Supplementary Information:

Acceleration of a ground-state reaction by selective femtosecond-infrared-laser-pulse excitation

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1. Schematic View of Alcoholysis Reactions

Supplementary Figure 1: Upper panel: Sketch of the alcoholysis reaction of phenylisocyanate (PHI) with cyclohexanol (CH-ol) forming the product cyclohexyl-carbanilate (CC). Lower panel: Absorption spectra of PHI solved in tetrahydrofuran (THF, red curve), CH-ol solved in THF (black curve), and the pure solvent THF (blue curve).

The alcoholysis reaction of phenylisocyanate (PHI) and cyclohexanol (CH-ol) is a thermal driven reaction and occurs upon mixing of PHI and CH-ol. Strong vibrational marker bands were found for CH-ol, the OH-stretching vibration, measured at 3500 cm\(^{-1}\) and calculated at 3816 cm\(^{-1}\), and for PHI, the NCO stretching vibration, at 2270 cm\(^{-1}\) (calc. 2362 cm\(^{-1}\)), the CH bending vibration at 1600 cm\(^{-1}\) (calc. 1648 cm\(^{-1}\)), and the NCO stretching vibration and CH bending vibration at 1512 cm\(^{-1}\) (calc. 1560 cm\(^{-1}\)). These vibrations are visible in Supplementary Fig. 1 and 2 and are not masked by tetrahydrofuran (THF) vibrations and can be used to follow the reaction time-resolved.
Supplementary Figure 2: (a) Absorption spectra of CH-ol in THF (black line), PHI in THF (red line), and THF (blue line) in the spectral range around 3000 cm\(^{-1}\) (a) and around 2000 cm\(^{-1}\) (b). (a) The OH-stretching vibration of CH-ol at 3500 cm\(^{-1}\). The calculated IR transition dipole moment (orange arrow), and the displacement of the atoms (blue arrows) of this normal mode is shown next to the absorption band. (b) The NCO-stretching vibration of PHI at 2270 cm\(^{-1}\). Moreover, the CH-bending vibration of PHI at 1600 cm\(^{-1}\), the NCO-stretching & CH-bending vibration of PHI at 1512 cm\(^{-1}\), and the CH-bending vibration of CH-ol at 1450 cm\(^{-1}\). The calculated dipole derivative unit vectors (orange arrows), and the displacement vectors (blue arrows) of the normal modes are shown next to the absorption bands.
Supplementary Figure 3: Absorption spectra of a 1:1 mixture of CH-ol and PHI in THF for different waiting times of 0 min, 60 min, 120 min, 180 min, and 300 min after mixing. Two identical samples were mixed, one was illuminated at ~3470 cm⁻¹ (FWHM ~ 50 cm⁻¹) at a repetition rate of 2 kHz (red lines), the other one was not illuminated (black lines). With increasing waiting time the cyclohexyl-carbanilate (CC) product rises. CC marker bands were identified: at 1730 cm⁻¹ (calculated 1784 cm⁻¹) the CO stretching vibration; at 1545 cm⁻¹ (calc. 1653 cm⁻¹) the CH-bending vibration, and at 1505 cm⁻¹ (calc. 1566 cm⁻¹) mainly the NH-bending vibration.

The progress of the alcoholysis reaction can be monitored by the CC product absorption bands at 1730 cm⁻¹, 1545 cm⁻¹, and 1505 cm⁻¹ presented in Supplementary Fig. 3. In addition, the NH-stretching vibration at 3300 cm⁻¹ (calc. 3630 cm⁻¹) (not shown in Supplementary Fig. 3) can also be used to follow CC formation. The CC absorption bands increase, while the PHI and CH-ol bands decrease. Illumination around 3470 cm⁻¹ accelerates the otherwise thermal driven reaction as can be seen by comparison of the illuminated sample (red lines) with the not illuminated sample (black lines).
2. **Theoretical Methods and Additional Results**

The initial step of the polymerization reaction has been mimicked by the alcoholysis reaction of PHI with CH-ol in explicit THF. Here, the experimental Arrhenius activation energy was found to be 6.7 kcal/mol [1]. First, geometry optimization and thermochemistry of stationary points, i.e. reactant, transition state, and product, have been performed in gas phase using DFT/B3LYP/6-31++G(d,p) [2]. The results are summarized in Supplementary Fig. 5 and Supplementary Tab. 1. Two different spatial conformations for the reactant (R1 and R2), one transition state (TS), and one product (P) have been obtained (see Supplementary Fig. 6). It was observed that the two reactant (or precursor) geometries for the reactive system (PHI + CH-ol), R1 and R2 are almost isoenergetic (their energy difference is around 1.4 kcal/mol). However, their structure is rather different. While R1 has a (nonlinear) N-H-O Hydrogen bond, R2 is similar to the TS, which has a cyclic, -C-O-H-O-, structure. Apart from this fact, the structures differ by the orientation of the CH-ol. We did not locate a transition state between R1 and R2, but it can be anticipated to exist. Similar to data reported in literature, the calculated
activation energies for R1 and R2 are found to be 30.1 to 31.5 kcal/mol, that is, 4.5 to 4.7 times the experimental values [1].

Due to this manifest discrepancy between the experimental results and the corresponding theoretical ones in gas phase, we included the effect of an explicit solvent, i.e. THF in the present case. Specifically, the stationary structures (PHI + CH-ol) of reactant, transition state, and product have been solvated with 26 THF molecules using a cluster model. Full geometry optimization for each system has been performed using the hybrid ONIOM model [3]. Here, the reactive molecular system (PHI + CH-ol) is studied at the B3LYP/6-31++G(d,p) level of theory, while the solvent molecules (THF) are described by the semi-empirical PM3 method.

For the ONIOM model the total energy is calculated as

\[ E_{\text{tot}} = E_{\text{B3LYP}}^{\text{react}} + E_{\text{PM3}}^{\text{solvent}} + E^{\text{int}} \]  

which can be rewritten as

\[ E_{\text{tot}} = E_{\text{B3LYP}}^{\text{react}} + E_{\text{PM3}}^{\text{react+solvent}} - E_{\text{PM3}}^{\text{solvent}} \]  

where \( E_{\text{tot}} \) is the total electronic energy, \( E_{\text{B3LYP}}^{\text{react}} \) is the electronic energy of the reactive system (PHI + CH-ol) using DFT/B3LYP, \( E_{\text{PM3}}^{\text{solvent}} \) is the electronic energy of the solvent (THF) using PM3, \( E_{\text{PM3}}^{\text{react+solvent}} \) is the electronic PM3 energy of the reactive system and solvent molecules (PHI + CH-ol + THF), and \( E^{\text{int}} \) is the interaction energy between the reactive system and solvent.

