

Supporting Information

Photopolymerization of dienoyl lipids creates planar supported poly(lipid) membranes with retained fluidity

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1. Lipid structures

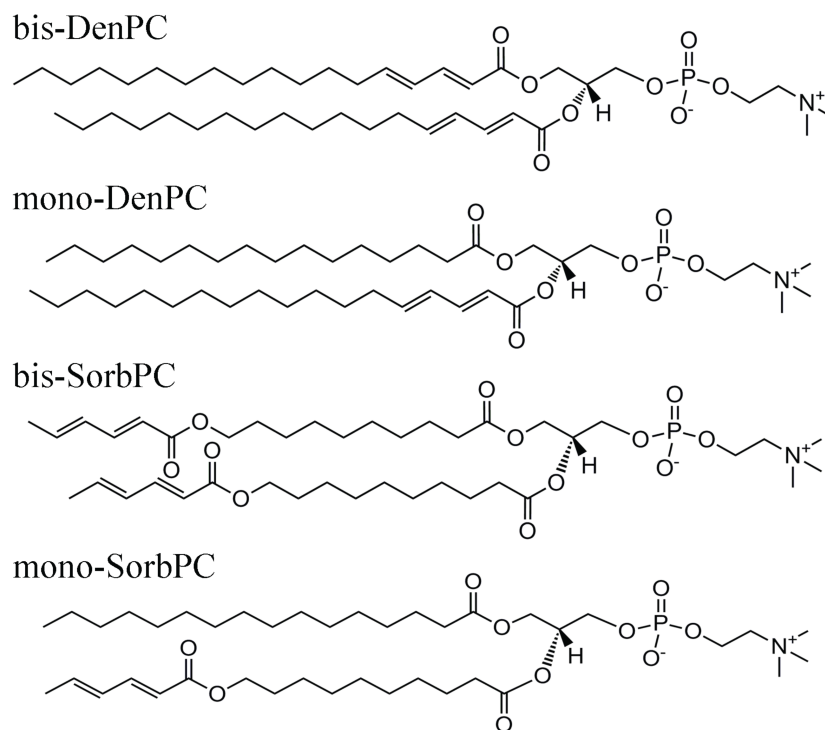


Figure S1. Polymerizable lipids.

2. Determination of UV polymerization time for PSLBs

To determine the amount of time necessary to polymerize a PSLB composed of dienoil lipids, bis-DenPC vesicles were irradiated with UV light for varying amounts of time and the progress of the reaction was monitored using UV-vis absorbance. The irradiation geometry was identical to that used for UV polymerization of PSLBs.

SUVs were formed by sonication as described in the Experimental section of the article. A glass slide was cleaned as described in the Experimental section and then treated with a silanizing agent, Surfasil Siliconizing Fluid (Thermo Scientific, Dubuque, IA), to minimize vesicle fusion on the glass surface. The slide was mounted into the sample chamber.

For each irradiation time investigated, a pre-irradiation UV spectrum and a post-irradiation UV spectrum were acquired (quartz cuvet, Spectral Instruments 440 spectrophotometer). Immediately after sonication, an aliquot of the SUV solution was used to obtain the pre-irradiation spectrum. Another aliquot of the solution was added to the sample chamber and irradiated using a low pressure Hg pen lamp held ca. 7.6 cm above the sample for a variable amount of time. The irradiated SUV sample was then removed from the sample chamber and the post-irradiation spectrum was measured. Irradiation times were 1, 5, 10, 15, 30, and 60 minutes.

Normalized absorbance spectra are shown in Figure S2. The normalization process follows: Baseline subtraction was performed for all spectra by subtracting the absorbance value at 400 nm from all wavelengths. To normalize the data for each set of pre- and post-polymerization spectra, the pre-polymerization absorbance at 261 nm was set to 1 by determining a normalization factor using

$$\text{normalization factor} = 1/(A_{\text{raw,pre},\lambda_{\text{max}}} - A_{\text{raw,pre},400\text{nm}})$$

where $A_{\text{raw,pre},\lambda_{\text{max}}}$ is the raw absorbance (before baseline subtraction) at λ_{max} in the pre-polymerization spectrum and $A_{\text{raw,pre},400\text{nm}}$ (before baseline subtraction) is the raw absorbance at 400 nm in the pre-polymerization spectrum. The baseline subtracted absorbance at all wavelengths in the pre- and post-polymerization spectra was then multiplied by the normalization factor.

