

Reactivity of multi-arm polyols towards isocyanates

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Table S1. Structure of the polyols

$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{HOCH}_2-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	<p>Pentaerythritol (PE)</p>
$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	<p>Trimethylol propane (TMP)</p>
$\text{HO} \left[\text{CH}_2-\text{CH}_2-\text{O} \right]_a \text{CH}_2-\text{C} \begin{array}{l} \left[\text{O}-\text{CH}_2-\text{CH}_2 \right]_b-\text{OH} \\ \\ \text{CH}_2 \\ \\ \left[\text{O}-\text{CH}_2-\text{CH}_2 \right]_c-\text{OH} \end{array} \text{CH}_2 \left[\text{O}-\text{CH}_2-\text{CH}_2 \right]_d \text{OH}$	<p>Pentaerythritol ethoxylate (PEEO)</p>
$\text{HO} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_2-\text{O} \end{array} \right]_a \text{CH}_2-\text{C} \begin{array}{l} \left[\text{O}-\text{CH}_2-\text{CH} \right]_b-\text{OH} \\ \\ \text{CH}_2 \\ \\ \left[\text{O}-\text{CH}_2-\text{CH} \right]_c-\text{OH} \\ \\ \text{CH}_3 \end{array} \text{CH}_2 \left[\begin{array}{c} \text{O}-\text{CH}_2-\text{CH} \\ \\ \text{CH}_3 \end{array} \right]_d \text{OH}$	<p>Pentaerythritol propoxylate (PEPO)</p>
$\begin{array}{c} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{O}-\text{CH}_2-\text{C} \\ \\ \text{H} \end{array} \right]_a \text{N} \\ \left[\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{CH}_2-\text{C} \\ \\ \text{CH}_3 \end{array} \right]_b \text{N} \\ \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{O} \\ \\ \text{CH}_3 \end{array} \right]_c \text{N} \\ \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_2-\text{O} \\ \\ \text{H} \end{array} \right]_d \\ \left[\begin{array}{c} \text{H} \\ \\ \text{C}-\text{CH}_2-\text{O} \\ \\ \text{CH}_3 \end{array} \right]_e \end{array}$	<p>Petol PA 500- 5D</p>

Table S2. Gradient table of the HPLC conditions used to separate the products of the reaction of Trimethylol propane and Phenyl-isocyanate (trimethylol propane excess). Column parameters: 150x4,6 mm VDSphere PUR 100 C18-M-SE, 5 μ m. The flow rate was 1 ml/min in all cases.

	Time (min)	MeOH (%)	Water (%)
1	0.00	45.0	55.0
2	8.00	45.0	55.0
3	20.00	70.0	30.0
4	25.00	80.0	20.0
5	30.00	80.0	20.0
6	30.10	45.0	55.0
7	36.00	45.0	55.0

Table S3. Gradient table of the HPLC conditions used to separate the products of the reaction of Pentaerythritol and Phenyl-isocyanate (pentaerythritol excess). Column parameters: 150x4,6 mm VDSphere PUR 100 C18-M-SE, 5 μ m. The flow rate was 1 ml/min in all cases.

	Time (min)	MeOH (%)	Water (%)
1	0.00	30.0	70.0
2	8.00	30.0	70.0
3	30.00	80.0	20.0
4	40.00	80.0	20.0
5	40.10	30.0	70.0
6	46.00	30.0	70.0

Table S4. Gradient table of the HPLC conditions used to separate the products of the reaction of Pentaerythritol ethoxylate and Phenyl-isocyanate (pentaerythritol ethoxylate excess). Column parameters: 150x4,6 mm VDSphere PUR 100 C18-M-SE, 5 μ m. The flow rate was 1 ml/min in all cases.