During the optimization process, structural changes occur for the solvent molecules that are not directly related to the reaction coordinate, but, e.g., reflect the flexibility at the surface of the cluster model. To avoid spurious effects due to such changes, the energy of the solvent is omitted from the total energy, thus giving the corrected energy

\[ E = E_{\text{B3LYP}}^{\text{react}} + E_{\text{PM3}}^{\text{react+solvent}} - E_{\text{PM3}}^{\text{react}} - E_{\text{PM3}}^{\text{solvent}} \]  

Thermochemical calculations are performed for the reactive system only, assuming the validity of the harmonic approximation. The results of the ONIOM calculations are summarized in Supplementary Tabs. 1-5.
Supplementary Figure 5: Energetics of the reaction of PHI and CH-ol at the DFT/B3LYP/6-31++G(d,p) level in gas phase and in solution (treated by the ONIOM approach); numbers are given in kcal/mol.

In solution, Supplementary Figs. 5 and 7 show that there are also two reactant geometries for the reactive system (PHI + CH-ol), R1 and R2. However, R1 is more stable than R2 (using the corrected energy, Eq. (3)) by about 9 kcal/mol. This means that in solution the cyclic nuclear conformation R2 is the minor fraction, whereas R1 is the major fraction. Given the similarity in structure between R2 and TS, as depicted in Supplementary Fig. 7, we expect that these are the relevant configurations that give rise to the rather low activation energy observed in experiment for this reaction (6.7 ± 0.2 kcal/mol) [1]. This is in accord with the observed small urethane product yield that points to either an ineffective excitation process or a minor fraction of nuclear conformations capable of reacting. Further support for the responsibility of R2 for the observed activation energy in experiment is the conformational change between R2 and TS. This change is mainly negligible for CH-ol compared to PHI (see the dipole moments of PHI and CH-ol in Supplementary Tab. 2). Conformational changes from R2 to TS show an NCO angle change of 0.6° (see Supplementary Tab. 3), a shortening of the distance between the NCO carbon and the OH oxygen by 0.1 Å, and a shortening of the distance between the NCO nitrogen and the OH hydrogen by 0.02 Å (see Supplementary Fig. 7). Moreover,
the interaction of the solvent with the R2 and TS conformations is stronger for CH-ol than for PHI (see Supplementary Tab. 4). These findings indicate to the stronger influence of the NCO-stretching vibration to the reaction coordinate as compared with the OH-stretching vibration, in accord with experiment. Furthermore, the shortening of the C-O distance is more pronounced than that of the N-H distance due to the stronger electrostatic interaction between the C and O atoms as compared with the N and H atoms (see the Mulliken partial atomic charges in Supplementary Tab. 5).

Concerning the energetics, we note that there is a substantial difference between the gas phase and solution results. Given the experimental activation energy of about 6.7 ± 0.2 kcal/mol the gas phase results are too large by factor of about 4.6. It turns out that the present ONIOM approach almost quantitatively reproduces the experimental value. In view of the various approximations such a quantitative agreement could be rather fortunate. However, it can be taken as an indication that the essential aspects of this part of the reaction are covered by the model.

Supplementary Figure 6: Geometries of the reaction of PHI and CH-ol at the DFT/B3LYP/6-31++G(d,p) level in gas phase.
Comparing the reactive systems in gas phase and in solution, one notices that the structural changes follow the order $P < R_1 < TS < R_2$. This can be seen by comparing the geometries in Supplementary Figs. 6 and 7. In addition, the change in dipole moments of gas phase and solution reactive systems (Supplementary Tab. 2) and the root mean square deviation (RMSD) of geometries between gas phase and solution reactive systems (Supplementary Tab. 3) confirm the same order. In addition, much of the change of the dipole moment of PHI is due the structure and here most notably the NCO angle, which changes from 145° (gas phase) to 174° (solution). An interesting observation concerns the TS geometry, which is much tighter in gas phase as compared with the solution phase. For instance, the C-O distance in the TS changes from 1.6 Å to 3.0 Å upon solvation. This also can be observed from the Mulliken partial atomic charges on the interacting atoms (see Supplementary Tab. 5).

It is important to mention that all configurations $R_1$, $R_2$, $TS$ and $P$ are stabilized in solution as compared with the gas phase. This is due to the strong interaction between the solvent molecules and the reactive systems (PHI + CH-ol) and their constituents PHI and CH-ol. This reactive system-solvent-interaction increased in the order $TS < R_2 < R_1 < P$. Therefore, if we calculate the energy of reactive systems ($R_1$, $R_2$, and $TS$) relative to energy of $P$ according to Eq. 3, we observe a stabilization of $TS$ and a destabilization of $R_2$ (see Supplementary Fig. 5), leading to the observed experimental activation energy.
In a more detailed analysis of the reactive system (PHI + CH-ol) itself, it was observed that the CH-ol-solvent-interaction is stronger than the PHI-solvent-interaction for all reactive systems (see Supplementary Tab. 4). Further, the solvation shell around CH-ol is tighter as compared to PHI, thus pointing to the stronger (attractive) interaction.

**Supplementary Table 1:** Energetics (in kcal/mol) of the reaction between PHI and CH-ol in gas phase and in THF solution (according to Eq. (3); the uncorrected energies are given in parentheses).

