Electronic Supplementary Information for

Into the polymer brush regime through the "grafting-to" method: Densely polymer-grafted rodlike viruses with an unusual nematic liquid crystal behavior

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1. Estimation of the conformation of the PEG chains on the virus surface

The conformation of the PEG chains tethered on a surface can be divided into two regimes: the "mushroom" or polymer brush.[1] This can be estimated based on the Flory dimension (R_F) of the grafted PEG, the distance between grafting points (D). When $D > R_F$, the grafted PEG chains adopt a "mushroom" conformation which normally occurs to low grafting density. In contrast, the grafted PEG chains adopt a "polymer brush" conformation when $D < R_F$.[2] R_F for the linear PEG can be estimated by $R_F = a N^{3/5}$, where a is the length of one monomer (0.35 nm for PEG), N is the total number of monomers. For PEG5k, $N = 113$, therefore, $R_F = 5.96$ nm.

To estimate the distance (D) between two grafted PEG chains, it is assumed that PEGs are homogenously and randomly distributed around the whole surface of the *fd* virus. The *fd* virus with a length of 880 nm and a size of 6.6 nm has a surface area of A_{fd} = 18700 nm^2. Therefore, each of the 2700 identical coat proteins (pVIII) contributes a surface area of A_{P8} = 6.93 nm^2 of space. The main grafting point of the PEG is either the N-terminal or the Lysine residue (Lys6) at the position of 6 of pVIII.

Based on the aforementioned surface area data, the distance between two *N*-terminals, two Lys6s, *N*-terminal and Lys6 of two neighboring pVIIIs, or *N*-terminal and Lys6 on the same pVIII can be estimated as in the range of 1 to 2.4 nm. The results were also consistent with the previous estimations based on the molecular structure.[3] In the case of *fd*-SC with more than 3500 PEGs per virus, each pVIII is grafted with at least one PEG. The distance between two PEGs, *D*, is therefore in the range of 1 to 2.4 nm,[3] no matter which amino group the two PEGs are coupled to. Hence $R_F > D$, PEG is in the brush conformation. In contrast, in the case of the *fd* virus grafted with only 400 PEGs per virus, only 400 pVIIIs in 2700 pVIIIs have the chance to be grafted with PEG if assuming one PEG can be grafted to only one pVIII. This means one PEG for every 6.75 coat proteins. The distance between two PEGs, *D*, is in the range of 6.75 × (1.6 to 2.4 nm) = 10.8 to 16.2 nm. Therefore, $R_F < D$ and the PEGs are in the "mushroom" conformation.

2. Estimation of the lateral pressure due to inter-chain repulsion of the grafted PEG

There are a large amount of work on the lipid membrane grafted with PEG of various Mw and grafting density.[4] Theory has been derived from the Alexnder and de Geness theory of polymer brush to calculate the lateral pressure on the membrane due to the inter-chain repulsion of the PEG chains. Especially, all of the parameters of PEG needed for the calculation are well-documented in literature. We think that the virus is basically a cylindrical membrane formed by the packing of several thousands of the coat proteins. The lateral pressure (Π_p^{brush}) can be calculated by the following equations[4]:

$$\Pi_p^{brush} = m_F k_B T n_p a_m^{2m_F} \left(\frac{X_p}{A_1}\right)^{m_F + 1} \quad (1)$$

where n_p is the number and a_m the size of monomer units in the polymer-PEG which for PEG with a Mw 5000 is 113 and 0.39 nm, respectively; The exponent m_F is 5/6 in

the de Gennes scaling theory, and is 2/3 in the mean-field theory.[4] Similar to the lipid membrane grafted with PEG, *X*p is the faction of the coat proteins that grafted with PEG, for *fd* grafted with 400 PEG per virus *X*p = 0.15, for that grafted with ca. 3500 PEG per virus, *X*p = 1 since each pVIII is grafted with at least on PEG. A_1 is the surface area occupied by each coat protein on the surface. k_B is Boltzmann's constant; T is the absolute temperature. With these parameters, Π_p^{brush} is calculated in the range of 2.28 ~ 3.45 mN m^{-2}.