	Time (min)	MeOH (%)	Water (%)
1	0.00	50.0	50.0

2	8.00	50.0	50.0
3	20.00	80.0	20.0
4	30.00	80.0	20.0
5	30.10	50.0	50.0
6	36.00	50.0	50.0

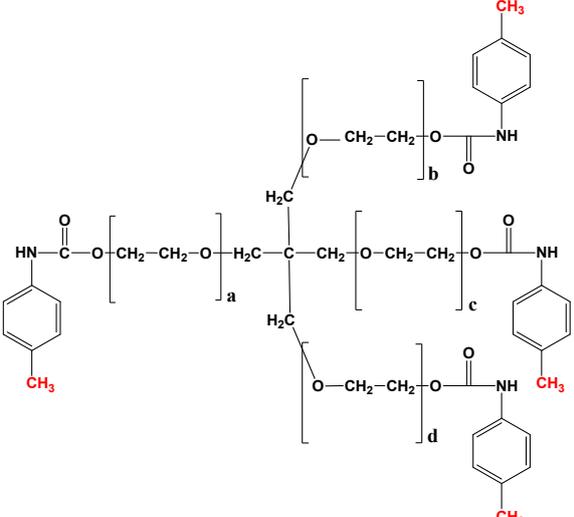
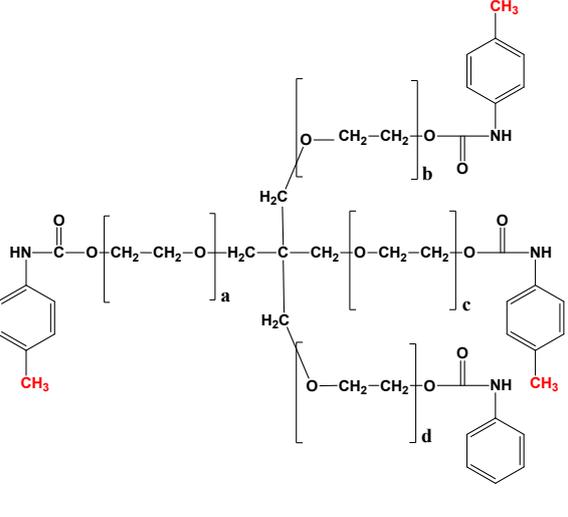
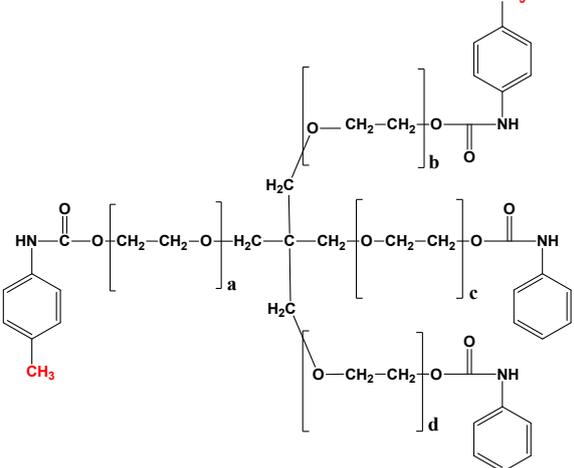
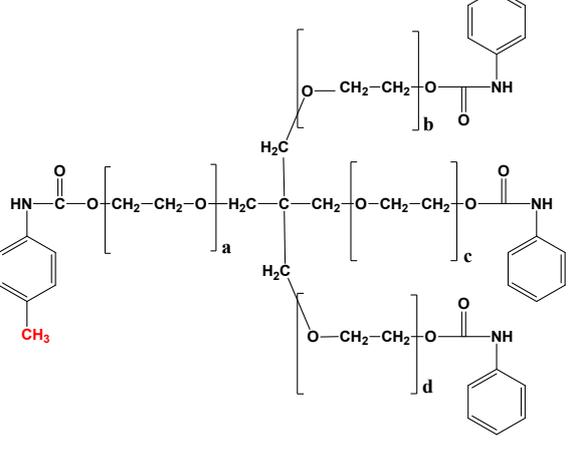
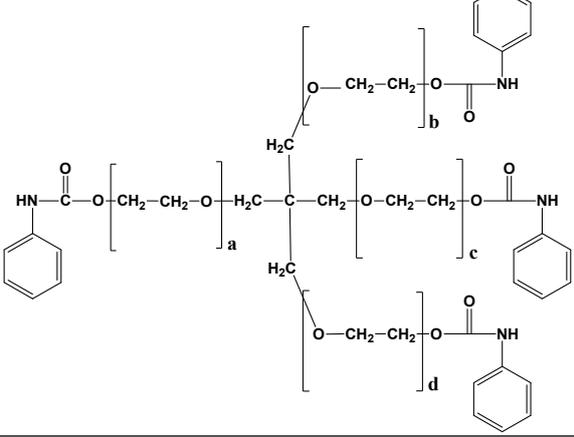
Table S5. Gradient table of the HPLC conditions used to separate the products of the reaction of Trimethylol propane and Phenyl-isocyanate (phenyl isocyanate excess). Column parameters: 150x4,6 mm VDSphere PUR 100 C18-M-SE, 5 μ m. The flow rate was 1 ml/min in all cases.