<table>
<thead>
<tr>
<th></th>
<th>R1 to TS</th>
<th>R1 to P</th>
<th>R2 to TS</th>
<th>R2 to P</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔE</td>
<td>32.1</td>
<td>-19.6</td>
<td>33.6</td>
<td>-18.2</td>
</tr>
<tr>
<td>ΔH</td>
<td>29.5</td>
<td>-18.3</td>
<td>30.9</td>
<td>-17.0</td>
</tr>
<tr>
<td>ΔG</td>
<td>33.8</td>
<td>-13.7</td>
<td>34.8</td>
<td>-12.7</td>
</tr>
<tr>
<td>E_{act}</td>
<td>30.1</td>
<td>-</td>
<td>31.5</td>
<td>-</td>
</tr>
<tr>
<td>solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔE</td>
<td>15.3 (2.2)</td>
<td>21.9 (27.1)</td>
<td>6.2 (7.5)</td>
<td>-31.0 (-21.7)</td>
</tr>
<tr>
<td>ΔH</td>
<td>14.2 (1.0)</td>
<td>20.5 (25.7)</td>
<td>5.6 (6.9)</td>
<td>-29.1 (-19.8)</td>
</tr>
<tr>
<td>ΔG</td>
<td>13.4 (0.2)</td>
<td>17.3 (22.5)</td>
<td>6.8 (8.1)</td>
<td>-23.9 (-14.6)</td>
</tr>
<tr>
<td>E_{act}</td>
<td>14.8 (1.6)</td>
<td>-</td>
<td>6.2 (7.5)</td>
<td>-</td>
</tr>
</tbody>
</table>

**Supplementary Table 2:** Dipole moment of reactive system (PHI + CH-ol) and its constituents in gas phase as well as in THF solution.

<table>
<thead>
<tr>
<th>dipole moment (Debye)</th>
<th>gas phase</th>
<th>solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reactive system</td>
<td>2.27</td>
<td>2.56</td>
</tr>
<tr>
<td>PHI</td>
<td>2.64</td>
<td>2.61</td>
</tr>
<tr>
<td>CH-ol</td>
<td>1.78</td>
<td>1.77</td>
</tr>
<tr>
<td><strong>R2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reactive system</td>
<td>1.72</td>
<td>3.45</td>
</tr>
<tr>
<td>PHI</td>
<td>2.86</td>
<td>2.77</td>
</tr>
<tr>
<td>CH-ol</td>
<td>1.78</td>
<td>1.76</td>
</tr>
<tr>
<td><strong>TS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reactive system</td>
<td>3.62</td>
<td>3.29</td>
</tr>
<tr>
<td>PHI</td>
<td>0.99</td>
<td>2.74</td>
</tr>
<tr>
<td>CH-ol</td>
<td>1.63</td>
<td>1.76</td>
</tr>
<tr>
<td><strong>P</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reactive system</td>
<td>2.50</td>
<td>2.54</td>
</tr>
</tbody>
</table>
**Supplementary Table 3**: NCO angle for reactive system in gas and solution as well as root mean square deviation (RMSD) between gas phase and solution reactive systems.

<table>
<thead>
<tr>
<th></th>
<th>NCO angle (°)</th>
<th>RMSD (Å)</th>
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<tbody>
<tr>
<td></td>
<td>gas phase</td>
<td>solution</td>
</tr>
<tr>
<td><strong>R1</strong></td>
<td>173.2</td>
<td>173.3</td>
</tr>
<tr>
<td><strong>R2</strong></td>
<td>173.7</td>
<td>173.4</td>
</tr>
<tr>
<td><strong>TS</strong></td>
<td>145.9</td>
<td>174.0</td>
</tr>
<tr>
<td><strong>P</strong></td>
<td>126.5</td>
<td>126.1</td>
</tr>
</tbody>
</table>

**Supplementary Table 4**: Interaction energy of reactive system (PHI + CH-ol) and its constituents with the solvent (in kcal/mol).

<table>
<thead>
<tr>
<th></th>
<th>reactive system-solvent-interaction</th>
<th>PHI-solvent-interaction</th>
<th>CH-ol-solvent-interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R1</strong></td>
<td>-29.9</td>
<td>-10.5</td>
<td>-19.5</td>
</tr>
<tr>
<td><strong>R2</strong></td>
<td>-23.2</td>
<td>-7.8</td>
<td>-15.5</td>
</tr>
<tr>
<td><strong>TS</strong></td>
<td>-17.3</td>
<td>-5.6</td>
<td>-11.9</td>
</tr>
<tr>
<td><strong>P</strong></td>
<td>-32.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Supplementary Table 5**: Mulliken partial atomic charges on the interacting atoms for reactive system in gas phase and in THF solution.

<table>
<thead>
<tr>
<th>Mulliken partial charges</th>
<th>gas</th>
<th>solution</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>PHI</td>
<td>CH-ol</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>C</td>
</tr>
<tr>
<td><strong>R1</strong></td>
<td>-0.39</td>
<td>0.66</td>
</tr>
<tr>
<td><strong>R2</strong></td>
<td>-0.28</td>
<td>0.73</td>
</tr>
<tr>
<td><strong>TS</strong></td>
<td>-0.45</td>
<td>0.58</td>
</tr>
<tr>
<td><strong>P</strong></td>
<td>-0.44</td>
<td>0.43</td>
</tr>
</tbody>
</table>
3. Experimental Methods and Additional Results

The formation of urethanes is a thermally driven reaction, which starts immediately after the components are mixed. CH-ol and PHI react forming the urethane product CC. For all experiments, we used equimolar concentration of CH-ol and PHI in THF with various concentrations and sample thicknesses.

The formation of polyurethanes is a thermally driven step-growth reaction, which starts immediately after the components are mixed. At the first step, TCD and TDI react forming the urethane product. The remaining unreacted functional OH and NCO groups allow a strain elongation by further urethane formation. In subsequent reaction steps a polyurethane polymer is formed. To get as large as possible polymer molecules the reactants should be of the equimolar concentration.

3.1. Sample preparation

3.1.1. Sample preparation for acceleration measurements of CH-ol & PHI

We dissolved 163 μl PHI in 337 μl THF resulting in a concentration of 3 mol/l. Accordingly 158 μl CH-ol were mixed with 342 μl THF to a concentration of 3 mol/l. For measurements with lower concentrations, we reduced the amount of PHI and CH-ol accordingly.

For the acceleration measurements 200 μl of both solutions were taken and mixed in a CaF₂ sample cell with 0.1 mm spacer thickness. The sample for the experiment had a concentration of 0.75 mol/l. The absorption of the $\nu$(OH) vibration of CH-ol was about 1 OD at 3470 cm$^{-1}$ (see Fig. 3a in the article). In the acceleration measurements, we tracked the formation of the $\nu$(CO) of CC to determine the reaction rate upon excitation around 3470 cm$^{-1}$ (with a laser pulse of 50 cm$^{-1}$ FWHM). Typical absorptions are depicted in Fig. 3b. The absorption change at 1512 cm$^{-1}$ of the $\nu$(NCO)$&\delta$(CH) of PHI was used to estimate absorption changes in the fs IR-pump IR-probe experiments (see Section 3.5.5). In these samples the $\nu$(NCO) absorption was above 10 OD.