Supplementary Figures

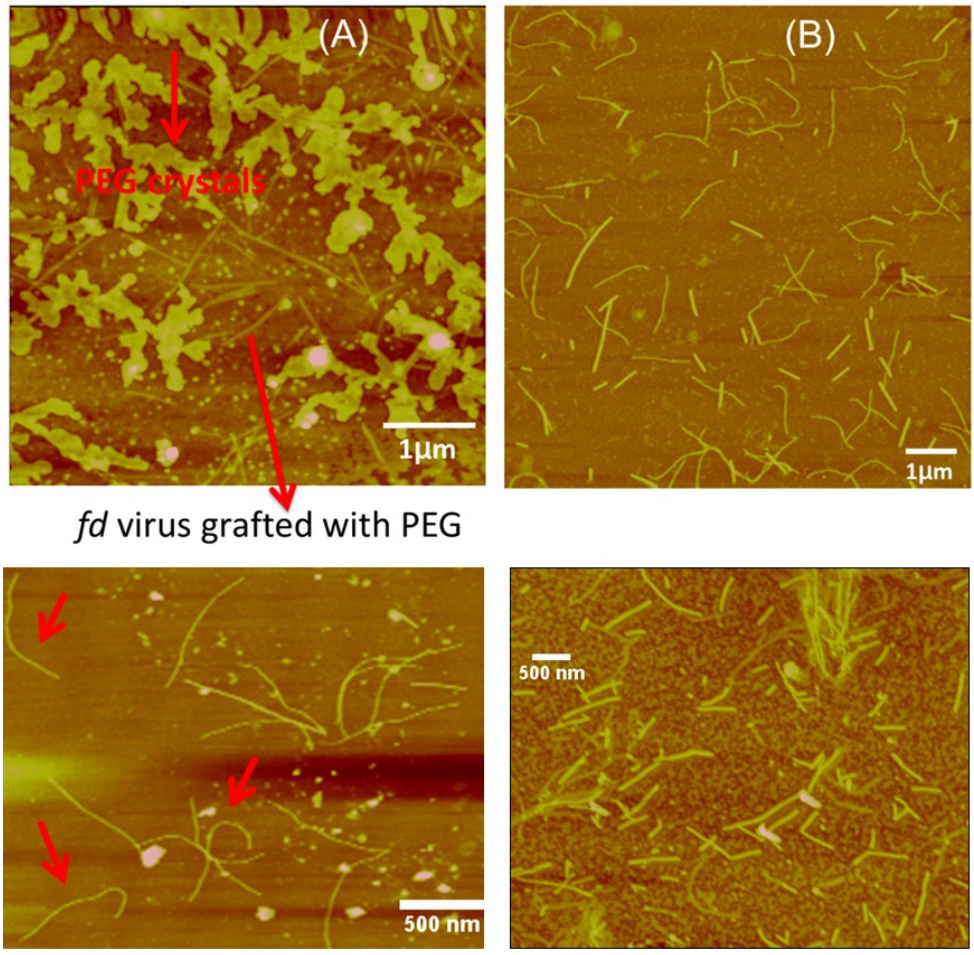

Figure S1. AFM of the densely PEGylated virus (*fd*-SC) without exhausting removal of the excess PEG (A) and the mixture of the densely PEGylated virus (*fd*-SC) with pure virus (B). In (A), PEG crystals are clearly visible as well as the straight

PEGylated viruses. (B) is a larger version of Figure 2D in the main text. (C) AFM of the intact *fd* virus alone. Curved viruses are highlighted by arrows. (D) AFM of the densely PEGylated virus (*fd*-SC) alone.

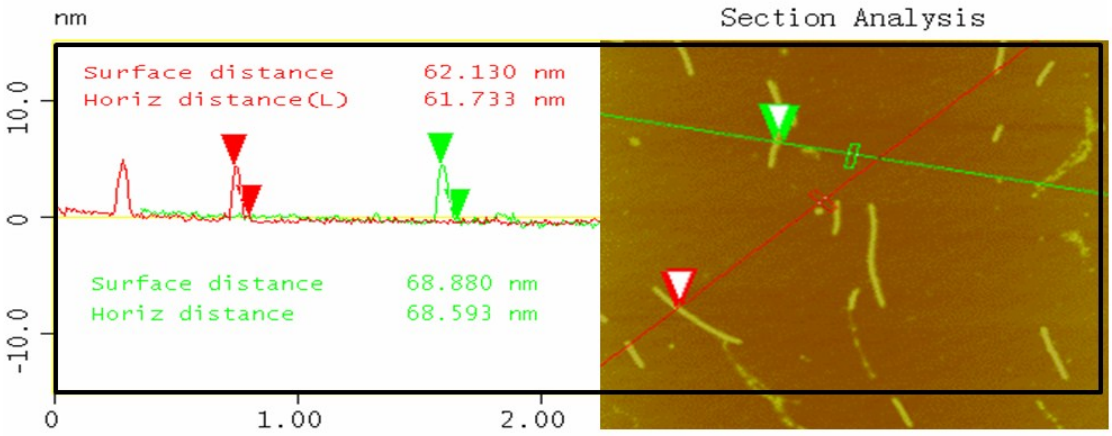

Figure S2. Section analysis of the densely PEGylated virus (*fd*-SC). The viruses have a monodisperse diameter in terms of either of the surface distance or the horizontal distance.