	Time (min)	MeOH (%)	Water (%)
1	0.0	50.0	50.0
2	8.00	50.0	50.0
3	8.10	80.0	20.0
4	14.00	80.0	20.0
5	14.10	50.0	50.0
6	20.00	50.0	50.0

Table S6. Gradient table of the HPLC conditions used to separate the products of the reaction of Pentaerythritol and Phenyl-isocyanate (pentaerythritol excess). Column parameters: 150x4,6 mm VDSphere PUR 100 C18-M-SE, 5 μ m. The flow rate was 1 ml/min in all cases.

	Time (min)	MeOH (%)	Water (%)
1	0.00	30.0	70.0
2	9.00	30.0	70.0
3	9.10	40.0	60.0
4	15.00	40.0	60.0
5	15.10	80.0	20.0
6	20.00	80.0	20.0
7	20.10	30.0	70.0
8	26.00	30.0	70.0

Table S7. The structure of PEPO derivatives, which may be present after derivatization of reaction products obtained from the PEPO-Phenyl isocyanate reaction.

	
<p>PEPO reacted with 4 PTI</p>	<p>PEPO reacted with 3 PTI and 1 PI</p>
	
<p>PEPO reacted with 2 PTI and 2 PI</p>	<p>PEPO reacted with 1 PTI and 3 PI</p>
	
<p>PEPO reacted with 4 PI</p>	

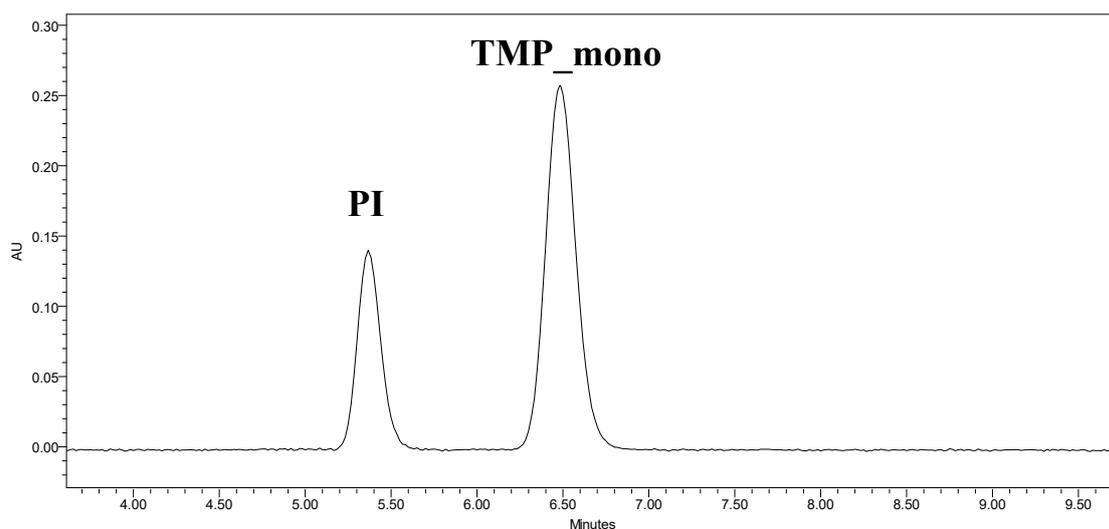


Figure S1. HPLC chromatogram of the reaction of TMP and PI (TMP excess). The separation was recorded at 233 nm. Reaction time: 5 min.