3.1.2. Sample preparation for acceleration measurements of TCD & TDI

TCD mother solution:

We dissolved 82.7 mg of TCD (165.4 g/mol) in 500 μl of nitrobenzene yielding a mother solution with 1 mol/l.

TDI mother solution:

We mixed 71.9 μl of TDI (174.2 g/mol) with 428.1 μl solvent, consisting of CHCl₃:CH in a ratio of 1:1. The resulting mother solution has a concentration of 1 mol/l.
We mixed 100 μl of both mother solutions (TDI and TCD) and diluted them with 400 μl nitrobenzene and 400 μl of the mixture CHCl₃:CH resulting in a concentration of 0.1 mol/l of both reactants. This solution was used for the acceleration measurements with pumping at 2270 cm⁻¹ and at 3070 cm⁻¹. The dilution was necessary to track the vibrational NCO absorption band decrease within some hours.

The acceleration measurements upon excitation of the ν(OH) of TCD at 3470 cm⁻¹ had to be performed in a mixture consisting of 100 μl of each mother solution (TDI and TCD), diluted with 100 μl of CHCl₃:CH and 100 μl of nitrobenzene (total volume of 400 μl) resulting in a reactant concentration of 0.25 mol/l. The adaption was necessary because the absorption in the 0.1 mol/l sample was too low for measuring any differences in the reaction rate.

3.1.3. Sample preparation for fs IR-pump IR-probe experiments

In all ultrafast measurements, the concentration ratio of CH-ol and PHI was the same (1:1). The extinction coefficient in the maximum of the ν(OH) absorption band of CH-ol is about 14 times and 6 times smaller than the extinction coefficient of the ν(NCO) absorption band of PHI, and the ν(CO) absorption band of CC, respectively. Thus, different concentrations and thicknesses were used for measurements in different spectral observation windows, otherwise the sample would absorb nearly all probe photons.

- In the 1500 cm⁻¹ region, 50 μm of 0.75 mol/l CH-ol and 0.75 mol/l PHI solved in THF were used.
- For the measurements of the PHI NCO-band at 2260 cm⁻¹, 50 μm of 0.375 mol/l CH-ol and 0.375 mol/l PHI in THF were used.
- The rise of CO-band at 1730 cm⁻¹ was detected within 100 μm of 1.5 mol/l CH-ol and 1.5 mol/l PHI in THF.

3.1.4. Drawing of polyurethane squares

Solution for photolithography:

We mixed 250 μl of both mother solutions (TDI and TCD), yielding in a concentration of 0.5 mol/l. From the resulting mixture 100 μl were taken and filled in a home build cuvette (two CaF₂ windows) with a 50 μm (or 25 μm) thick PTFE spacer (see Supplementary Fig. 8).
3.2. Cuvette for acceleration measurements

Supplementary Figure 8: Home built cuvette for acceleration and photolithography measurements. Two different spacers were tested: (i) One spacer exhibits two chambers filled with the same sample. One of the chambers is excited with IR light, the other one is not illuminated. (ii) One spacer exhibits only one big chamber. Here, two identical samples and cells were used, one was excited with IR light, the other one was not.

3.3. Acceleration measurements

All acceleration measurements were performed in the following way: The sample mixture was merged and within one to two minutes the sample was filled into two identical sample cells both consisting of two CaF₂ windows (25 mm diameter) with a Teflon spacer of 100 µm (or sometimes 50 µm) thickness. (i) The IR spectrum of both samples were taken (0 min) and then sample A was illuminated with the already running IR pulse OPA [4]. The other sample B was put next to the sample scanner, keeping the conditions as similar as possible. After a given time (e.g. 60 min) the procedure (i) was repeated. The acceleration measurements were stopped when about 30%-40% of the sample was consumed. The absorption of the investigated band was always smaller or about 1 OD.

Concentrations of CH-ol and PHI were in the range of about 0.75 mol/l in THF with a 0.1 mm spacer thickness, providing a reasonable absorption around 3500 cm⁻¹ and 1730 cm⁻¹. Here, we chose a high concentration because the high activation energy results in a slower reaction.

Concentrations of TCD and TDI were in the range of about 100 mmol/l, resulting in a concentration of NCO and OH groups of about 200 mmol/l. Since absorption of the NCO stretching vibration is stronger than the OH stretching vibration, we increased the concentrations by 2.5 times to get reasonable absorption strengths for excitation at 3490 cm⁻¹ (50 cm⁻¹ FWHM).

We developed a sample holder for the IR spectrometer Bruker Equinox 55 to ensure a very reproducible positioning of the sample.

The reaction rates were determined by
- CH-ol & PHI mixtures: following the integral increase of the CO absorption at 1730 cm\(^{-1}\) upon excitation around 3470 cm\(^{-1}\) for CH-ol and PHI mixtures (see Fig. 3b in the article)
- TCD & TDI mixtures: following the decrease of the NCO absorption band (at 2270 cm\(^{-1}\)) upon excitation around 2270 cm\(^{-1}\) (Supplementary Fig. 11a) or the integral decrease of the OH absorption band (at 3500 cm\(^{-1}\)) upon excitation around 3070 cm\(^{-1}\) (Supplementary Fig. 10) or around 3490 cm\(^{-1}\) (Supplementary Fig. 9a and 9b).

The IR laser pulses were generated by a home built OPA. The IR pulses had energies between 2 µJ and 4 µJ, a repetition rate of 2 kHz and a spectral width (FWHM) of 50 cm\(^{-1}\) around its central frequency. A typical IR pulse spectrum is plotted in Supplementary Fig. 11a. For more information on the IR pulses see Kozich et al. [4]

For more information on analysis of the reaction rates and how we determined the activation energy see Kössl et al. [1]

The acceleration of the reaction was determined by calculating the ratio of the rate constants with illumination and without illumination. Since experimental errors or sample fluctuations can occur, we repeated the measurements several times by following the same procedure to obtain a statistic for the results. The distribution of results is presented in Supplementary Fig. 11c-e and 11g.

