

Supporting Information

The rate equations and parameters for the PMDI and SSMCC decay curves obtained by solving the differential equations after replacing the n_i 's using **Eq. (4)** are given here. For the imide A1 and A2 in PMDI the equation is

$$I_A = I_A^0 e^{-kx} \quad (9)$$

I_A^0 is the area of either imide peak in the pristine spectra; k is the rate constant for the imide decay; and x is the total exposure in MGy. As expected, the imide A1 and A2 peaks have the same rate constant and differ only by an overall factor corresponding to their differing cross sections (detection probabilities). For the imine and nitrile peaks then the equations are

$$I_B = \frac{\sigma_B}{\sigma_A} \left(\frac{I_A^0 k_1}{k} \right) (1 - e^{-k_1 x}) \quad (10)$$

$$I_C = \frac{\sigma_C}{\sigma_A} \left(\frac{I_A^0 k_2}{k} \right) (1 - e^{-k_2 x}) \quad (11)$$

I_A^0 is again the area of either imide peak in the pristine spectra; k_1 is the rate constant for the decay from imide to imine; k_2 is the rate constant for the decay from imide to nitrile; k is the rate constant for the imide decay (i.e. $k = k_1 + k_2$); σ_A , σ_B , and σ_C are the different cross sections (detection probabilities) of the imide A1, imine, and nitrile orbitals, respectively; and x is the total exposure in MGy. Terms involving the areas of the imine or nitrile peaks in the pristine spectra are omitted, as these peaks are not present in the pristine spectra. Fitting these equations to the imide, imine, and nitrile reaction curves is straightforward, as there are relatively few free parameters due to the constraints that $k = k_1 + k_2$ and $k_1 = k_2$.

Table 5: Reaction Rate Equation Parameters for PMDI TEY Data

Parameter	Value
I_A^0	1.0
k_I [MGy ⁻¹]	5.1*10 ⁻⁴
k_2	5.1*10 ⁻⁴
σ_B/σ_A	1.35
σ_C/σ_A	0.87

*For PMDI, the subscript A corresponds to imide (A1 or A2), B to imine, and C to nitrile.

Table 6: Reaction Rate Equation Parameters for SSMCC TEY Data

Parameter	Value
I_A^0	1.05
I_B^0	0.91
k_I [MGy ⁻¹]	8.8*10 ⁻²
k_2	8.6*10 ⁻²
k_3	8.6*10 ⁻²
k_4	3.5*10 ⁻³
k_5	3.5*10 ⁻³
σ_B/σ_A	0.87
σ_C/σ_A	0.36
σ_C/σ_B	0.41
σ_D/σ_A	0.27
σ_D/σ_B	0.30

*For SSMCC, the subscript A corresponds to imide B2, B to imide B1, C to imine, and D to nitrile.

For the imide B2 in SSMCC, the rate equation is

$$I_A = I_A^0 e^{-k_A x} \quad (12)$$

I_A^0 is the area of the imide B2 peak in the pristine spectrum; k_A is the rate constant for all of imide 2's first order reactions(i.e. $k_A = k_1 + k_2 + k_3$); and x is the total exposure in MGy. This is a first order reaction of imide B2 yielding imide B1, imine, or nitrile. For the imide B1 peak, the rate equation is

$$I_B = I_B^0 e^{-k_B x} + \frac{\sigma_B}{\sigma_A} \left(\frac{I_A^0 k_1}{k_B - k_A} \right) (e^{-k_A x} - e^{-k_B x}) \quad (13)$$