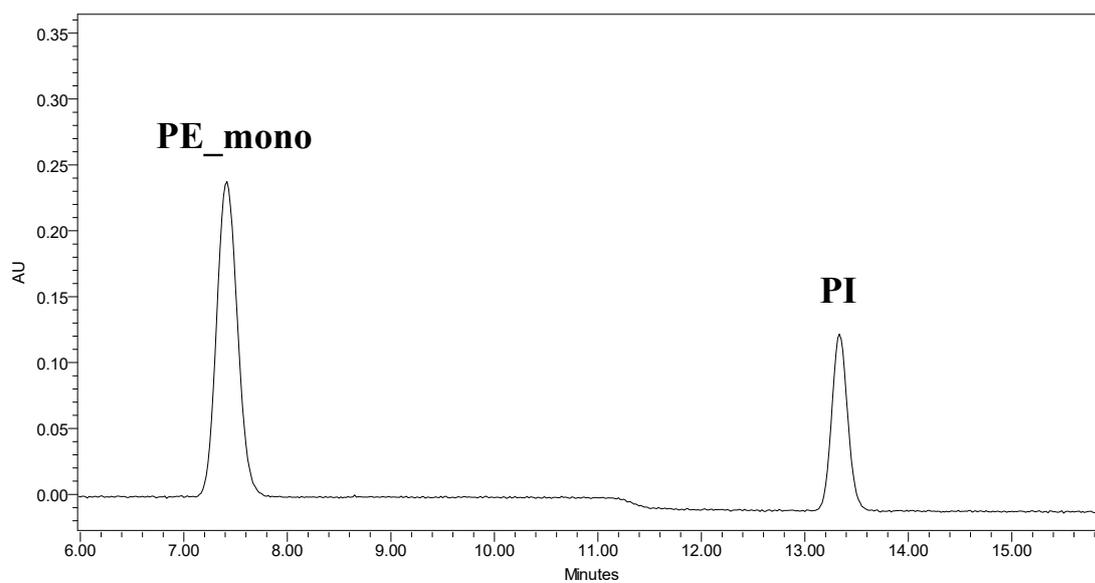


Figure S2. HPLC chromatogram of the reaction PE and PI (PE excess). The separation was recorded at 233 nm. Reaction time: 4 min.

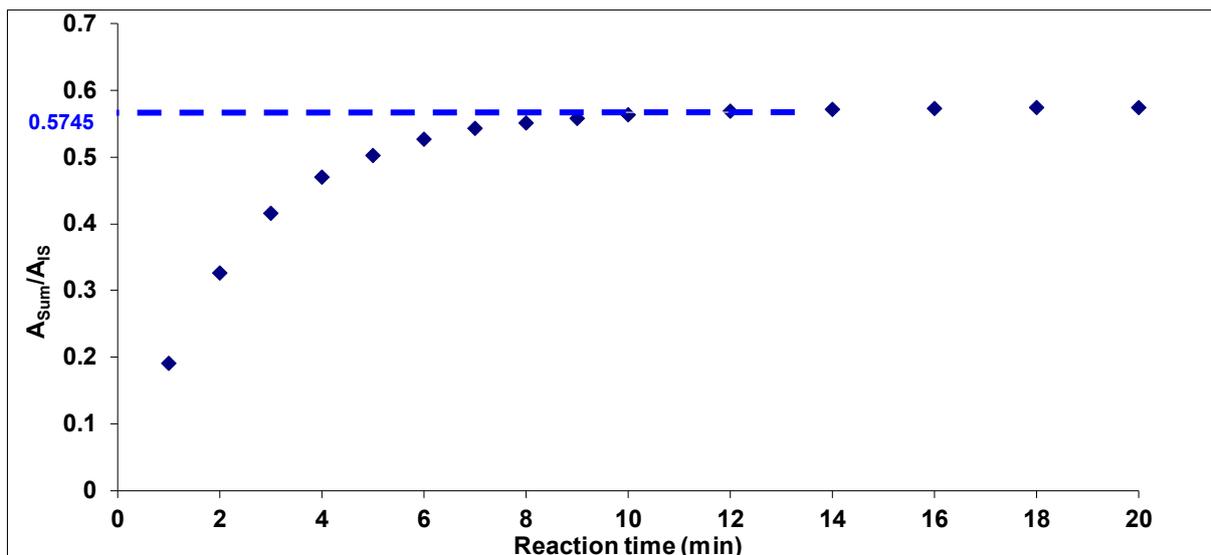


Figure S3. A_{sum}/A_{IS} in the function of time in the case of TMP. It is unambiguously visible that total peak area reaches a maximum after ca. 10 minutes. It means that all of unreacted TMP disappears from the reaction mixture after 10 minutes. Similar graphs were obtained in the case of other reactions as well.