In Figure S2, the disappearance of the band at 261 nm is the result of monomer to polymer conversion.¹ Figure S3 is a plot of the post-polymerization normalized absorbance at 261 nm as a function of irradiation time. After 10-15 minutes, the absorbance reaches a minimum. Thus nearly 100% photopolymerization of dienoyl lipids occurred within 15 min of irradiation which is consistent with previous reports.²⁻⁵ To minimize potential photodegradation of PSLBs and photobleaching of rhodamine-PE, the photopolymerization time was therefore limited to 30 minutes for all UV polymerized PSLBs. No decrease in rhodamine-PE fluorescence intensity was measured after 30 minutes of UV irradiation of doped PSLBs.

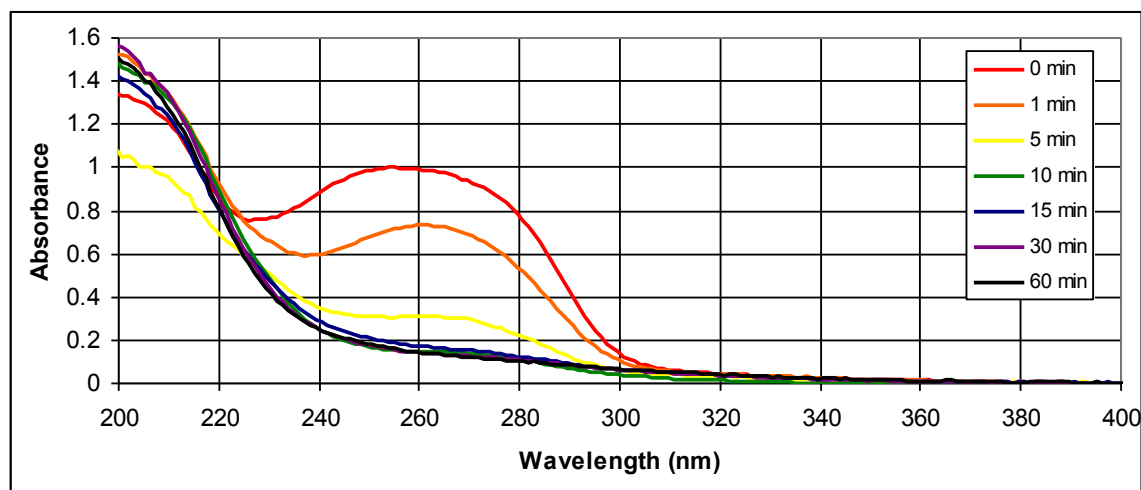


Figure S2. Normalized absorbance spectra of bis-DenPC vesicles as a function of UV irradiation time. The 0 min spectrum was taken before irradiation.

