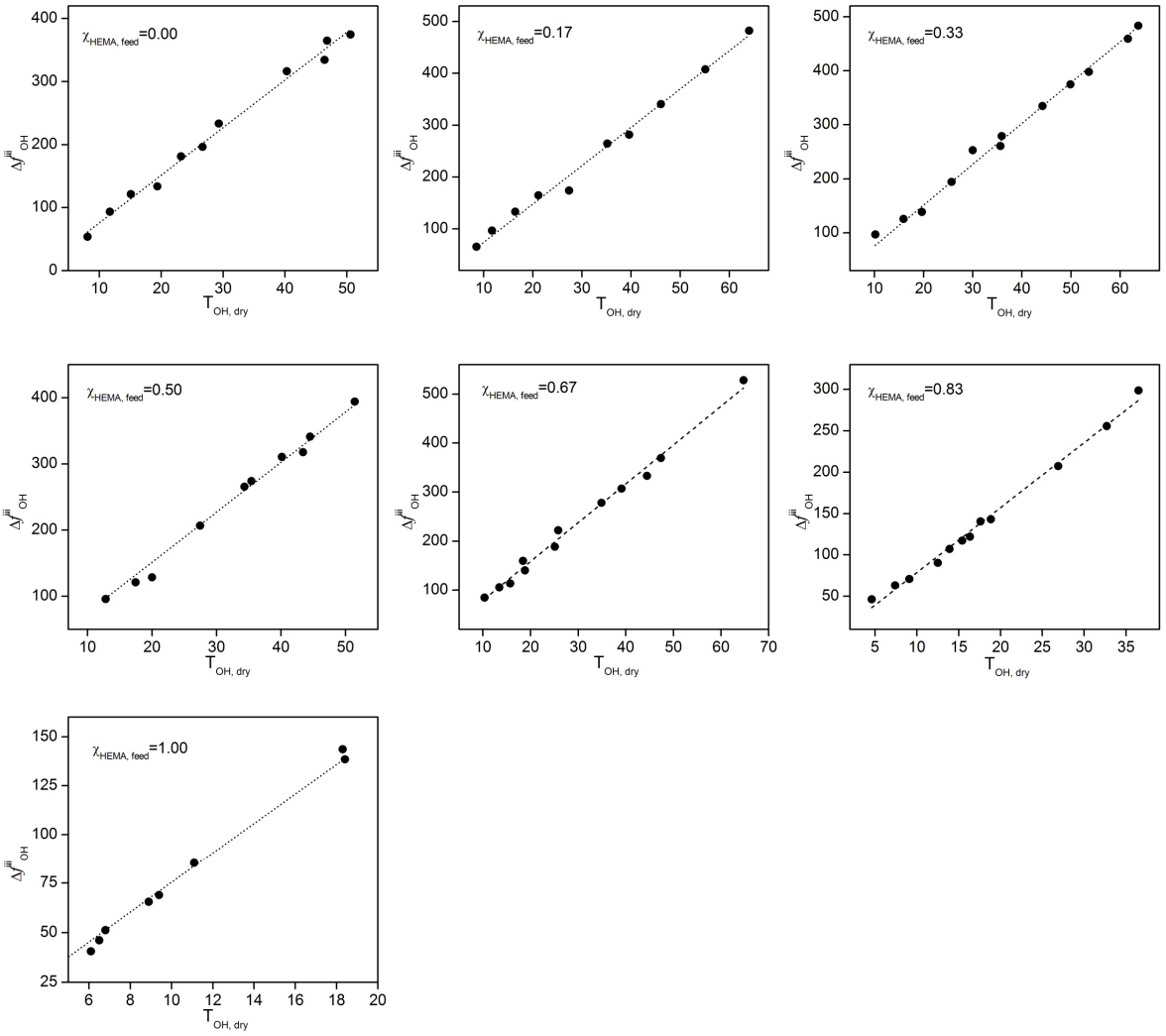

Fig. S3 The relations between Δf^{iii}_{OH} and $T_{OH,\,dry}$ for each $\chi_{HEMA,feed}$. For each $\chi_{HEMA,feed}$, the values of Δf^{iii}_{OH} and $T_{OH,\,dry}$ were measured for films of various thickness. The slopes $k_{2,\,dry}$ was fitted linearly from the curves and all $R^2>0.98$.