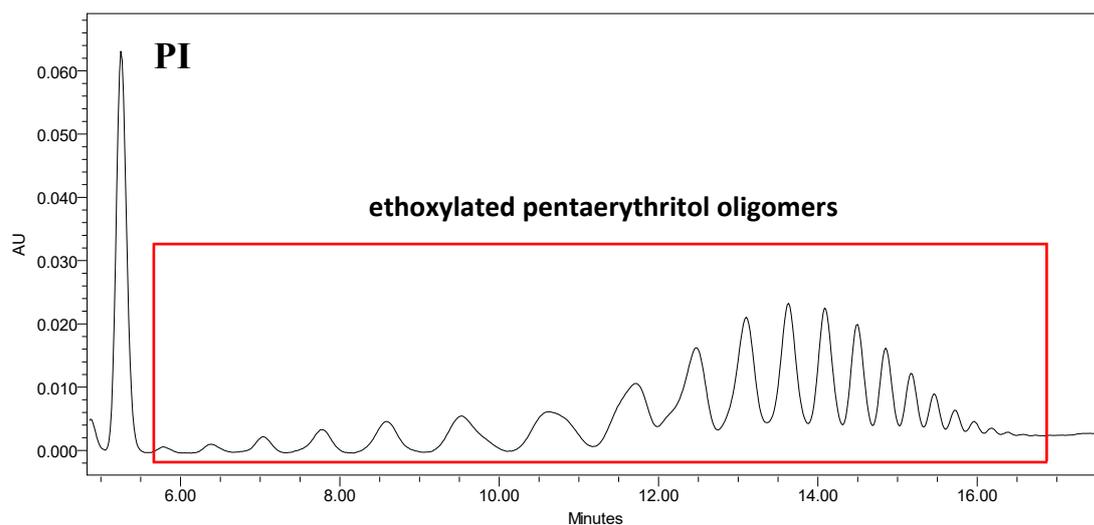


Figure S4. HPLC chromatogram of the reaction of pentaerythritol ethoxylate and phenyl isocyanate (pentaerythritol ethoxylate excess). The separation was recorded at 233 nm. Reaction time: 7 min.

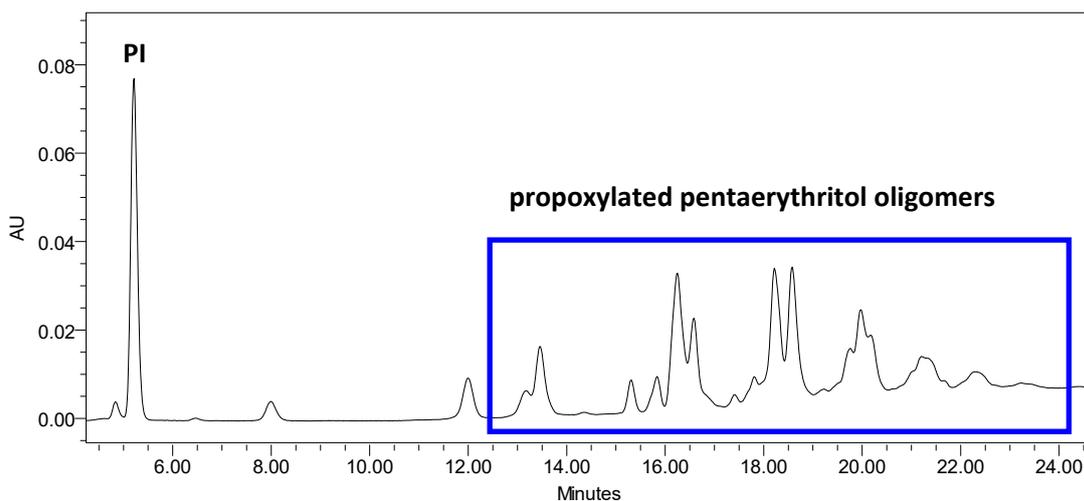


Figure S5. HPLC chromatogram of the reaction of pentaerythritol propoxylate and phenyl isocyanate (pentaerythritol propoxylate excess). The separation was recorded at 233 nm. Reaction time: 14 min.