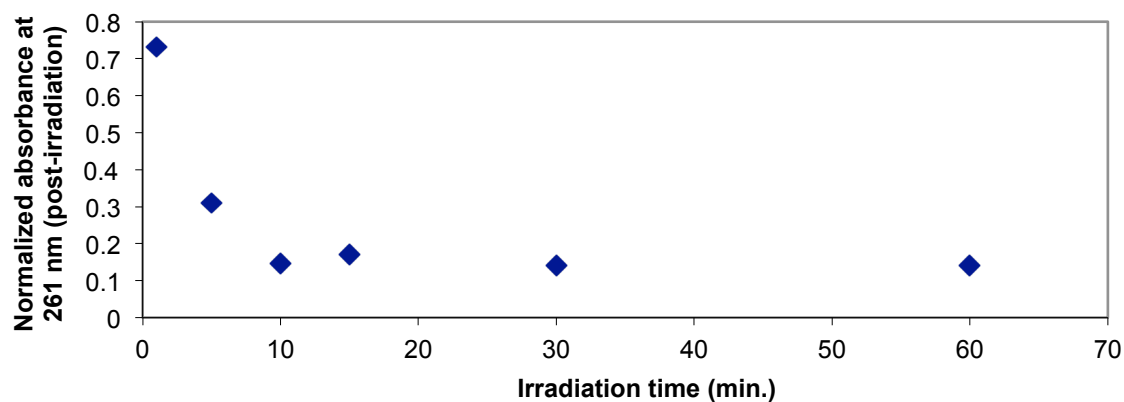
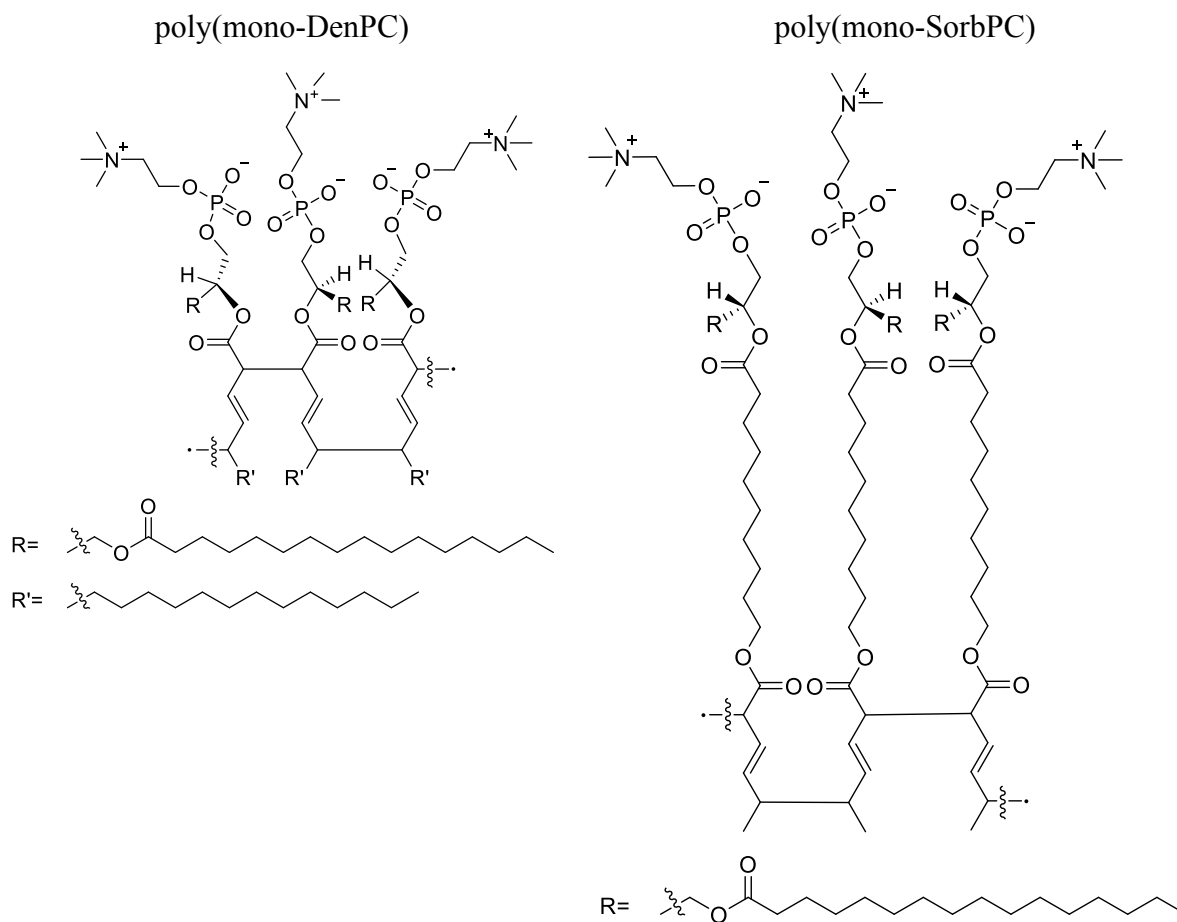


Figure S3. Normalized absorbance at 261 nm plotted as a function of UV irradiation time. The non-zero absorbance values at long irradiation times result from the sloped background that is not accounted for by the baseline subtraction procedure.

