Supporting Information

Uncatalyzed Reactions of 4,4’-Diphenylmethane-Diisocyanate with Polymer Polyols as Revealed by Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry

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I. Estimation of the relative MALDI-TOF MS response factors

The intensities of the reference were compared to those of the different series, and the corresponding relative response factors were estimated by means of eq. S1.

\[ I_{\text{ref}} = p_1 I_A + p_2 I_B + p_3 I_C + p_4 I_D \]  

(S1)

where \( p_1 = \frac{q_{\text{ref}}}{f_{\text{ref}}} f_A \), \( p_2 = \frac{q_{\text{ref}}}{f_{\text{ref}}} f_B \), \( p_3 = \frac{q_{\text{ref}}}{f_{\text{ref}}} f_C \) and \( p_4 = \frac{q_{\text{ref}}}{f_{\text{ref}}} f_D \). \( q \) is the concentration ratio of the reference and the starting polymer triol (PPG_GL), \( I_{\text{ref}} \), \( I_A \), \( I_B \), \( I_C \) and \( I_D \) stand for the MALDI-TOF MS intensities for the reference and series \( A_n \), \( B_n \), \( C_n \) and \( D_n \), respectively, while \( f_{\text{ref}}, f_A, f_B, f_C \) and \( f_D \) are the MALDI-TOF MS response factors for the reference and the series \( A_n, B_n, C_n \) and \( D_n \), respectively. The relative MALDI-TOF MS response factors of the oligomer series with respect to that of series \( A_n \) were obtained as \( f_A/f_B = p_2/p_1 \), \( f_A/f_C = p_3/p_1 \) and \( f_A/f_D = p_4/p_1 \).

For polymer diols (PPG, PTHF, PCLD) eq. S1 reduces to eq. S2

\[ I_{\text{ref}} = p_1 I_A + p_2 I_B + p_3 I_C \]  

(S2)

II. Derivation of eq. 21

Using eqs. 10-12, from eq. 12 the time (t) can be expressed as

\[ t = \frac{-\ln(X_{A_n})}{4k_1} \]  

(S3)

Substituting eq. S3 into eq. 11, we get eq. S4.

\[ X_{B_n} = \frac{1}{k_2} \left( X_{A_n} - e^{\frac{-\ln(X_{A_n})}{2k_1}} \right)^{\frac{k_2}{2k_1}} \]  

(S4)

Denoting \( k_2/2k_1 \) as \( \alpha \) and substituting it into eq. S4, after rearrangement, eq. S5 can be obtained which is equivalent to eq. 21.

\[ X_{B_n} = \frac{X_{A_n}^{\alpha} - X_{A_n}}{1-\alpha} \]  

(S5)
III. Derivation of eq. 23

Using eqs. 17-20, from eq. 17 the time \( t \) can be expressed as

\[
t = \frac{-\ln(X_{A_n})}{6k_1}
\]  
(S6)

Substituting eq. S6 into eq. 19, we get eq. S7.

\[
X_{C_n}(t) = \frac{2k_2}{3k_1} \frac{e^{-\ln(X_{A_n}) \frac{k_3}{3k_1}}}{(1 - \frac{2k_2}{3k_1})(1 - \frac{k_3}{3k_1})} \left\{ X_{A_n} - e^{-\ln(X_{A_n}) \frac{k_3}{3k_1}} \right\}
\]
(S7)

\[
+ \frac{1}{(1 - \frac{2k_2}{3k_1})(1 - \frac{k_3}{2k_2})} \left\{ e^{-\ln(X_{A_n}) \frac{k_3}{3k_1}} - e^{-\ln(X_{A_n}) \frac{2k_2}{3k_1}} \right\}
\]

Substituting \( \alpha = 2k_2/3k_1 \) and \( \beta = k_3/2k_2 \), into eq. S7 and taking into account that \( \alpha \beta = k_3/3k_1 \), eq. S8 can be obtained which is equivalent to eq. 23.

\[
X_{C_n} = \frac{\alpha}{(1 - \alpha)(1 - \alpha \beta)} (X_{A_n} - X_{\alpha A_n} \beta) + \frac{\alpha}{(1 - \alpha)(1 - \beta)} (X_{\alpha A_n} - X_{\alpha A_n})
\]  
(S8)
IV. Figures

**Fig. S1.** Product distributions *versus* time in the PTHF-MDI reaction determined by MALDI-TOF MS. The solid lines represent the fitted curves calculated by eqs. 10-12. Experimental conditions: $[\text{MDI}]_0 = 0.32 \text{ M}$, $[\text{PCLD}]_0 = 0.01 \text{ M}$ and $T = 80 \degree\text{C}$.

**Fig. S2.** ESI-MS/MS spectrum of the $[\text{PPG,GL+3MDI+3CH}_3\text{OH+2Na}]^{2+}$ adduct ion with a number of repeat units $n=16$. ESI-MS/MS spectrum was obtained at collision energy of 142 eV.