Chemical auxiliary-free polymerization yielding non-linear PEG for protein-resistant application

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Supporting Information

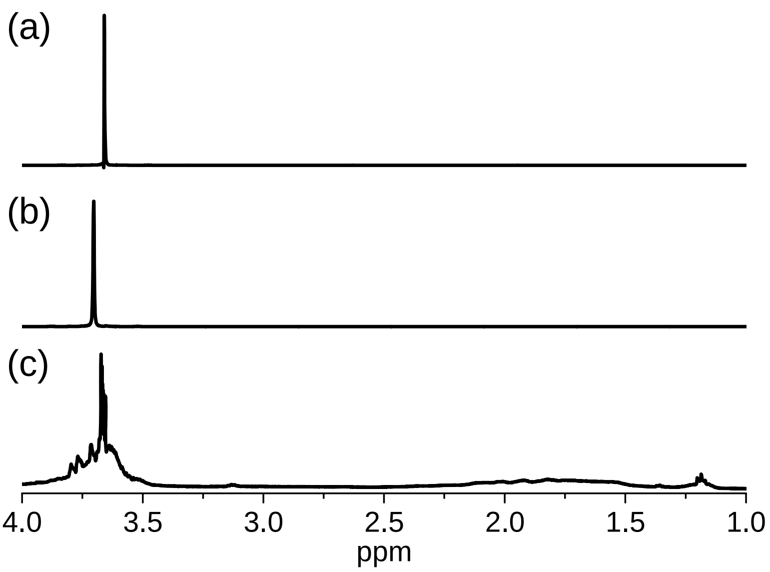


Figure S1 ^{1}H NMR spectra of (a) ethylene glycol, (b) commercial linear PEG, and (c) our NLPEG, respectively, which were obtained in D_2O and room temperature.

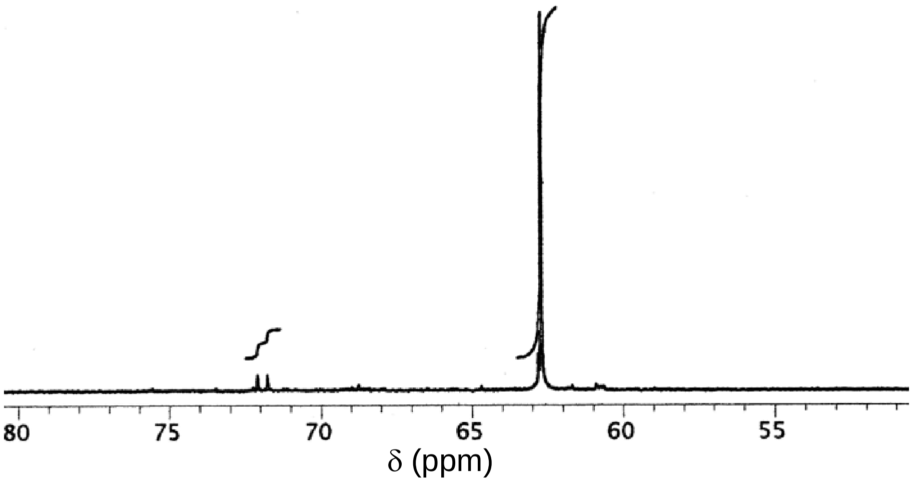


Figure S2 ^{13}C NMR inverse gated spectrum with the integration of signal intensity showing that the repeating units of NLPEG contain CH and CH_2 at a ratio of 1: 12.

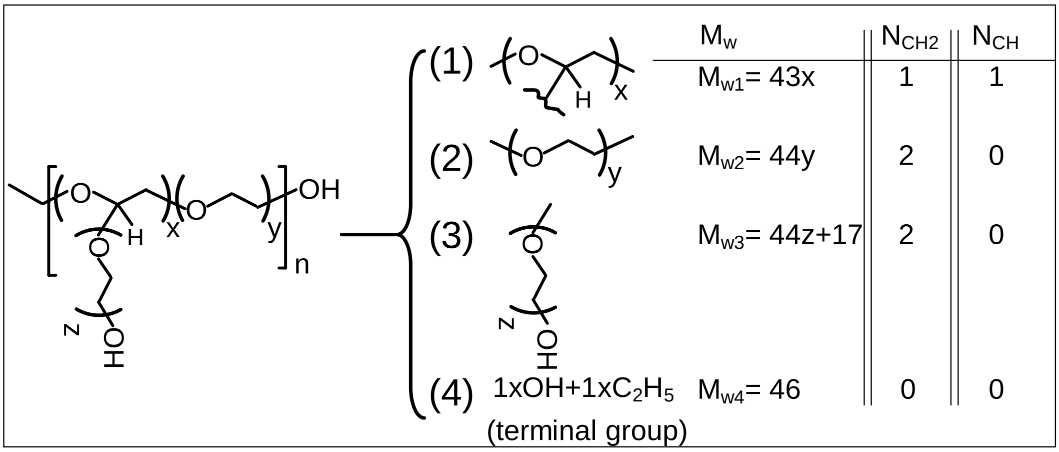
The calculation of DB value: Regarding the calculation of the degree of branching (DB), the DB was commonly determined according to the following equation:

$$DB = \frac{D+T}{D+L+T} \approx \frac{2D}{2D+L}$$

In which D, T and L are that the fractions of dendritic, terminal and linear units in the resulting polymer are obtained from the integration of the respective signals in IG ^{13}C NMR-spectra. For example, while the ratio of CH/CH_2 was 1:12, the methane carbon (CH) and the methylene carbon (CH_2) presented dendritic units and linear units, respectively. Thus, D = 1, L = 12, so that DB = (2 x 1)/(2 x 1 + 12) = 0.143 (shown in table 1 the fourth row of DB values) and so on.

Electronic Supplementary Material (ESI) for RSC Advances

Details of Structure Analysis: To aid the explanation and understanding of table 1, the calculation processes were written as following. Since the ratio of CH/CH_2 was 1:12 ± 3, which was estimated by seven different samples. This result illustrated that the DB values of our novel polymer have a distribution from a minimum value (1:9) to a maximum value (1:15). Thus, we listed in the table 1 that was based all possibilities. Additionally, these parameters of repeating units (e.g., x, y, z and n) of each segment need to be defined as an integer.



Total Molecular weight (M_w) $= (M_{w1}+M_{w2}+M_{w3}) \times n + M_{w4}$

$= (43x+44y+44z+17)\times n+46$ ------------(**eq.1**)

If Mw = 2000 $\longrightarrow$ $(43x+44y+44z+17)\times n+46 = 2000$

$43nx+44\,n(y+z)+17n = 1954$------------(**eq.2**)

If r = CH/CH2=1/9

thus, the number of CH2 (N_{CH2}) = x + 2y + 2z

thus, the number of CH (N_{CH}) = x

$\longrightarrow \dfrac{x}{x+2y+2z} = \dfrac{1}{9}$

$\longrightarrow$ y + z = 4x------------(**eq.3**)

(Note that, X ≠ 0, z ≠ 0, to avoid the side chain disappearance of NLPEG).

⇨ To combine **eq. 2** and **eq. 3** $\longrightarrow$ 219nx + 17n=1954 ----(**eq.4-1**)

so that

If r = CH/CH2=1/10 $y + z = \frac{9}{2}x$ $\longrightarrow$ 241nx + 17n=1954 ----(**eq.4-2**)

If r = CH/CH2=1/11 $y + z = 5x$ $\longrightarrow$ 263nx + 17n=1954 ----(**eq.4-3**)

If r = CH/CH2=1/12 $y + z = \frac{11}{2}x$ $\longrightarrow$ 285nx + 17n=1954 ----(**eq.4-4**)

If r = CH/CH2=1/13 $y + z = 6x$ $\longrightarrow$ 307nx + 17n=1954 ----(**eq.4-5**)

If r = CH/CH2=1/14 $y + z = \frac{13}{2}x$ $\longrightarrow$ 329nx + 17n=1954 ----(**eq.4-6**)

If r = CH/CH2=1/15 $y + z = 7x$ $\longrightarrow$ 351nx + 17n=1954 ----(**eq.4-7**)

Parameters in eq. 4-1 219nx+17n = 1954 and y + z = 4x		
x = 1	y + z = 4	n = 8.3 ≒ 8
x = 2	y + z = 8	n = 3.9≒ 4
x = 3	y + z = 12	n = 3.1 ≒ 3
x = 4	y + z = 16	n = 2.2 ≒ 2
x = 5	y + z = 20	n = 1.8 ≒ 2
x = 6	y + z = 24	n = 1.5 ≒ 2
X = 7	y + z = 28	n = 1.26 ≒ 1