Changing the IR pulse focus in the sample from 150 µm to 75 µm or to 1-2 mm does not influence the acceleration of the reaction. Thus, we conclude that the observed acceleration effect is not due to a multi-photon process.
Supplementary Figure 9: Absorption spectra of a 1:1 mixture of TDI and TCD in nitrobenzene at delay times of 0 min, 45 min, and 90 min after merging without (black curves) and with IR pulse excitation at around 3490 cm$^{-1}$ (red curves); a) the OH stretching vibration of TCD around 3500 cm$^{-1}$ decreases, while the NH stretching vibration of the urethane product around 3300 cm$^{-1}$ increases with time and illumination; b) the CO stretching vibration of the urethane group around 1760 cm$^{-1}$ increases with time and illumination.
**Supplementary Figure 10:** Absorption spectra of a 1:1 mixture of TDI and TCD in nitrobenzene at delay times of 0 min, 45 min, 90 min, and 180 min after merging without (black curves) and with IR pulse excitation at around 3070 cm⁻¹ (red curves); the OH stretching vibration of TCD around 3500 cm⁻¹ decreases, while the NH stretching vibration of the urethane product around 3300 cm⁻¹ increases with time. Illumination has no or negligible effect on the increase or decrease of the absorption bands.
Supplementary Figure 11: Acceleration measurements: TCD & TDI upper panel, CH-ol & PHI lower panel. (a) Reaction as a function of time with IR pulse excitation (red lines) at 2270 cm⁻¹ and without illumination (black lines); pump pulse spectrum (blue line), structures of TCD and TDI; (b) Reaction as a function of time with IR pulse excitation (red lines) at 3490 cm⁻¹ and without illumination (black lines); structure of the formed urethane product; (c)-(e) measured acceleration ratios upon excitation at different vibrations. CH excitation is dominated by the solvent absorption at 3070 cm⁻¹, and leads to no acceleration. (f) Reaction as a function of time; illumination with IR pulses at 3470 cm⁻¹ (red lines), without (black lines); vibrations are indicated. (g) Measured reaction rates.
3.4. Temperature effects

3.4.1. Thermal Imaging

To check whether the sample is heated by the IR excitation pulses at a repetition rate of 2 kHz over time, we measured the spatially resolved average temperature distribution within the sample with a FLIR A600 thermal imaging camera, while exciting the sample. For this experiment the sample was not moved, and the IR pulses illuminated the same sample spot. The thermal sensitivity of the camera from spot to spot was better than 0.05°C. We observed no temperature increase of the sample at the illuminated spot higher than 0.1 °C. Thus, no average thermal heating of the sample over time takes place. Note, this does not show whether a transient temperature change on a ps to ns time scale occurs, that completely equilibrates on a time scale of 0.5 ms to 33 ms.

Supplementary Figure 12: Temperature scan of the sample upon IR illumination; resolution (0.1 x 0.1 mm, frame rate 30 Hz); diameter of IR focus of 0.3 mm. The IR pulse with energy of 4 µJ hits the sample at the spot SP5. The measured average temperature was 22.2°C, not deviating from other spots in the sample (22.2 °C – 22.3 °C, see upper left inset). The camera measures the temperature with a frame rate of 30 Hz.
3.4.2. Thermal CO-band shift

Supplementary Figure 13: Difference spectra of the CO-stretching vibration after heating the sample by 2.5K. The CO-band shifts to higher energies.

3.5. Estimates

3.5.1. Calculation of the temperature effect of 6°C for 24% acceleration (CH-ol & PHI)

The reaction rate $k$ is given by the Arrhenius equation

$$k = A e^{\frac{-E_a}{k_b T}}$$

where $E_a$ is the activation energy, $k_b$ the Boltzmann constant and $A$ the pre-exponential factor. The influence of the temperature on the reaction rate changes $\Delta k$ are given by

$$\Delta k = \frac{E_a}{k_b T^2} A e^{\frac{-E_a}{k_b T}} \cdot \Delta T$$

A change of 24% reaction rate for an activation energy of about 2300 cm$^{-1}$ is

$$\frac{\Delta k}{k} = 0.24 = \frac{E_a}{k_b T} \cdot \frac{\Delta T}{T}$$

$$\Delta T = 0.24 \cdot \frac{200 \text{ cm}^{-1}}{2300 \text{ cm}^{-1}} \cdot 295 K \approx 6 K$$

From this estimation, we can conclude that an increase in reaction rate of 24% can be achieved by heating the sample by some Kelvin.

3.5.2. Heating the CH-ol & PHI in THF by fs IR pulses acceleration measurements

The heat capacity of THF Cp(THF) is 124 J/(molK), and of PHI Cp(CH-ol) is 157 J/(molK). The IR pulse energy can be calculated that is necessary to increase the temperature of the sample by 6 K. For simplicity, we assume only THF molecules to be in the volume (adding CH-ol or PHI does not
change the results significantly). In the acceleration experiments the focal radius was 0.15 mm, the sample thickness 0.1 mm, resulting in an excited volume $V = 0.007 \text{ mm}^3$ per IR pulse.

The amount of substance in this volume is $n = 8.72 \times 10^{-8}$ mol, and the effective heat capacity $C_{\text{eff}} = C_p(\text{THF}) \times n(\text{THF})$ is $\sim 11 \mu\text{J/K}$. Since we excited the sample with about 3 $\mu\text{J}$, we would expect an average temperature increase of 0.3 K, in agreement with our temperature measurements (see Supplementary Fig. 12).

Upon increasing the focal radius, the temperature increase is strongly reduced at constant IR pulse energy. Since we observed no change in reaction acceleration upon increasing the focal diameter to 1-2 mm, we can exclude heating effects as the origin of reaction acceleration.

3.5.3. Heating the CH-ol & PHI in THF during fs IR-pump IR-probe experiments

The heat capacity of THF $C_p(\text{THF})$ is 124 J/(mol K), and of PHI $C_p(\text{CH-ol})$ is 157 J/(mol K). The IR pulse energy can be calculated that is necessary to increase the temperature of the sample by 6 K. For simplicity, we assume only THF molecules in the volume (adding CH-ol or PHI does not change the results significantly). In the IR-pump IR-probe experiments (probing the $\nu(\text{NCO})$ range, Fig. 4b) the focal radius was bigger or equal to 0.075 mm, and the sample thickness 0.05 mm resulting in an excited volume $V = 0.00088 \text{ mm}^3$ per IR pulse.

The amount of substance in this volume is $n = 1.1 \times 10^{-8}$ mol, and the effective heat capacity $C_{\text{eff}} = C_p(\text{THF}) \times n(\text{THF})$ is $\sim 1.33 \mu\text{J/K}$. We excited the sample with about 3 $\mu\text{J}$ at an optical density of $\sim 0.2 \text{ OD}$ at 3500 cm$^{-1}$ (the pump pulse spectrum is shown in Supplementary Fig. 14a), resulting in an effective pulse energy of 1.1 $\mu\text{J}$. This would lead to a temperature increase of 0.8 K.