I_A^0 is the same as in the imide B2 rate equation; I_B^0 is the area of the imide B1 peak in the pristine spectrum; σ_A and σ_B , are the different cross sections (detection probabilities) of the imide B2 and imide B1 orbitals, respectively (as mentioned previously, their ratio is $\sigma_B/\sigma_A = I_B^0/I_A^0$ because $n_A^0 = n_B^0$); k_A is again the sum of the rate constants for imide B2's first order reactions; k_B is the sum of the rate constants for imide B1's first order reactions (i.e. $k_B = k_4 + k_5$); and x is the total exposure in MGy. The first term corresponds to the first order reactions of imide B1 yielding imine or nitrile, and the second term corresponds to the imide B1 produced by the reaction of imide B2. For the imine and nitrile peaks, the rate equations are

$$I_C = \frac{\sigma_C}{\sigma_A} \left(\frac{I_A^0 k_2}{k_A} \right) (1 - e^{-k_A x}) + \frac{k_4}{k_B} \left[\frac{\sigma_C}{\sigma_A} \left(\frac{I_A^0 k_1}{k_A} \right) (1 - e^{-k_A x}) - \frac{\sigma_C}{\sigma_A} \left(\frac{I_A^0 k_1}{k_B - k_A} \right) (e^{-k_A x} - e^{-k_B x}) + \frac{I_B^0 \sigma_C}{\sigma_B} (1 - e^{-k_B x}) \right] \quad (14)$$

$$I_D = \frac{\sigma_D}{\sigma_A} \left(\frac{I_A^0 k_3}{k_A} \right) (1 - e^{-k_A x}) + \frac{k_5}{k_B} \left[\frac{\sigma_D}{\sigma_A} \left(\frac{I_A^0 k_1}{k_A} \right) (1 - e^{-k_A x}) - \frac{\sigma_D}{\sigma_A} \left(\frac{I_A^0 k_1}{k_B - k_A} \right) (e^{-k_A x} - e^{-k_B x}) + \frac{I_B^0 \sigma_D}{\sigma_B} (1 - e^{-k_B x}) \right] \quad (15)$$

I_A^0 , I_B^0 , k_A , and k_B are defined as before; σ_A , σ_B , σ_C , and σ_D are the different cross sections (detection probabilities) of the imide B2, imide B1, imine, and nitrile orbitals, respectively; k_I , k_2 , k_3 , k_4 , and k_5 are defined as before; and x is the total exposure in MGy. The first term in this equation corresponds to a reaction of imide B2 yielding imine or nitrile. The bracketed term in this equation corresponds to a reaction of imide B1 yielding imine or nitrile. The first and second terms in the brackets account for the increase in imide B1 due to the decay of imide B2. The third term in the brackets accounts for the initial amount of imide B1. Terms involving the areas of the imine or nitrile peaks in the pristine spectra are omitted, as these peaks are not present in the pristine spectra. The approximate parameters used in the above reaction rate equations to fit the data for PMDI and SSMCC are given in **Table 5** and **Table 6**. The double hump structure seen in the imine and nitrile curves in **Figure 5** can be explained by the two different imides converting to imine or nitrile. Since imide B2 decays more quickly than imide B1, the first increase in the imine and nitrile curves is due to conversion of imide B2. The imine and nitrile growth stalls when little imide B2 remains, then increases again due to the slower conversion of imide B1.

The constraints given above for the various rate constants (i.e. $k_A = k_1 + k_2 + k_3$ and $k_B = k_4 + k_5$) as well as the assumptions that $k_2=k_3$ and $k_4=k_5$ reduce the number of free parameters in the fits of the decay curves to the following: k_A , k_B , k_I , and the cross section ratios σ_C/σ_A , σ_C/σ_B , σ_D/σ_A , and σ_D/σ_B for both imine and nitrile curves. The rate constant k_A is determined by fitting **Eq. (12)** to the decay curve of imide B2, for which k_A is the only free parameter. The rate constants k_I and k_B are determined by fitting **Eq. (13)** to the decay curve of imide B1, with $k_I < k_A$. Fitting **Eq. (14)** and **Eq. (15)** to the imine and nitrile curves, respectively, then determines

the cross section ratios for the bonds, as k_2 , k_3 , k_4 , and k_5 are predetermined by the above constraints, and k_A , k_I , and k_B are known from fitting the decay curves for other bonds with their respective equations. The scaling for the imide B2 and imide B1 peaks is determined by their initial areas in the pristine spectra. As expected from the similar cross-sections and the 1:1 ratio between the imides in the undamaged molecule, the peak areas are approximately the same in the pristine spectra.