Parameters in eq. 4-2 (241nx + 17n= 1954) and y + z = (9/2)x		
x = 1	y + z = 4.5[b]	n = 7.6≒ 8
x = 2	y + z = 9	n = 3.9 ≒ 4
x = 3	y + z = 13.5	n = 2.6 ≒ 3
x = 4	y + z = 18	n = 1.9 ≒ 2
x = 5	y + z = 22.5	n = 1.6 ≒ 2
x = 6	y + z = 27	n = 1.3 ≒ 1
x = 7	y + z = 31.5	n = 1.1 ≒ 1

Parameters in eq. 4-3 (263nx + 17n = 1954) and y + z = 5x		
x = 1	y + z = 5	n = 7.0 ≒ 7
x = 2	y + z = 10	n = 3.6 ≒ 4
x = 3	y + z = 15	n = 2.4 ≒ 2
x = 4	y + z = 20	n = 1.8 ≒ 2
x = 5	y + z = 25	n = 1.5 ≒ 2
x = 6	y + z = 30	n = 1.2 ≒ 1
x = 7	y + z = 35	n = 1.1 ≒ 1

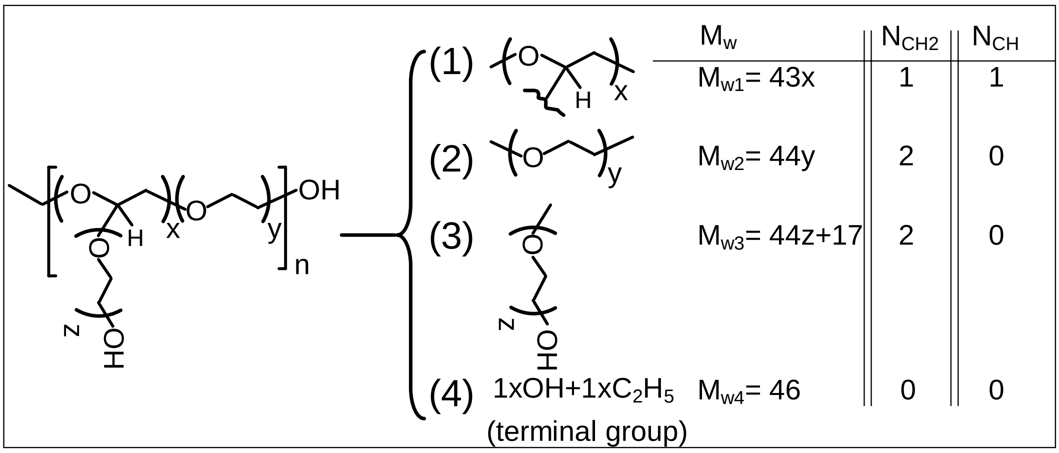
Parameters in eq. 4-4 (285nx + 17n = 1954) and y + z = (11/2)x		
x = 1	y + z = 5.5	n = 6.5 ≒ 7
x = 2	y + z = 11	n = 3.3 ≒ 3
x = 3	y + z = 16.5	n = 2.2 ≒ 2
x = 4	y + z = 22	n = 1.7 ≒ 2
x = 5	y + z = 27.5	n = 1.4 ≒ 1
x = 6	y + z = 33	n = 1.1 ≒ 1
x = 7	y + z = 38.5	n = 0.97 ≒ 1

Parameters in eq. 4-5 (307nx + 17n = 1954) and y + z = 6x		
x = 1	y + z = 6	n = 6.0 ≒ 6
x = 2	y + z = 12	n = 3.1 ≒ 3
x = 3	y + z = 18	n = 2.1 ≒ 2
x = 4	y + z = 24	n = 1.6 ≒ 2
x = 5	y + z = 30	n = 1.3 ≒ 1
x = 6	y + z = 36	n = 1.0 ≒ 1
x = 7	y + z = 42	n = 0.92 ≒ 1

Parameters in eq. 4-6 (329nx + 17n = 1954) and y + z = (13/2)x		
x = 1	y + z = 6.5	n = 5.6 ≒ 6
x = 2	y + z = 13	n = 2.9 ≒ 3
x = 3	y + z = 19.5	n = 1.9 ≒ 2
x = 4	y + z = 26	n = 1.5 ≒ 2
x = 5	y + z = 32.5	n = 1.2 ≒ 1
x = 6	y + z = 39	n = 0.98 ≒ 1
x = 7	y + z = 45.5	n = 0.84 ≒ 1

