Supporting Information

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

Tibor Nagy[1], Borbála Antal[1], Anita Dékány-Adamoczky[1], József Karger-Kocsis[2]
Miklós Zsuga[1], Sándor Kéki[1*]

[1] *Department of Applied Chemistry, University of Debrecen, Egyetem tér1, H-4032 Debrecen, Hungary*

[2] *Department of Polymer Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3, H-1111 Budapest, Hungary*

Corresponding author's e-mail: keki.sandor@science.unideb.hu

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.

$$I_{ref} = p_1 I_A + p_2 I_B + p_3 I_C + p_4 I_D \quad \text{(S1)}$$

where $p_1 = qf_{ref}/f_A$, $p_2 = qf_{ref}/f_B$, $p_3 = qf_{ref}/f_C$ and $p_4 = qf_{ref}/f_D$, q is the concentration ratio of the reference and the starting polymer triol (PPG_GL), I_{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_{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

$$I_{ref} = p_1 I_A + p_2 I_B + p_3 I_C \quad \text{(S2)}$$

II. Derivation of eq. 21

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

$$t = \frac{-\ln(X_{A_n})}{4k_1} \quad \text{(S3)}$$

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

$$X_{B_n} = \frac{1}{\frac{k_2}{2k_1} - 1}\left(X_{A_n} - e^{-\ln(X_{A_n})\frac{k_2}{2k_1}} \right) \quad \text{(S4)}$$

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

$$X_{B_n} = \frac{X_{A_n}^{\alpha} - X_{A_n}}{1 - \alpha} \quad \text{(S5)}$$

III. Derivation of eq. 23

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

$$t = \frac{-\ln(X_{A_n})}{6k_1} \tag{S6}$$

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

$$\begin{aligned} X_{C_n}(t) = {} & \frac{\frac{2k_2}{3k_1}}{(1-\frac{2k_2}{3k_1})(1-\frac{k_3}{3k_1})}\left(X_{A_n} - e^{\ln((X_{A_n})\frac{k_3}{3k_1}} \right) + \\ & + \frac{1}{(1-\frac{2k_2}{3k_1})(1-\frac{k_3}{2k_2})}\left(e^{\ln((X_{A_n})\frac{k_3}{3k_1}} - e^{\ln((X_{A_n})\frac{2k_2}{3k_1}} \right) \end{aligned} \tag{S7}$$

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.

$$X_{C_n} = \frac{\alpha}{(1-\alpha)(1-\alpha\beta)}(X_{A_n} - X_{A_n}^{\alpha\beta}) + \frac{\alpha}{(1-\alpha)(1-\beta)}(X_{A_n}^{\alpha\beta} - X_{A_n}^{\alpha}) \tag{S8}$$

