Poly(ethylene glycol) Brushes

Poly(ethylene glycol) (-CH_2-CH_2-O-) molecules of different molecular weights (assume each is perfectly monodisperse) have been covalently attached to gold by a reactive terminal thiol group on one end. The dry surface coverage on gold was determined experimentally:

Molecular weight (kDa)	2	5	10	20	30
Surface coverage (ng/cm^2)	306	449	631	631	404

(A) Calculate and plot the expected height of the brush vs molecular weight. The monomer length is 0.28 nm and the Kuhn length is 0.72 nm.

The heights of the brushes in water were also determined independently:

Molecular weight (kDa)	2	5	10	20	30
Height (nm)	6.5	12.1	23.6	38	29

(B) Compare the values to those calculated. Do the brushes appear to be strongly stretched in reality? (Motivate your answer.)

To calculate the height according to the Alexander - de Gennes brush we need the grafting density Γ in number of polymers per area. Instead we get it in mass per area, which we can call Γ_{mass}. If M is given per mole the conversion is:

$$\Gamma = \frac{\Gamma_{\text{mass}}}{M} N_{\text{A}}$$

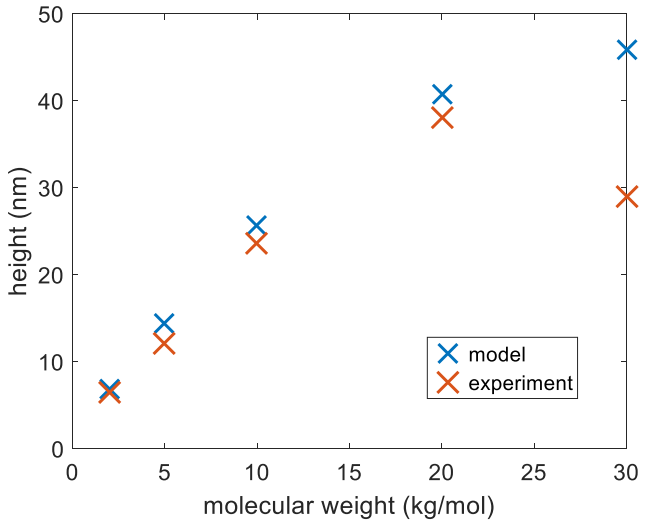
This gives the new table:

Molecular weight (kgmol^{-1})	2	5	10	20	30
Surface coverage (nm^{-2})	0.92	0.54	0.38	0.19	0.08

The monomer weight is m = 44 gmol^{-1} and $N = M/m$. We also need to rescale before getting the brush height:

$$H = \left[\frac{\Gamma}{3}\right]^{\frac{1}{3}} b^{\frac{2}{3}} a \frac{M}{m}$$

For a = 0.28 nm and b = 0.72 nm we can plot the result:



The agreement is quite good for all M except the largest 30 kgmol^{-1}, just a small factor off. So the brushes are strongly stretched up to 20 kgmol^{-1}. Note that the plot should not be linear even for strongly stretched brushes, because the grafting density is not constant! Any discussion on linearity of the plot is only relevant is the grafting density is the same.

A decent alternative is to compare the heights with the contour lengths and calculate the stretching in percent. Since the percentages are quite high it is fairly safe to say they are strongly stretched.

Data is taken from Emilsson et al. ACS Applied Materials and Interfaces 2015, 7 (14), 7505-7515.