Experiments probing the $\nu(\text{CO})$ (Fig. 4c) were performed with 0.1 mm spacer thickness and focal radius of 0.095 mm (and optical density of the $\nu(\text{OH})$ of about 2OD).

3.5.4. Number of photons per OH group

Here, we estimate how many photons per OH group are available at the IR focus during the fs IR-pump IR-probe experiments.

We used CH-ol and PHI concentrations of 0.75 mol/l (probing the $\nu(\text{NCO})$& $\delta(\text{CH})$ around 1500 cm$^{-1}$, Fig. 4a), 0.375 mol/l, or 1.5 mol/l and sample thicknesses of 0.05 mm, 0.05 mm, or 0.1 mm, respectively. For the OH groups with 0.75 mol/l we have to $4.5 \times 10^{20}$ groups per cm$^3$. The volume that we excited by the pump pulse with focal radius of about 0.075 mm or bigger at a sample thickness of 0.05 mm is $V = \pi(0.0075)^2 \text{ cm}^2 \times 0.005 \text{ cm} = 8.8 \times 10^{-7} \text{ cm}^3$. This results in a number of OH groups in the pump pulse volume of about $4 \times 10^{14}$ or more.
With an average pump energy of 3 mW at 1 kHz repetition rate (3 × 10^{-6} J/pulse) at 3500 cm⁻¹, and an absorption of 1.0 OD we have an effective pump energy per pulse of 2.7 µJ. We get the number of photons per pump pulse N from the energy per photon $E_p$:

$$E_p = h \times \nu = h \times c \times 3500 \text{ cm}^{-1} = 7 \times 10^{-20} \text{ J/photon}$$

results in $N = 3.9 \times 10^{13}$

On average, less than every 10th OH group was excited by a photon.

### 3.5.5. Estimation of fs IR-pump IR-probe signal strength

Here, we roughly estimate the signal change by a single IR pulse. At the beginning of the reaction between CH-ol and PHI the change of optical density of PHI is at least ~0.04 OD / hour. This change is directly visible from Supplementary Fig. 14b. We illuminated the sample (radius of 12 mm) with fs IR pulses of ~0.3 mm (0.25 mm – 0.35 mm) focal diameter and 2 kHz repetition rate by scanning the sample volume line by line. Thus, the illumination is spatially and temporally (on a minute time scale) averaged over the complete sample by this method, resulting in an averaged reaction rate increase of 24% (see Supplementary Fig. 11g). The average OD change due to illumination is at least 0.24 x 0.04 OD/hour ~0.01 OD / hour.

Supplementary Figure 14: Absorbance change as a function of time (acceleration measurements) of a CH-ol and PHI mixture in THF with IR pulse illumination at 3470 cm⁻¹ (red lines) and without illumination (black lines). (a) Magnification of the spectral range of the $\nu$(OH) and $\nu$(NH) (from Fig. 3a). Pump pulse spectrum at 3500 cm⁻¹ (blue line) of the fs IR pump – IR probe experiments presented in Fig. 4. (b) Magnification of the peak at 1512 cm⁻¹ of Fig. 3b. Here, the decrease in absorption with (red lines) and without illumination (black lines) as a function of time are clearly visible. Without illumination, we see an absorption change from 0.97 OD to 0.93 OD in the first hour (0.04 OD / hour).

In our fs IR-pump IR-probe experiment we used a focal beam radius of about (0.075±0.01) mm and a cell radius of 12 mm. We illuminate the complete sample cell by scanning the pump beam over the sample line by line. The laser repetition rate is 1 kHz with every second pump pulse is blocked. The expected OD change in the illuminated volume could be a factor of ~2.5 × 10⁴ higher, if the light intensity in the focus would be applied to the complete sample volume at the same photon density.
With this photon density we can compare the signal from the acceleration measurement with the signal from the fs IR-pump – IR-probe measurement.

During the measurement of 1 hour we emit about $0.5 \times 1000 \times 3600 = 1.8 \times 10^6$ pump pulses, while scanning the sample. The estimated change in OD per pulse is about $\text{Absorption change} = \frac{0.01 \text{ OD/hour} \cdot 2.5 \times 10^4}{1.8 \times 10^6 \text{ pulses/hour}} \sim 0.14 \times 10^{-3} \text{ OD/pulse}$

Thus, we expect a signal change in the $\nu$(NCO)&$\delta$(CH) bleaching band at 1512 cm$^{-1}$ in the order of some tenth of mOD, (≈ 0.1 mOD) as observed in Fig. 4a.

Another possible way to estimate the signal strength of the $\nu$(NCO)&$\delta$(CH) bleaching band at 1512 cm$^{-1}$ is to assume that only the number of photons and the number of illuminated molecules are responsible for the acceleration.

In the acceleration measurements we used a pump pulse with 2 kHz and a pulse energy of 3 µJ at 3470 cm$^{-1}$ (50 cm$^{-1}$ FWHM). The focal diameter was about 0.3 mm and the sample thickness 0.1 mm at a concentration of 0.75 mol/l of PHI and 0.75 mol/l of CH-ol in THF. The observed signal change due to acceleration was 0.01 OD in the first hour. We already concluded that every reaction was initiated by absorption of one photon.

Now, we can simply compare the number of photons and number of molecules in the excited volume in the acceleration and fs IR-pump – IR-probe measurements (fs IR-IR):

The repetition rate of the pump pulses in the acceleration measurements is 4 times higher than in the fs IR-IR. The focal Volume is 8 times bigger in the acceleration measurements. This results in an estimated signal change of $\frac{0.01 \text{ OD}}{32} = 0.0003 \text{ OD} = 0.3 \text{ mOD}$ in good agreement with the results displayed in Fig. 4a.