Parameters in eq. 4-7 (351nx + 17n = 1954) and y + z = 7x		
x = 1	y + z = 7	n = 5.3 ≒ 5
x = 2	y + z = 14	n = 2.7 ≒ 3
x = 3	y + z = 21	n = 1.8 ≒ 2
x = 4	y + z = 28	n = 1.4 ≒ 1
x = 5	y + z = 35	n = 1.1 ≒ 1
x = 6	y + z = 42	n = 0.92 ≒ 1
x = 7	y + z = 49	n = 0.80 ≒ 1

Note that, the sum of y + z is integer, if is non-integer that should be culled. All calculations allow the n value to be maximized. The gray rows were chosen to list in table 1, based on the x and n had supposed minimum and maximum value, respectively.



Total Molecular weight $(M_w) = (M_{w1} + M_{w2} + M_{w3}) \times n + M_{w4}$

$= (43x + 44y + 44z+17) \times n + 46$ ------------(**eq.1**)

If $Mw = 25000 \longrightarrow (43x+44y+44z+17)\times n + 46 = 25000$

$43nx+44\,n(y+z)+17n = 24954$ ---------(**eq.2**)

If r = CH/CH2=1/9

thus, the number of CH2 $(N_{CH2}) = x + 2y + 2z$

thus, the number of CH $(N_{CH}) = x$ $\longrightarrow \dfrac{x}{x + 2y + 2z} = \dfrac{1}{9}$

$\longrightarrow y + z = 4x$------------(**eq.3**)

(Note that, X ≠ 0, z ≠ 0, to avoid the side chain disappearance of NLPEG.)

⇨ To combine **eq. 2** and **eq. 3** $\longrightarrow 219nx + 17n = 24954$ ---(**eq.4-1**)

so that

If r = CH/CH2=1/10 $y + z = \frac{9}{2}x \longrightarrow 241nx + 17n = 24954$ ---(**eq.4-2**)

If r = CH/CH2=1/11 $y + z = 5x \longrightarrow 263nx + 17n = 24954$ ---(**eq.4-3**)

If r = CH/CH2=1/12 $y + z = \frac{11}{2}x \longrightarrow 285nx + 17n = 24954$ ---(**eq.4-4**)

If r = CH/CH2=1/13 $y + z = 6x \longrightarrow 307nx + 17n = 24954$ ---(**eq.4-5**)

If r = CH/CH2=1/14 $y + z = \frac{13}{2}x \longrightarrow 329nx + 17n = 24954$ ---(**eq.4-6**)

If r = CH/CH2=1/15 $y + z = 7x \longrightarrow 351nx + 17n = 24954$ ---(**eq.4-7**)

Parameters in eq. 4-1 219nx+17n = 24954 and y + z = 4x		
x = 1	y + z = 4	n = 105.7 ≒ 106
x = 2	y + z = 8	n = 54.8 ≒ 55
x = 3	y + z = 12	n = 37.0 ≒ 37
x = 4	y + z = 16	n = 27.9 ≒ 28
x = 5	y + z = 20	n = 22.4 ≒ 22
x = 6	y + z = 24	n = 18.7 ≒ 19
X = 7	y + z = 28	n = 16.1 ≒ 16

Parameters in eq. 4-2 (241nx + 17n= 24954) and y + z = (9/2)x		
x = 1	y + z = 4.5	n = 96.7 ≒ 97
x = 2	y + z = 9	n = 50.0 ≒ 50
x = 3	y + z = 13.5	n = 33.7 ≒ 34
x = 4	y + z = 18	n = 25.4 ≒ 25
x = 5	y + z = 22.5	n = 20.4 ≒ 20
x = 6	y + z = 27	n = 17.1 ≒ 17
x = 7	y + z = 31.5	n = 14.6 ≒ 15

Parameters in eq. 4-3 (263nx + 17n = 24954) and y + z = 5x		
x = 1	y + z = 5	n = 89.1 ≒ 89
x = 2	y + z = 10	n = 46.0 ≒ 46
x = 3	y + z = 15	n = 31.0 ≒ 31
x = 4	y + z = 20	n = 23.3 ≒ 23
x = 5	y + z = 25	n = 18.7 ≒ 19
x = 6	y + z = 30	n = 15.6 ≒ 16
x = 7	y + z = 35	n = 13.4 ≒ 13

