Supplementary Material (ESI) for *PCCP*
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Supporting Information for

Phase Transition Kinetics in Langmuir and Spin-Coated Polydiacetylene Films

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1. AFM images of SC PDA films

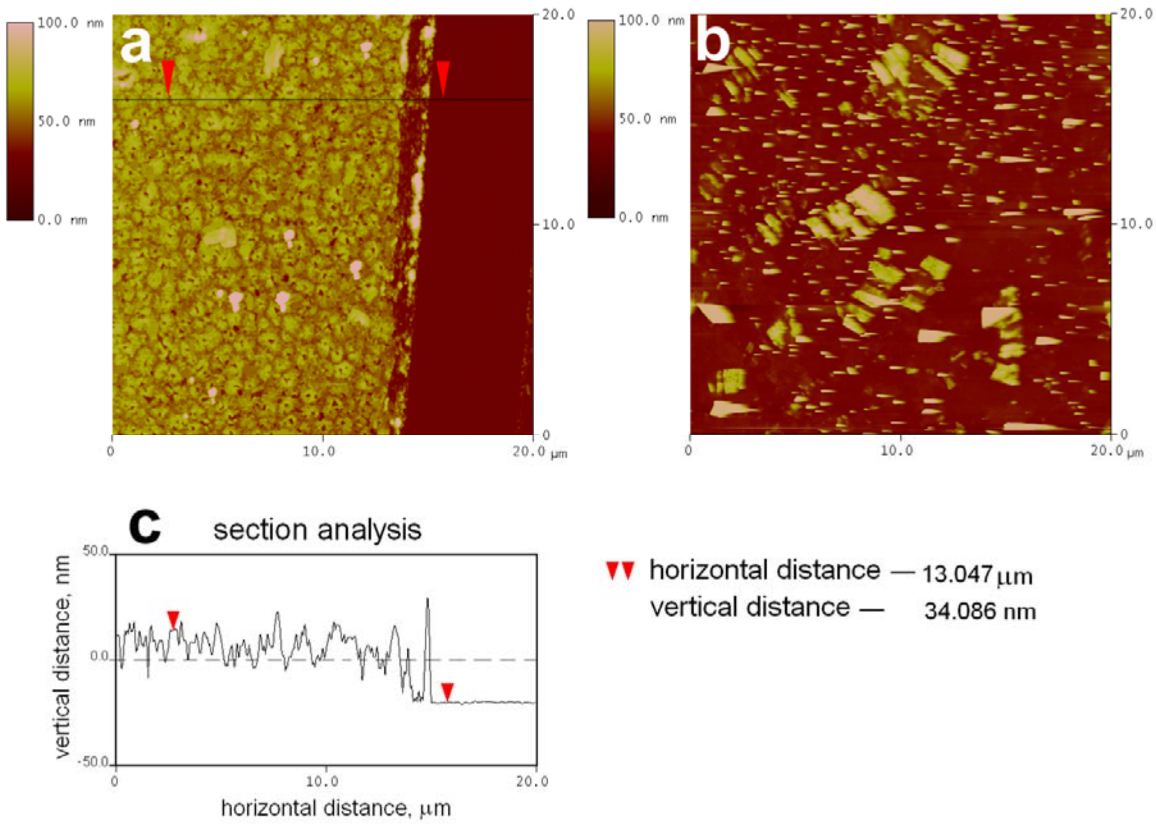


Figure S1: AFM images of SC PDA film (a) before and (b) during the degradation stage; (c) Section analysis along the black line shown in (a). Note the good coverage of the PDA film in (a) with the well-defined step from the film to the quartz substrate while image (b) depicts fragments remaining from the degraded film.

2. <u>The kinetic model</u>

2.1 Simple Kinetic Model

M – Monomer phase (the unpolymerized part of the film)
P – Polymer phase (the polymerized part of the film)
D – Degradation phase (the part of the film that was damaged and eventually removed from the substrate)

Two exposure–dependent kinetic constants, k_1 and k_5 $(Wscm^{-2})^{-1}$, were defined in order to describe the transformation rate in each stage of the reaction as a function of UV dose. The phase transitions of PDA are schematically presented by Formula (1):

(1) $M \xrightarrow{k_1} P \xrightarrow{k_5} D$

The M→P transition is described by k_1 and the P→D transitions are described by k_5.