3.5.6. Estimation of the overall quantum yield upon fs excitation at 3500 cm$^{-1}$

Here, we estimate the overall quantum yield upon fs excitation at 3500 cm$^{-1}$ from Fig. 4c displaying the rise of the $\nu$(CO) vibration of CC. In Fig. 4c the final $\nu$(CO) signal is about 0.75 mOD. In this experiment, we used CH-ol and PHI concentrations of 1.5 M and a sample thickness of 0.1 mm. The focal pump diameter was about 0.19 mm and the probe diameter was smaller about 0.13 mm. We do not take the different diameter sizes of pump and probe beam into account and estimate the number of OH groups in the excited volume. The volume is $V=\pi(0.0095)^2 \text{ cm}^2 \times 0.01 \text{ cm} = 2.8 \times 10^{-6} \text{ cm}^3$. Since
we used a concentration of 1.5 mol/l = 1.5 \times 10^{-3} \text{ mol/cm}^3, with 6.023 \times 10^{23} \text{ OH groups per mol, we had } 9.0 \times 10^{20} \text{ OH groups per cm}^3. The number of OH groups \( N \) in the excited volume is

\[ N = 2.5 \times 10^{15}. \]

The pump beam had an excitation energy of 3 \times 10^{-6} \text{ J}. We assume all photons to be absorbed. Thus, about 4.3 \times 10^{13} \text{ photons (see Sec. 3.5.4) were absorbed. About every 60 th OH group absorbs a photon. Since the total absorption of the OH-stretching vibration at 3500 \text{ cm}^{-1} \text{ in the sample was about } 2.0 \text{ OD, we would expect a total bleaching signal of about } 33 \text{ mOD.}

The observed signal at 1730 \text{ cm}^{-1} \text{ was about } 0.75 \text{ mOD. The extinction coefficient of the CC } \nu \text{(CO) vibration is about 6 times higher than that of the } \nu \text{(OH), hence the corresponding signal at the } \nu \text{(OH) vibration resulting from the alcoholysis reaction is expected to be about } 0.125 \text{ mOD.}

The comparison of 33 \text{ mOD and } 0.125 \text{ mOD results in a overall quantum yield of about } 0.3 \%.

Note, this is an estimation of the overall quantum yield. The error of this estimation is huge and we expect the overall quantum yield to be in the range of 0.05\% to 0.6\%. The main error source is the focal diameter.

Direct comparison of the absorption strengths of the \( \nu \text{(OH) vibration at } 3500 \text{ cm}^{-1} \text{ and the } \nu \text{(NCO)}&\delta \text{(CH) at } 1512 \text{ cm}^{-1} \text{ (see Supplementary Fig. 14a, 14b, and 3) shows, that both are of similar strength. Thus, the estimated bleaching signal is about } 0.1 \text{ mOD, in agreement with the bleaching signal in Fig. 4a.}
3.6. Femtosecond IR pump – IR probe results

3.6.1. Hydrogen bonding between CH-ol and CC

Supplementary Figure 15: Left: Comparison of the CC CO-stretching vibration for two different CH-ol:CC ratios, both solvated in THF. The sharp features in both spectra are caused by vapor water lines and can be ignored. Increasing the amount of CH-ol leads to a rise of the red-shifted and broadened shoulder. This is a strong indicator for H-bond formation. Right: The difference of both is presented. The H-bonding causes a peak shift of around 10 cm⁻¹ and broadens the band by factor of 2 to 3.

3.6.2. Comparison to pure relaxation dynamics (IVR)

Supplementary Figure 16: (a) Transient spectra of CH-ol in THF after excitation of the OH-stretching vibration at 3500 cm⁻¹. We assign the broad feature as the tail of changes of δ(CH)-vibration at 1450 cm⁻¹ (Supplementary Fig. 2b), or δ(OH)-vibration at lower wavenumbers. No sharp features are observed, neither at 1515 cm⁻¹ nor at 1505 cm⁻¹. Right: IR pump – IR probe data at magic angle. (b) Transient data of CH-ol in THF upon excitation of the OH stretching vibration at 3500 cm⁻¹. The time axis is linear up to 1 ps, logarithmic from 1 ps to 100 ps. Excited state absorption (positive signal) is visible around 3250 cm⁻¹, bleaching signals at 3470 cm⁻¹, and ‘hot’ ground state absorption around 3530 cm⁻¹ for longer delay times. Excitation energy of 1.5 µJ, 0.75 M CH-ol concentration, focal pump diameter about 200 µm, probe diameter about 150 µm, 0.05 mm thickness.
Supplementary Figure 17: 

(a) Transient spectra of CH-ol & PHI in THF after excitation of the OH-stretching vibration at 3500 cm$^{-1}$ as shown in the article (Fig 4a). 
(b) Transient spectra of PHI in THF after excitation of the NCO-stretching vibration at 2270 cm$^{-1}$. The positive band of pure PHI is nearly featureless and decays on a fast time scale. Hence, the observed signals in the mixture is not due to heating of the PHI or excitation of the NCO-stretching via VER.

Supplementary Figure 18: 

(a) Transient spectra of CH-ol & PHI in THF after excitation of the OH-stretching vibration at 3500 cm$^{-1}$ as shown in the article (Fig. 4b). 
(b) Transient spectra of PHI in THF after excitation of the NCO-stretching vibration at 2270 cm$^{-1}$. The positive and the negative band of pure PHI exhibit a different shape and decay much faster within some ps. Additionally, the bleaching position is different due to the different ESA. Thus, we conclude that the observed signal in the mixture is not due to excitation of the NCO mode, or heating the NCO mode via VER.

3.6.3. Subtraction of the CH-ol & CC relaxation dynamic

As shown in Section 3.6.1, CH-ol and CC are forming an H-bond. The H-bond leads to an effective coupling between both molecules. This coupling causes visible signals in the ultrafast dynamics even for small concentrations of CC as presented in Supplementary Fig. 19 and 20.
We mixed a 10:1 mixture of CH-ol and CC to record the pure CC relaxation dynamics (Supplementary Fig. 19a, and Supplementary Fig. 19b red line). In Supplementary Fig. 19a the \( \nu(\text{CO}) \) vibration of CC upon excitation of the \( \nu(\text{OH}) \) of CH-ol at 3500 cm\(^{-1}\) is shown. Since, we observe clear signals, energy is transferred from the CH-ol \( \nu(\text{OH}) \) to the CC \( \nu(\text{CO}) \) via the H-bond coupling: We observe a fast positive component around 1700 cm\(^{-1}\) decaying on a time scale of \( \sim 4 \) ps. On this time scale the bleaching band has negligible strength, and we attribute the positive signal to the decay of the excited \( \nu(\text{CO})^* \) vibrational mode of CC overlapping with the bleaching band. With the decay of the \( \nu(\text{CO})^* \) vibration, the bleaching band increases and a blue-shifted band emerges around 1740 cm\(^{-1}\) with about 8 ps. We assign this process to heating of CC via IVR (see Supplementary Fig. 13).