Parameters in eq. 4-4 (285nx+17n = 24954) and y + z = (11/2)x		
x = 1	y + z = 5.5	n = 82.6 ≒ 83
x = 2	y + z = 11	n = 42.5 ≒ 43
x = 3	y + z = 16.5	n = 28.6 ≒ 29
x = 4	y + z = 22	n = 21.6 ≒ 22
x = 5	y + z = 27.5	n = 17.3 ≒ 17
x = 6	y + z = 33	n = 14.4 ≒ 14
x = 7	y + z = 38.5	n = 12.4 ≒ 12

Parameters in eq. 4-5 (307nx + 17n = 24954) and y + z = 6x		
x = 1	y + z = 6	n = 77.0 ≒ 77
x = 2	y + z = 12	n = 39.5 ≒ 40
x = 3	y + z = 18	n = 26.6 ≒ 27
x = 4	y + z = 24	n = 20.0 ≒ 20
x = 5	y + z = 30	n = 16.1 ≒ 16
x = 6	y + z = 36	n = 13.4 ≒ 13
x = 7	y + z = 42	n = 11.5 ≒ 12

Parameters in eq. 4-6 (329nx+17n = 24954) and y + z = (13/2)x		
x = 1	y + z = 6.5	n = 72.1 ≒ 72
x = 2	y + z = 13	n = 37.0 ≒ 37
x = 3	y + z = 19.5	n = 24.9 ≒ 25
x = 4	y + z = 26	n = 18.7 ≒ 19
x = 5	y + z = 32.5	n = 15.0 ≒ 15
x = 6	y + z = 39	n = 12.5 ≒ 13
x = 7	y + z = 45.5	n = 10.8 ≒ 11

Parameters in eq. 4-7 (351nx + 17n = 24954) and y + z = 7x		
x = 1	y + z = 7	n = 67.8 ≒ 68
x = 2	y + z = 14	n = 34.7 ≒ 35
x = 3	y + z = 21	n = 23.3 ≒ 23
x = 4	y + z = 28	n = 17.6 ≒ 18
x = 5	y + z = 35	n = 14.0 ≒ 14
x = 6	y + z = 42	n = 11.8 ≒ 12
x = 7	y + z = 49	n = 10.1 ≒ 10

Note that, the sum of y + z is integer, if is non-integer that should be culled. All calculations allow the n value to be maximized. The gray rows were chosen to list in table 1, based on the x and n had supposed minimum and maximum value, respectively.

Details of yield analysis

(1) If r = CH/CH2 = **12**	39 $HOCH_2CH_2OH$ →	(repeating unit of NLPEG)$_{39}$
(1) mole ratio	39	1
(2) molecular weight	62	Mw = **2** kDa
(3) mole	110.7/62 = 1.785 mmol	X
(4) yield (%)		Y

⟹ 39/1 = 1.785/X

X = 0.0458 mmol = 91.5 mg

Y = 22.6/91.5 x 100 % = 25 %

(2) If r = CH/CH2 = **12**	572 $HOCH_2CH_2OH$ →	(repeating unit of NLPEG)$_{572}$
(1) mole ratio	572	1
(2) molecular weight	62	Mw = **25** kDa
(3) mole	110.7/62 = 1.785 mmol	X
(4) yield (%)		Y

⟹ 572/1 = 1.785/X

X = 3.121×10^{-3} mmol = 78.0 mg

Y = 23.1/78.0 x 100 % = 30 %

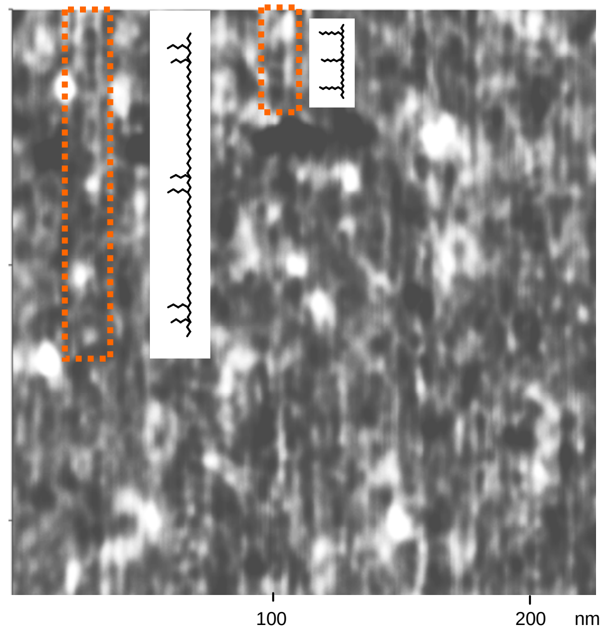


Figure S3 AFM image of NLPEG.