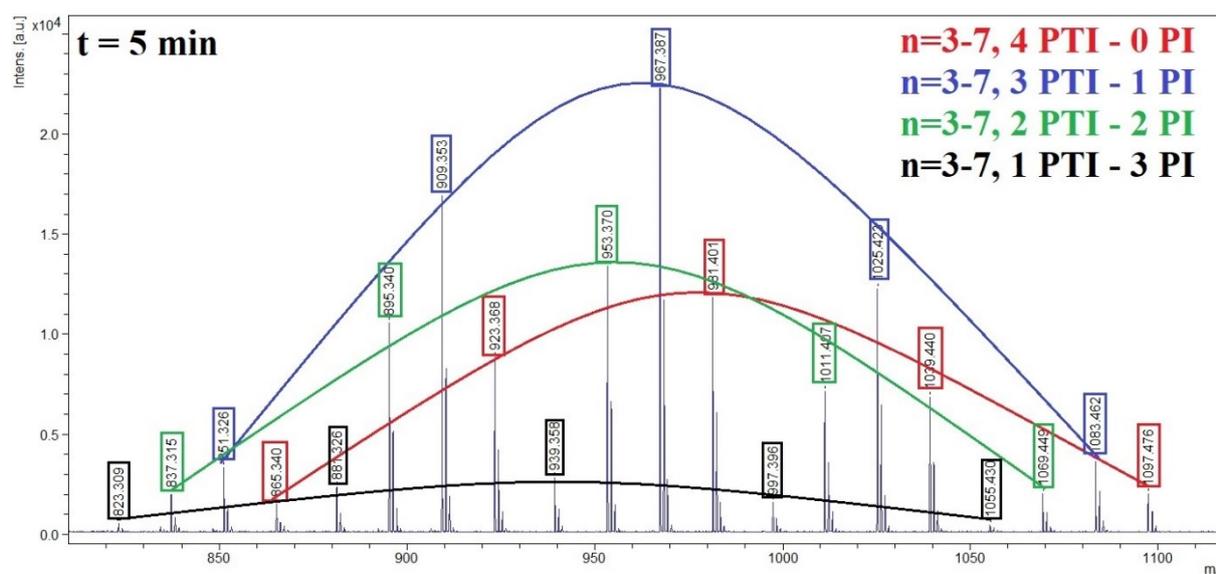


Figure S6. The different series of PEPO derivatives after derivatization in the case of high isocyanate excess. Colors represent the series that reacted with the same number of PTI and PI. Reaction time: 5 min.