Since, no formation of a product occurs in the CH-ol & CC mixture, we compared the dynamics of CH-ol & CC with CH-ol & PHI upon excitation of the OH-stretching vibration at 3500 cm\(^{-1}\). The transient signal of the CH-ol & PHI mixture was subtracted from the transient PHI & CH-ol data. Prior subtraction, the spectra were scaled to have the same strength at the blue-shifted hot band around 1740 cm\(^{-1}\). This is shown in Supplementary Fig. 19b. As a result, we receive the formation of the \( \nu(\text{CO}) \) vibration of CC due to alcoholysis of CH-ol and PHI.

To give more validity to this approach, we also compared the first half of our scans from the PHI & CH-ol data with the second half (see Supplementary Fig. 20, left column). In Supplementary Fig. 20 left column, the absorbance difference spectra of the first half (thick lines), and second half (thin lines) are presented for different delay time intervals. Since the CC product concentration is increasing with time, the signal around 1700 cm\(^{-1}\) is stronger in the second half of the experiment (thin lines). Moreover, a significant difference between the first and second half of the experiment is observed at 1730 cm\(^{-1}\) with a strongly reduced bleaching signal in the first half of the experiment. After scaling of the first half of the experiment (Supplementary Fig. 20, left column) to the same signal strength around 1740 cm\(^{-1}\) (and 1700 cm\(^{-1}\)) of the second half of the experiment (see also Supplementary Fig. 19b), and subtraction of the second half a new absorption rises at the CO position indicating product formation, shown in Supplementary Fig. 20, last column. Due to short time difference between both halves, the resulting signal is weaker compared to the CC&CH-ol subtraction presented in Supplementary Fig. 19b, because part of the rising product signal is also subtracted.
Supplementary Figure 19: (a) Transient spectra of CH-ol & CC upon excitation at 3500 cm\(^{-1}\) for different delay times. (b) Transient spectra of CH-ol & PHI and CH-ol & CC, both solved in THF after excitation of the OH-stretching vibration at 3500 cm\(^{-1}\). The spectra were averaged from 30 ps to 100 ps to minimize noise; both signals are constant over the averaged time range. A scaling factor of 1.5, determined by minimizing the difference of the positive bands, was used to compensate for variations in the sample concentrations. After scaling, both signals are almost identical except at 1730 cm\(^{-1}\). By subtracting CH-ol & CC from the CH-ol & PHI signal, we removed the unwanted contribution of the CH-ol & CC interaction. Thus, the resulting difference mainly shows the formation of the CO-stretching band.

Supplementary Figure 20: Comparison of the averaged transient spectra of the first half hour and second half hour of measurement. Left: Unscaled averaged spectra, thick lines display the first half and thin lines the second half. The gross of the signal, attributed to the CC relaxation, grows with time. This is expected, as the CC concentration rises with time. Middle: The same signals, scaled to match in the hot-band of CC, small differences are only observed around 1730 cm\(^{-1}\). Right: Subtraction of the scaled scans (fresh sample – old sample) shows a positive signal at the position of the \(\upsilon(CO)\) mode, revealing the rise of the product. The time constant of the rise is consistent with the other data ((10 ± 3) ps.).
3.6.4. Selected transients

Supplementary Figure 21: Selected transients of CH-ol & PHI after excitation of the OH-stretching vibration at 3500 cm\(^{-1}\). Top left: PHI \(\nu\) (NCO) bleach increases around 2260 cm\(^{-1}\), no rise of a hot-band is observed. Top right: Rise of the PHI \(\nu\) (NCO) & \(\delta\) (CH) bleach at 1515 cm\(^{-1}\) and rise of the CC \(\delta\) (NH) band at 1505 cm\(^{-1}\). Bottom left: Difference of the measurements of CH-ol and PHI and CH-ol and CC: Rise of the CC \(\nu\) (CO)-stretch at 1730 cm\(^{-1}\). All observed bands show changes with a \((10\pm3)\) ps time constant. The larger noise for the NCO-bleach at 2260 cm\(^{-1}\) originates in the high absorption of the band and is due to a lower number of shots (only 4000 shots) compared to the other spectral ranges (around 30 000 shots).
3.6.5. Reproducibility – NCO region 24h old sample

Supplementary Figure 22: Selected transients and averaged spectra of 24h old CH-ol & PHI sample after excitation of the OH-stretching vibration at 3500 cm$^{-1}$. The concentration of CH-ol and PHI of the fresh was two times higher than after 24 h. Since, around 2260 cm$^{-1}$ there are no contributions of the CC product, these data should show the same dynamics as presented in Fig. 4b. The absorbance difference spectra agree well with the spectra in Fig. 4b, but exhibit a better signal to noise ratio due to longer averaging. Transients also corroborate the data shown in Fig. 4b and Supplementary Fig. 21.

3.7. Photolithography

Polyurethane squares were written in a solution of TCD/TDI mixture solved in nitrobenzene, cyclohexane, and chloroform. This specific solution enabled us to solve TCD and TDI, but the polymer was poorly solved. The polymer square is not visible in the sample cell if the solvent is still present, due to low scattering. Thus, we opened the cell and removed the solvent (see Supplementary Fig. 23). The special alcohol with three Cl groups were chosen, because of their strong electronegativity and scattering cross-section. Electron microscopy experiments enable to visualize the chlorine atoms. Unfortunately, the polymer structure was not detectable, since the sample melted during the experiment.

Measurements with a Raman microscope are presented in Supplementary Fig. 24. We determined 20 times higher Raman signals with the focus located on the polymer square compared to measurements with the focus next to the polymer square.
Supplementary Figure 23: Polymer squares generated by femtosecond IR pulse illumination at 2270 cm\(^{-1}\). Distances were determined with the dnt DigiMicro Mobile camera. The solvent is removed to visualize the squares. Left panel: 4 x 4 mm square written with a focal diameter of 150 µm. Right panel: 3 x 3 mm square written with a focal diameter of 75µm. A small remaining part of the solvent and its effect on the transparency of the sample is visible in the upper left corner.

Supplementary Figure 24: Raman intensities on the polymer square (blue line) and next to the polymer square (black line) measured by a Raman microscope. The grey line displays the 26 times amplified intensities of the black line.
4. References