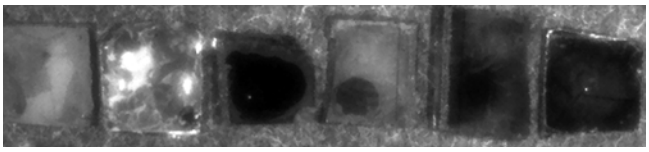


Figure S4 The experiment of protein resistance was performed by the adsorption of FITC conjugated BSA on SiN wafer with pre-grafted various polymers from left to right including: SiN alone, PDMS, LPEG (1 kDa), LPEG (6 kDa), star-PEG and our NLPEG (2 kDa). To compare the pictures, the fluorescence intensity of our NLPEG is closer to background intensity (black area of each picture).

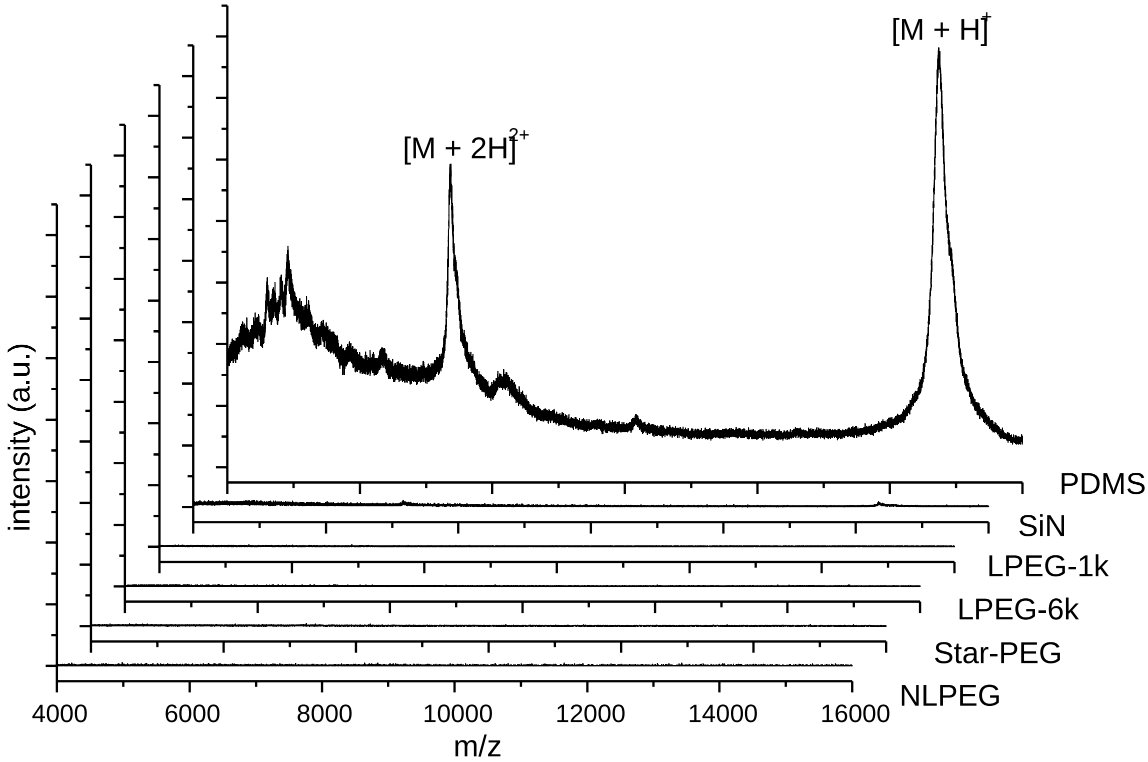


Figure S5 MALDI-TOF mass spectra of a lysozyme on a hydrophilic SiN which was pre-modified various polymers including PDMS, LPEG (1k), LPEG (6k), commercial star-PEG and NLPEG. As a result, no significant difference appears in various polymer coatings, except for PDMS coating. This result illustrates that our NLPEG can repel lysozyme as well as other PEG. Matrix: sinapinic acid.