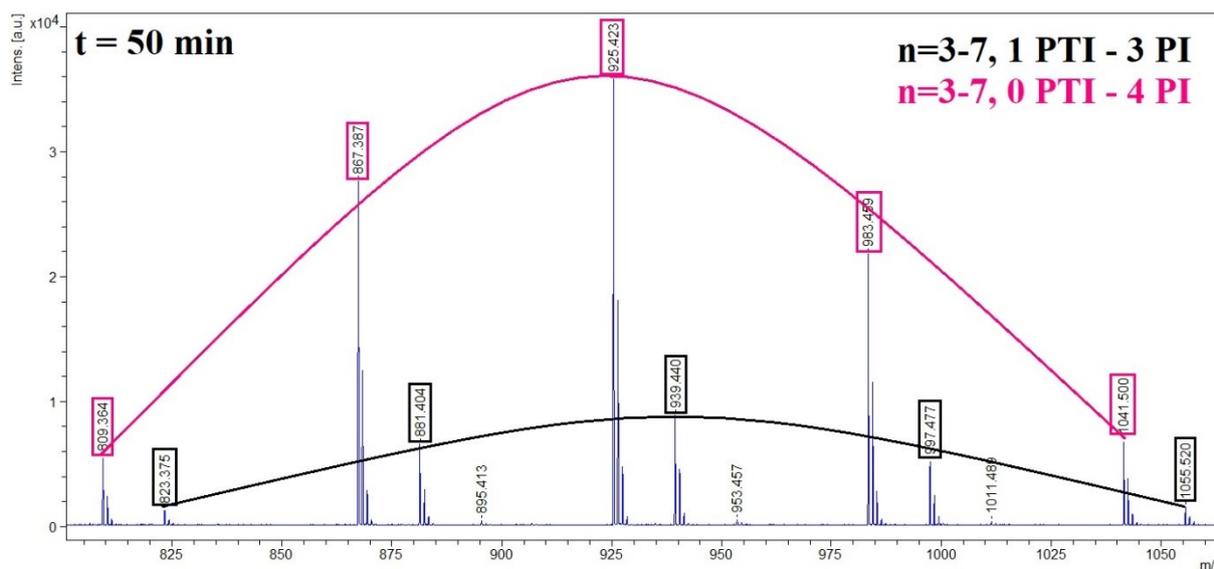


Figure S7. The different series of PEPO derivatives after derivatization in the case of high isocyanate excess. Colors represent the series that reacted with the same number of PTI and PI. Reaction time: 50 min.

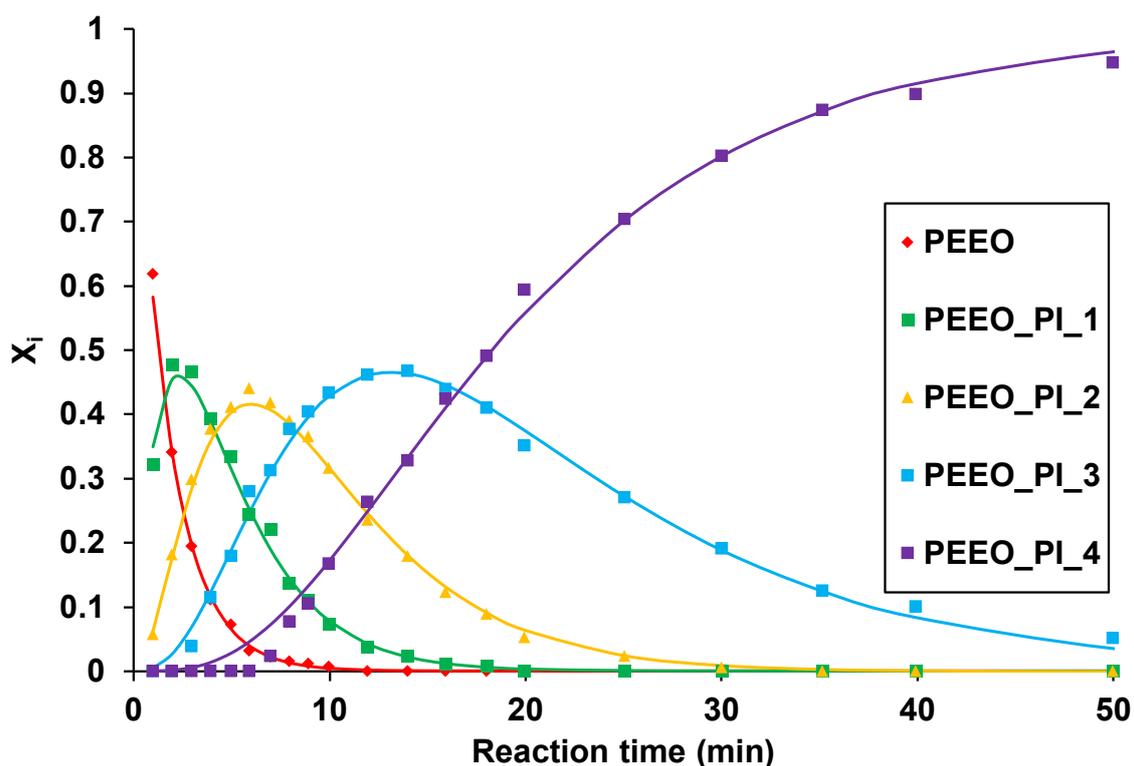


Figure S8. The change of the amount of derivatives in time in the case of the reaction of PEEO and PI. Reaction conditions: $[PEEO]_0 = 0.01$ M, $[PI]_0 = 0.16$ M, solvent: DMSO, temperature = 30 °C. Standard deviation of the rate constants was lower than 5 % in all cases.