IV. Figures

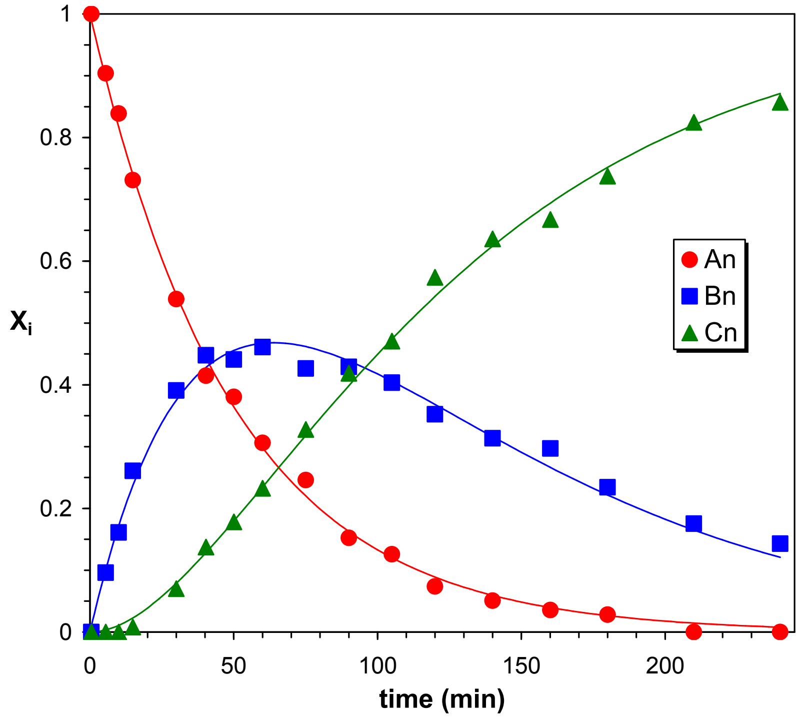

Fig. S1. Product distributions *versus* time in the PTHF-MDI reaction determined by MALDI-TOF MS. The solid lines represent the fitted curves calculated by eqs. 10-12. Experimental conditions: $[MDI]_o = 0.32$ M, $[PCLD]_o = 0.01$ M and T = 80 ^oC.

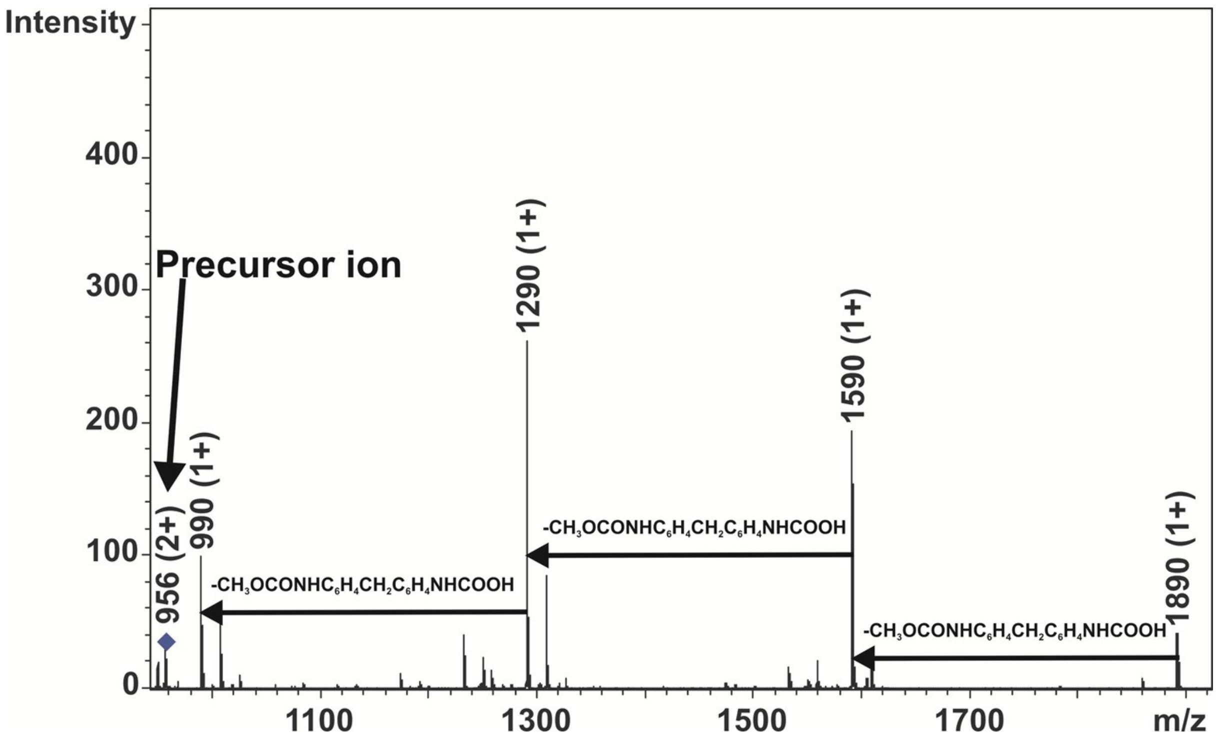

Fig. S2. ESI-MS/MS spectrum of the $[PPG\_GL+3MDI+3CH_3OH+2Na]^{2+}$ adduct ion with a number of repeat units n=16. ESI-MS/MS spectrum was obtained at collision energy of 142 eV.