3. Representative structures of linearly polymerized lipids



4. Comparison of fitting mono- and biexponential models to a recovery curve

The goodness of fitting a model to a recovery curve was evaluated based on the residuals plot (see examples in Fig. S4) and the adjusted coefficient of determination, R_{adj}^2 ,

$$R_{adj}^2 = 1 - (1 - R^2) \left(\frac{n-1}{n-p} \right)$$

$$R^2 = 1 - \left[\left(\sum_{i=1}^n (y_i - \hat{y}_i)^2 \right) \left(\sum_{i=1}^n (y_i - \bar{y})^2 \right)^{-1} \right]$$

where n is the number of data points, p is the number of variables in the model, y_i is the fluorescence intensity ratio ($F(t)$ in eq 1 in the article), \bar{y} is the mean of y_i , and \hat{y}_i is the predicted value of y_i .

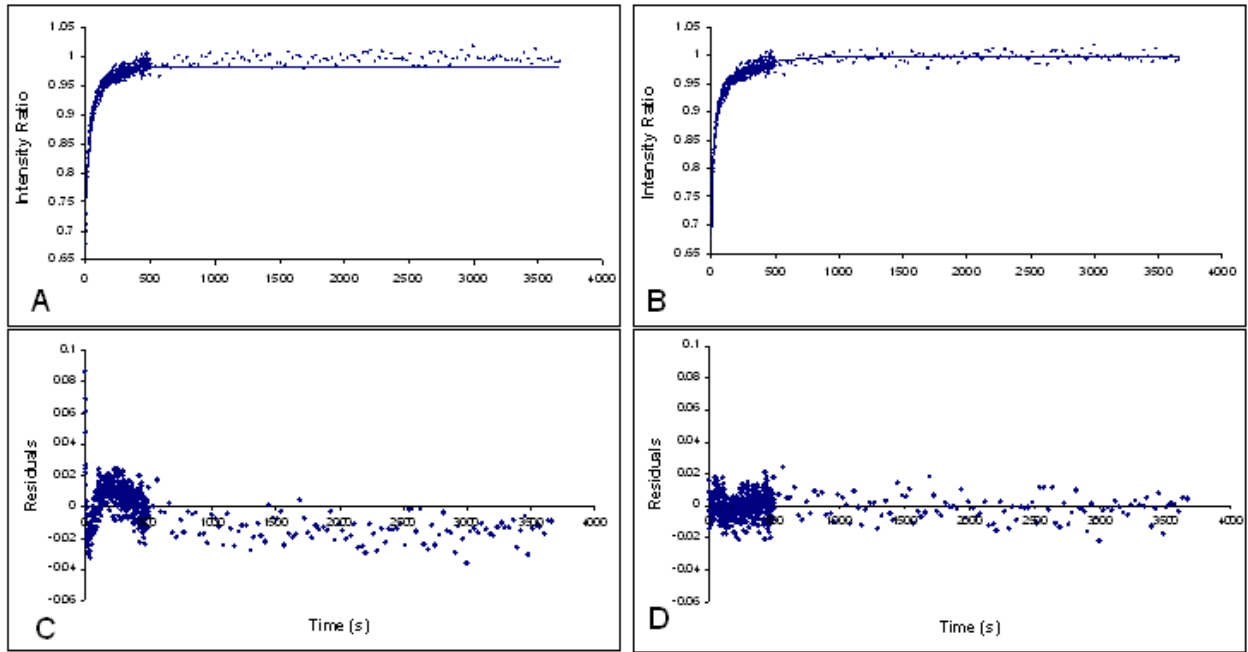


Figure S4. FRAP recovery curve for an unpolymerized bis-SorbPC PSLB fit to: (A) a monoexponential model and (B) a biexponential model. Solid lines are the fits to the data. The R_{adj}^2 values in (A) and (B) were 0.9051 and 0.9708, respectively. (C) and (D) show the residuals for the fits in (A) and (B), respectively.

5. References

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