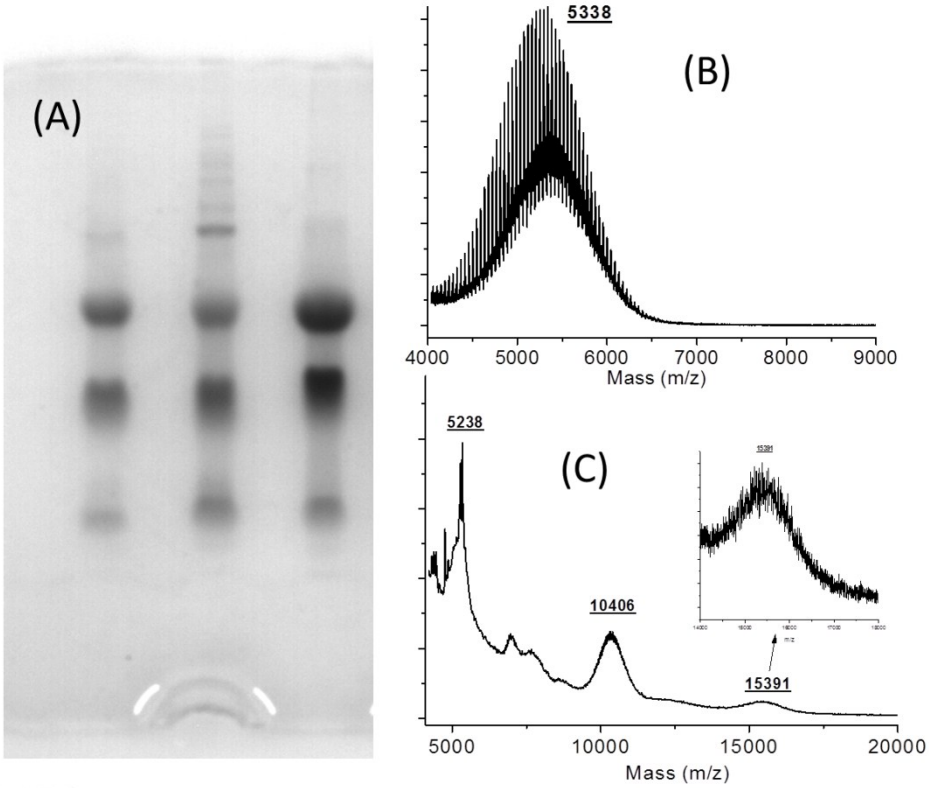

Figure S3. (A) SDS-PAGE of the PEGylated virus via grafting the *fd* virus with mPEG-SPA at various ratios of PEG to the surface amino acid group of the virus. Lanes from the left to right: 300:1, 400:1 and 500:1, respectively. (B) MALDI-TOF MS of the mPEG-SC used in the current work for PEGylation. (C) MALDI-TOF MS of the PEGylated fd virus with mPEG-SPA. A peak corresponding to ungrafted pVIII is clearly visible.

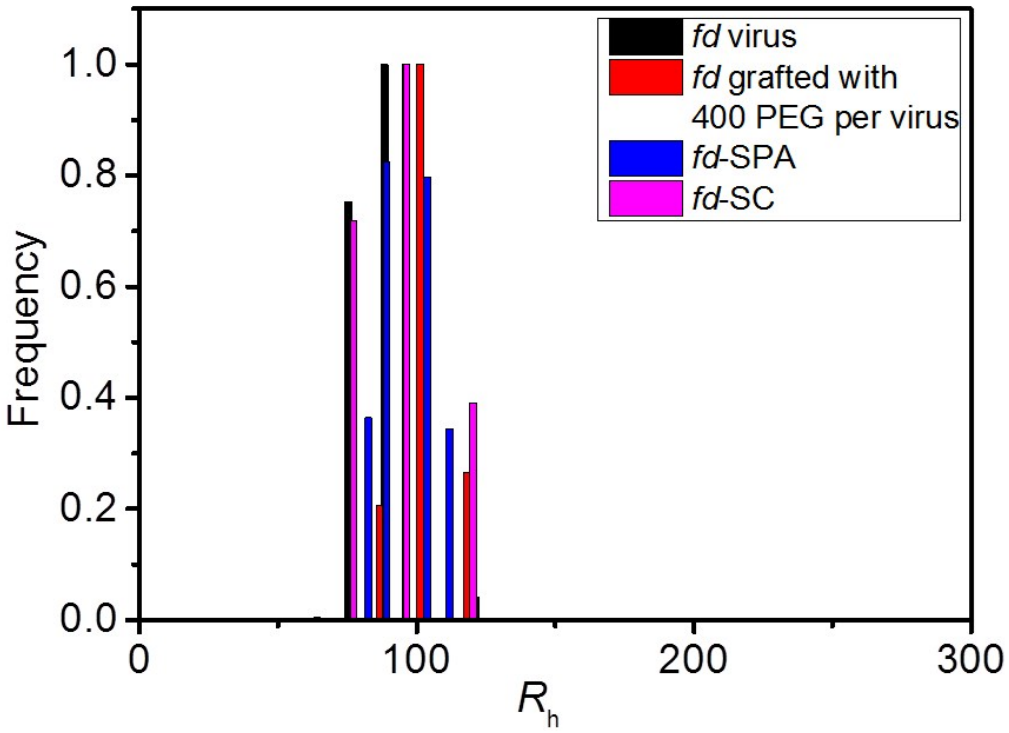

Figure S4. Size distribution of the (PEGylated) *fd* viruses as probed by dynamic light scattering. The scattering angle was 30°. The concentration of the virus is 6.0×10^{-5} mg mL^{-1}.

Reference

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