Setting the initial amount of monomer to unity, the fractions of the monomer M, polymer P and degradation stage D as a function of radiation exposure, H, $(Wscm^{-2})$ can be calculated using Equations (2)-(4):

(2) $$\frac{dM}{dH} = -k_1 M \rightarrow M = M_0 e^{-k_1 H}$$

(3) $$\frac{dP}{dH} = k_1 M - k_5 P \rightarrow P = \frac{k_1}{k_5 - k_1}(e^{-k_1 H} - e^{-k_5 H})$$

(4) $$\frac{dD}{dH} = k_5 P \rightarrow D = 1 + \frac{k_1 e^{-k_5 H} - k_5 e^{-k_1 H}}{k_5 - k_1}$$

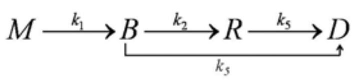
2.2 Unidirectional Kinetic Model

The following phases are present:

M – Monomer phase (the unpolymerized part of the film with starting amount of M_0)
B – Blue phase (the polymerized part of the film in the blue phase)
R – Red phase (the polymerized part of the film in the red phase)
D – Degradation phase (the part of the film that was damaged)

Three exposure–reciprocal kinetic constants, k_1, k_2 and k_5 $(Wscm^{2})^{-1}$, were defined in order to describe the transformation rate in each stage of the reaction as a function of UV dose. The phase transitions of PDA are schematically presented by:

(5)



The phases evolve with flux H of UV radiation according to:

(6) $$\frac{dM}{dH} = -k_1 M$$

(7) $$\frac{dB}{dH} = k_1 M - k_2 B - k_5 B$$

(8) $$\frac{dR}{dH} = k_2 B - k_5 R$$

(9) $$\frac{dD}{dH} = k_5 R + k_5 B = k_5 (B + R)$$

The solution for *M* is

(10) $$M = e^{-k_1 H}$$

with all quantities in units of the starting monomer M_0 proceed by considering the sum B+R so that

(11) $$\frac{dP}{dH}=\frac{d(B+R)}{dH}=k_1M-(B+R)k_5$$

(12) $$B+R=\frac{k_1}{k_5-k_1}(e^{-k_1H}-e^{-k_5H})$$

To solve D to place Eq. (12) in to Eq. (9)

(13) $$\frac{dD}{dH}=k_5R+k_5B=k_5(R+B)=k_5[\frac{k_1}{k_5-k_1}(e^{-k_1H}-e^{-k_5H})]$$

(14) $$D=1+\frac{k_1e^{-k_5H}-k_5e^{-k_1H}}{k_5-k_1}$$

For B we plot:

(15) $$\frac{dB}{dH}=k_1M-k_2B-k_5B=k_1M-B(k_2+k_5)$$

(16) $$B=\frac{k_1}{(k_2+k_5-k_1)}(e^{-k_1H}-e^{-(k_2+k_5)H})$$

And finally to solve R:

(17) $$\frac{dR}{dH}=k_2B-k_5R$$

(18) $$R=\frac{k_1(k_2e^{-k_1H}-(k_2+k_5-k_1)e^{-k_4H}+(k_5-k_1)e^{-(k_2-k_5)H}}{(k_2+k_5-k_1)(k_5-k_1)}$$

2.3 Reversible Kinetic Model

The following phases are present:

M – Monomer phase (the unpolymerized part of the film with starting amount of M_0)

B – Blue phase (the polymerized part of the film in the blue phase)

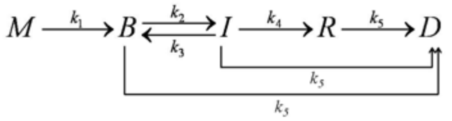
I – Intermediate phase (intermediate phase in the blue to red transition)

R – Red phase (the polymerized part of the film in the red phase)

D – Degradation phase (the part of the film that was damaged)

Five exposure–reciprocal kinetic constants, k_1-k_5 $(Wscm^2)^{-1}$, were defined in order to describe the transformation rate in each stage of the reaction as a function of UV dose. The phase transitions of PDA are schematically presented by:

(19)



We derive here the solution for the kinetic equations, including the putative new phase I. The M equation is solved by $M=e^{-k_1H}$ (normalizing the initial monomer to unity), hence the B and I equations can be written in a matrix form as

(20) $$\frac{d}{dH}\begin{pmatrix}B\\I\end{pmatrix}=\begin{pmatrix}k_1e^{-k_1H}\\0\end{pmatrix}-\hat{F}\begin{pmatrix}B\\I\end{pmatrix}$$

where

(21) $\hat{F} = \begin{pmatrix} k_2 + k_5 & -k_3 \\ -k_2 & k_3 + k_4 + k_5 \end{pmatrix} = a_0 \hat{I} + a_1 \hat{\sigma}_x + a_2 \hat{\sigma}_y + a_3 \hat{\sigma}_z$

where $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$ are standard Pauli matrices and $\hat{I}$ is a unit matrix. The coefficients are:

(22) $a_0 = \frac{1}{2}\left(k_2 + k_4 + 2k_5 + k_3\right)$

(23) $a_1 = -\frac{1}{2}\left(k_2 + k_3\right)$

(24) $a_2 = \frac{1}{2}\left(k_2 - k_3\right)$

(25) $a_3 = \frac{1}{2}\left(k_2 - k_3 - k_4\right)$

We rewrite the matrix in terms of a unit vector $\vec{n}$ and a vector $\hat{\boldsymbol{\sigma}}$ of the Pauli matrices:

(26) $\hat{F} = a_0 \hat{I} + \alpha \hat{\boldsymbol{\sigma}} \cdot \vec{n}$

(27) $\vec{n} = \frac{1}{2}\left(a_1,\ ia_2, a_3\right)$

(28) $\alpha = \sqrt{a_1^2 + a_3^2 - a_2^2} = \frac{1}{2}\sqrt{4k_2k_3 + \left(k_2 - k_3 - k_4\right)^2} > 0$

Using identities of Pauli matrices we have:

(29) $e^{\alpha H \hat{\boldsymbol{\sigma}} \cdot \vec{n}} = \cosh\left(\alpha H\right)\hat{I} + \sinh\left(\alpha H\right)\hat{\boldsymbol{\sigma}} \cdot \vec{n}$

The kinetic equation can be written in terms of:

(30) $\begin{pmatrix} B \\ I \end{pmatrix} = e^{-\hat{F}H} \begin{pmatrix} \tilde{B} \\ \tilde{I} \end{pmatrix}$

so that

(31) $\frac{d}{dH}\begin{pmatrix} \tilde{B} \\ \tilde{I} \end{pmatrix} = e^{\hat{F}H} \begin{pmatrix} k_1 \mathrm{e}^{-k_1 H} \\ 0 \end{pmatrix}$

Using the identity above for the exponent we get:

(32) $e^{\hat{F}H} = e^{a_0 H}\hat{I}\left[\cosh\left(\alpha H\right)\hat{I} + \sinh\left(\alpha H\right)\left(\hat{F} - a_0\hat{I}\right)\frac{1}{\alpha}\right]$

(33) $e^{\hat{F}H}\begin{pmatrix} k_1 \mathrm{e}^{-k_1 H} \\ 0 \end{pmatrix} = \left[e^{a_0 H}\cosh\left(\alpha H\right)\hat{I} + e^{a_0 H}\sinh\left(\alpha H\right)\frac{1}{\alpha}\begin{pmatrix} a_3 & a_1 + a_2 \\ a_1 - a_2 & -a_3 \end{pmatrix}\right]\begin{pmatrix} k_1 \mathrm{e}^{-k_1 H} \\ 0 \end{pmatrix}$

Hence the kinetic equation becomes:

(34) $\frac{d}{dH}\begin{pmatrix} \tilde{B} \\ \tilde{I} \end{pmatrix} = \begin{pmatrix} e^{a_0 H}\cosh\left(\alpha H\right)k_1 e^{-k_1 H} + \frac{1}{\alpha}e^{a_0 H}\sinh\left(\alpha H\right)a_3 k_1 e^{-k_1 H} \\ \frac{1}{\alpha}e^{a_0 H}\sinh\left(\alpha H\right)\left(a_1 - a_2\right)k_1 e^{-k_1 H} \end{pmatrix}$

After a straightforward integration and transforming back to B and N variables we obtain

(35) $\begin{pmatrix} B \\ I \end{pmatrix} = e^{-\hat{F}H}\begin{pmatrix} \tilde{B} \\ \tilde{I} \end{pmatrix} = e^{-a_0 H}\left[\cosh\left(\alpha H\right)\hat{I} - \frac{\sinh\left(\alpha H\right)}{\alpha}\begin{pmatrix} a_3 & a_1 + a_2 \\ a_1 - a_2 & -a_3 \end{pmatrix}\right]\begin{pmatrix} \tilde{B} \\ \tilde{I} \end{pmatrix}$

so that finally

(36) $B = \frac{1}{2}k_1\left\{\frac{e^{-k_1 H} - e^{-a_0 H - \alpha H}}{a_0 - k_1 + \alpha}\left(1 + \frac{a_3}{\alpha}\right) + \frac{e^{-k_1 H} - e^{-a_0 H + \alpha H}}{a_0 - k_1 - \alpha}\left(1 - \frac{a_3}{\alpha}\right)\right\}$

(37) $I = \frac{1}{2} k_1 \frac{a_1 - a_2}{\alpha} \left\{ \frac{e^{-k_1 H} - e^{-a_0 H - \alpha H}}{a_0 - k_1 + \alpha} - \frac{e^{-k_1 H} - e^{-a_0 H + \alpha H}}{a_0 - k_1 - \alpha} \right\}$

The kinetic equations for the polymer content P=B+I+R are identical to those of the model Eq. (1) so that we can use the solution for P and D of that model, and for the red phase:

(38) $R = P - B - I$