2.3. Calculation of *x*, *y*, *z* and *l*.

The value of *x*, *y*, *z* and *l* could be calculated from the copolymer composition $\chi_{HEMA,final}$ and carboxylation efficiencies e_{OEGMA} and e_{HEMA} with eq. (S7). Results were represented in Table 1 and Figure S4:

$$\begin{aligned} x &= n_{OEGMA_{COOH}} = n(1-\chi_{HEMA,final})e_{OEGMA} \\ y &= n_{HEMA} = n\chi_{HEMA,final}(1-e_{HEMA}) \\ z &= n_{OEGMA} = n(1-\chi_{HEMA,final})(1-e_{OEGMA}) \\ l &= n_{HEMA_{COOH}} = n\chi_{HEMA,final}e_{HEMA} \end{aligned} \qquad \text{(S7)}$$

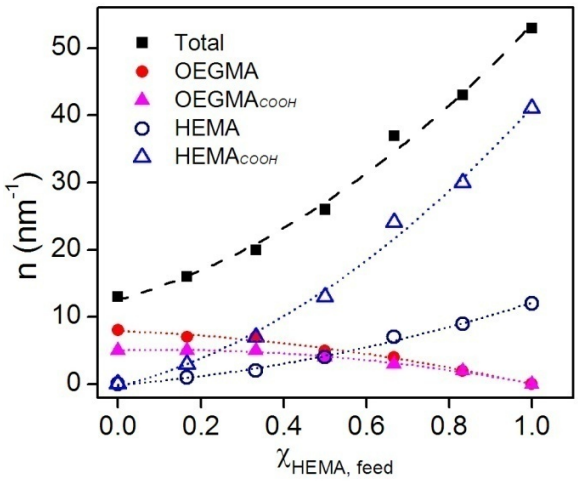

Fig. S4 The distribution of monomer units (shown as thickness-normalized degree of polymerization, n) in a polymer chain over different feed ratios. The pink solid triangles represent for the number of $OEGMA_{COOH}$ (*x*), blue hollow dots for HEMA (*y*), red solid dots for OEMGA (*y*), blue hollow triangles for $HEMA_{COOH}$ (*l*) and the black solid squares for the total amount of them (n).

2.4. Predetermination of t_{PBS}.

First, the swelling ratios ($t_{OH,\ PBS}$ and $t_{COOH,\ PBS}$, for polymers before or after carboxylation, respectively) of homopolymer poly(OEGMA) and poly(HEMA) in PBS were measured by QCM (Table S1).

Table S1 The swelling ratio of homopolymers poly(OEGMA) and poly(HEMA) in PBS.

homopolymer	$t_{OH,\,PBS}$	$t_{COOH,\,PBS}$
poly(OEGMA)	3.20	2.72
poly(HEMA)	1.87	8.72

As the swelling ratio was the ratio of wet thickness ($T_{COOH,\,PBS}$ and $T_{OH,\,PBS}$) to $T_{OH,\,dry}$, the value of it could also be interpreted as the one-nanometer chain's length when swelling in PBS. We tried to determine the length (height) of one unit of each of the four components in PBS ($\tau_{i,\,PBS}$):

in poly(OEGMA):

$$\tau_{OEGMA,PBS} = \frac{t_{OH,PBS}}{n}$$

$$\tau_{OEGMA_{COOH},PBS} = \frac{t_{COOH,PBS} - z \cdot \tau_{OEGMA,i}}{x}$$

in poly(HEMA): (S8)

$$\tau_{HEMA,PBS} = \frac{t_{OH,PBS}}{n}$$

$$\tau_{HEMA_{COOH},PBS} = \frac{t_{COOH,PBS} - y \cdot \tau_{HEMA,i}}{l}$$

Results were listed in Table S2.

Table S2 Length (height) of one unit of each of the four components in PBS.

Component	τ_{PBS} (nm)
OEGMA	0.25
$OEGMA_{COOH}$	0.15
HEMA	0.04
$HEMA_{COOH}$	0.20

We have determined the distribution of the four components in carboxylated poly(OEGMA-r-HEMA) (*x*, *y*, *z* and *l*; Table 1, Figure S4). With the information of each of them's length (height) in PBS, the

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overall wet thickness of surface-tethered polyelectrolyte could be estimated by summing them up:

$$T_{COOH,PBS} = (\tau_{OEGMAcooh,i} \cdot x + \tau_{HEMA,i} \cdot y + \tau_{OEGMA,i} \cdot z + \tau_{HEMAcooh,i} \cdot l) \cdot T_{OH,dry}$$
$$= (0.15x + 0.04y + 0.25z + 0.20l) \cdot T_{OH,dry}$$

Thus the swelling ratio $t_{COOH, PBS}$ is:

$$t^*_{COOH,PBS} = T_{COOH,PBS} / T_{OH,dry} = 0.15x + 0.04y + 0.25z + 0.20l \quad (11)$$

(*For the sake of simplicity, $t_{COOH, PBS}$ was denoted t_{PBS} in the communication main text.)