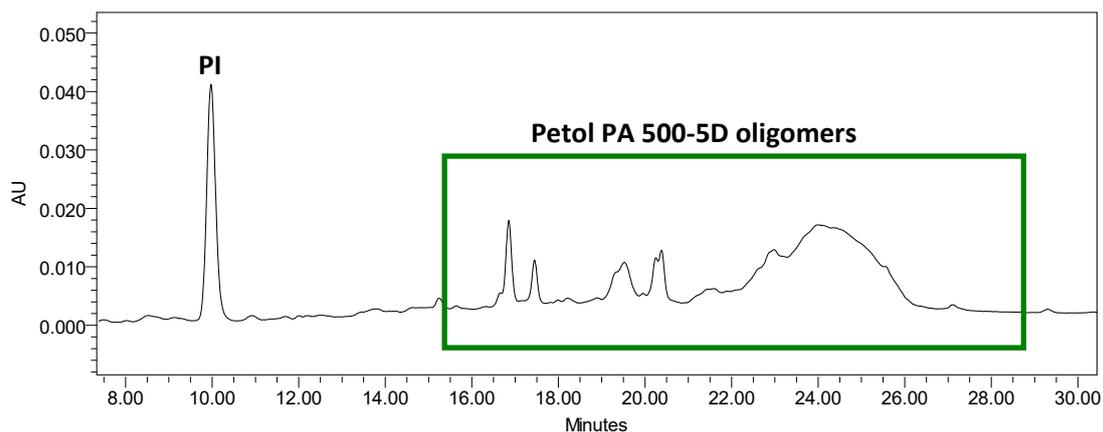


Figure S9. HPLC chromatogram of the reaction of Petol PA 500-5D and phenyl isocyanate (Petol excess). The separation was recorded at 233 nm. Reaction time: 3 min.

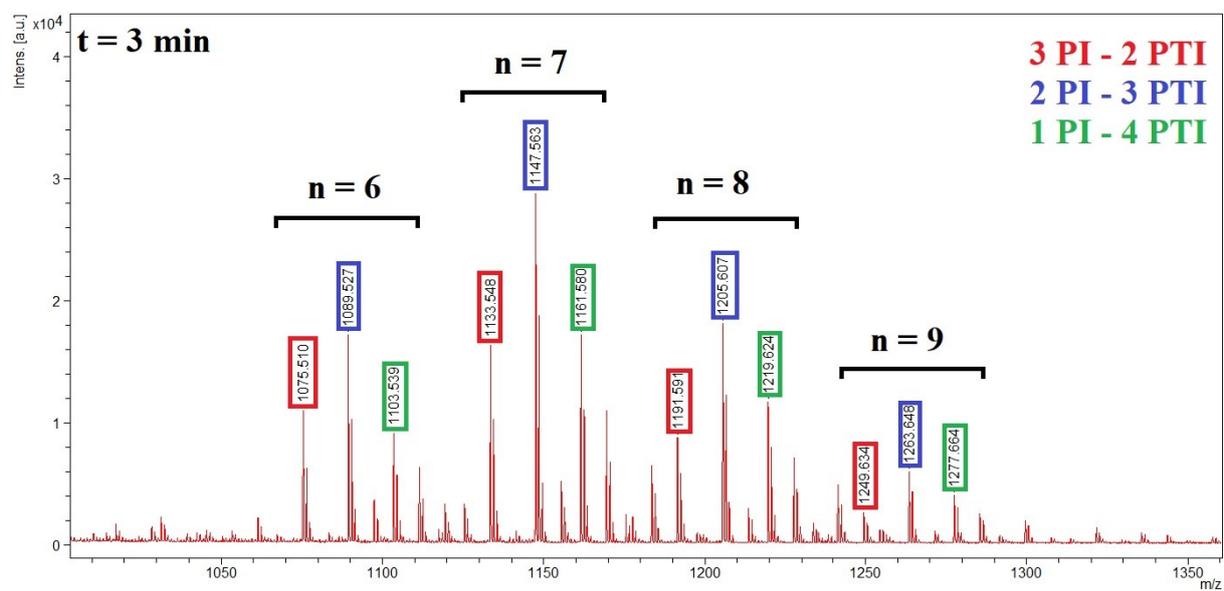


Figure S10. MALDI-TOF MS spectrum of the reaction of Petol PA 500-5D and phenyl isocyanate (phenyl isocyanate excess). Reaction time: 3 min.