With the same method, swelling ratio in water could also be predetermined (data not shown).

3. Validation of the method for predetermining swelling ratios.

3.1. The experimental swelling ratios.

Table S3 List of the experimental swelling behaviours of poly(OEGMA-*r*-HEMA) in three surrounding environments: dry, water or PBS.

$\chi_{HEMA,feed}$	Experimental swelling ratio[a]			
	$t_{COOH, dry}$	$t_{OH, water}$	$t_{COOH, water}$	$t_{COOH, PBS}$
0.17	1.11	2.94	1.81	2.96
0.33	1.17	3.20	2.24	3.89
0.50	1.24	2.80	2.11	4.26
0.67	1.36	3.06	2.20	6.30
0.83	1.45	2.46	2.12	7.52

3.2. Comparison between predicted and experimental values.

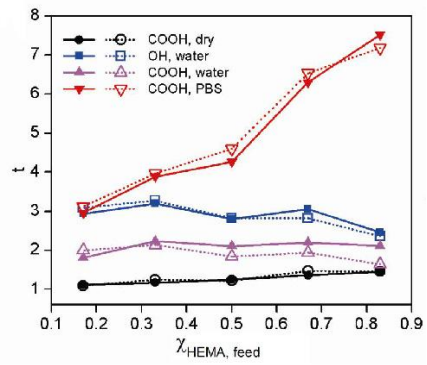

Fig. S5 The comparison of the predicted and experimental swelling ratios in different states. Data in solid symbol are experimental results, and in hollow one are predicted results.

4. Calculation of polymer chain density σ

As the initiator density was low (χ_I^{sol}=2.5%, < 10%), one could assume that the initiator efficiency was 100%, which meant polymer chain density equaled initiator density. As for the calculation of initiator density, we adopted the structural model described by J. Christopher Love *et al.*, in which the sulfur atoms were positioned in the 3-fold hollows of the Au (111) lattice (Figure S6).[4] So when χ_I^{sol}=100%, the initiator density was:

$$\sigma_{100} = \frac{\frac{3}{6}}{\frac{1}{2}\times\frac{\sqrt{3}}{2}\times a^2} = \frac{2}{\sqrt{3}a^2} = 4.637 \text{ chains nm}^{-2}$$

As for χ_I^{sol}=2.5%, $\sigma_{2.5}$=2.5% σ_{100}=0.116 chains nm^{-2}

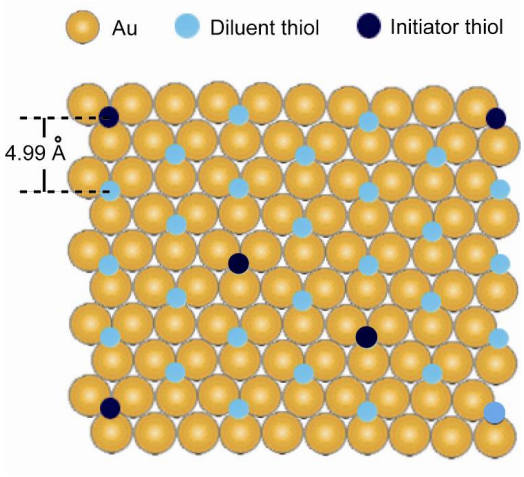

Fig. S6 The structure model adopted to calculate the polymer chain density.

5. Calculation of reactivity ratios based on Mayo-Lewis model.

As we have successfully got a series of feed and respective final ratios for copolymerization of HEMA and OEGMA, a $\chi_{HEMA,final}$-$\chi_{HEMA,feed}$ curve was achieved. Hence we employed Mayo-Lewis model[5] and applied the equation below to fit the curve subsequently acquire the reactivity ratios of each monomer in this copolymerization. The fitting curve is shown in Figure S2(b), R^2=0.998, r_{HEMA}=2.47±0.27, r_{OEGMA}=0.83±0.1.

$$\chi_{HEMA,final} = \frac{r_{HEMA}\chi_{HEMA,feed}^{\ 2} + \chi_{HEMA,feed}(1-\chi_{HEMA,feed})}{r_{HEMA}\chi_{HEMA,feed}^{\ 2} + 2\chi_{HEMA,feed}(1-\chi_{HEMA,feed}) + r_{OEGMA}(1-\chi_{HEMA,feed})^2}$$

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