Supplementary information

Reactions leading to the formation of the polymeric shell:

![Chemical reactions](image)

**Figure SI-1.** Three principal reactions leading to the formation of the polymer. Reaction with alcohol leads to the formation of urethane, while reaction with amine leads to the formation of urea linkages.

Isocyanate prepolymer (average functionality per molecule around 3) can react with alcohols (glycerol and polyvinylalcohol), water (leading to the formation of an amine) and the resulting amine. Since the functionality of isocyanate (and other reactive components) is >2, the resulting polymer is cross-linked.

When the oil phase containing isocyanate prepolymer is mixed with the first aqueous phase, isocyanate prepolymer starts to react with polyvinylalcohol (the concentration of which on the surface of droplets is high due to its surface activity) and water (which is the main component of the aqueous phase). This reaction is still comparatively slow, since no catalyst is present in the system yet. Further, the second aqueous phase is added, which contains DABCO as the catalyst and glycerol as the tri-functional alcohol. All three reactions shown in fig. SI-1 are catalyzed by DABCO.

When the DABCO and the glycerol are added, the main phase of the reaction starts. The nascent shell, most probably containing PVA in its structure, is formed very fast. From now on, the reactive species have to penetrate the shell in order to react with the isocyanate in the oil phase. The extent of the reaction with each type of complimentary monomer is determined by its partitioning between the two phases. Thus, PVA is probably too big to penetrate the membrane and will not react anymore. In contrast, water and glycerol are small enough to penetrate through the membrane. As the result, the cross-linked polymer containing urethane and urea linkages is formed.
Description of the process of particles formation.

Figure SI-2. The process of the particles formation represented as two processes taking place simultaneously. 1. Phase separation process induced by evaporation of co-solvent. 2. Interfacial polymerization induced by the addition of the second complimentary monomer and the catalyst.

The formation of core-shell particles with the liquid core can be imagined as two parallel processes: phase separation and interfacial polymerization. If only phase separation would be used (and no reaction of isocyanate with water would take place), one would virtually end up with the droplets of hydrocarbon surrounded with the liquid isocyanate after co-solvent evaporation. If only interfacial polymerization would be employed, one would end up with particles containing the mixture of the core material and the co-solvent as the core material.

On the influence of the oil phase composition on particle size.

The amount of the co-solvent necessary to make the isocyanate prepolymer and liquid hydrocarbon miscible is nearly two times less in the case of CO compared to three other core materials (Table 1). Further, one has to consider that isocyanate prepolymer is a relatively viscose, honey-like liquid (1,800 cP), while hydrocarbons and ethyl acetate are considerably less viscose. Thus, the overall viscosity of the initial oil phase in the case of CO is higher than in all other cases. Usage of shear-type mixer can explain formation of the emulsions with the slightly broader particle size distribution in case of more viscose dispersed phase 1. The smaller particle size in the case of TD can be explained by the reduction of Ostwald ripening due to the lower solubility of TD in water compared to the other hydrocarbons2, 3. In the cases of N- Hep and N-Non, both the composition of the oil phase and hydrophobicity of the components are very similar. Hence, the particle size distributions are almost identical.

FT-IR spectroscopy: why the particles with the same composition but different size have different spectra in the ATR mode

Probably, as the shell thickness of the particles increases, some screening/shielding of the IR light happens, so that the absorption bands corresponding to the core material appear to be less pronounced even if the composition is the same (see TGA in fig.11). Therefore, FTIR in ATR mode can be used for quantitative determination of core-shell ratio only in the case of particles with the same size/size distribution; otherwise the results will be incorrect. This problem, most probably, can be avoided by performing the measurements in a transmission mode using KBr pellets.
The Antoine equation:
\[ \log_{10} p = A - \frac{B}{C + T}, \]

where \( p \) is the vapor pressure, \( T \) is temperature and \( A, B \) and \( C \) are component-specific constants.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( T_b, \text{K} )</th>
<th>Antoine equation parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Hep</td>
<td>371</td>
<td>4.02832 1268.636 -56.199</td>
<td>4</td>
</tr>
<tr>
<td>Isooctane</td>
<td>372</td>
<td>3.93679 1257.84 -52.415</td>
<td>4</td>
</tr>
<tr>
<td>CO</td>
<td>422</td>
<td>3.98805 1438.687 -63.024</td>
<td>5</td>
</tr>
<tr>
<td>N-Non</td>
<td>424</td>
<td>4.06245 1430.377 -71.355</td>
<td>6</td>
</tr>
<tr>
<td>Dodecane</td>
<td>&gt;487</td>
<td>4.10549 1625.928 -92.839</td>
<td>4</td>
</tr>
<tr>
<td>TD</td>
<td>&gt;526</td>
<td>4.13735 1739.623 -105.616</td>
<td>7</td>
</tr>
</tbody>
</table>

Simulation of the weight loss kinetics
Let us imagine a sample containing microparticles with a broad size distribution. The size of the particles varies between 100 nm and 1000 nm (\( D_{\text{max}} = 400 \) nm). We divide this sample into 10
imaginary fractions, each with the particle radius equal $R_n=100, 200, 300\ldots1000$ nm. The volume fraction of each fraction is known.

The evaporation of the core material from 100 nm particles is 100 times faster than from 1000 nm ones, because

$$\frac{dm}{dt} \propto \frac{1}{R^2}$$

Simulation of the weight loss kinetics for each fraction of particles as well as their sum, which represents the mass loss of the whole sample, is shown in the figure below.

The shape of the obtained graph is very similar to the one obtained in the reality (fig.12). Consequently, the assumption that non-linearity of $m(t)$ can be caused by the broad size distribution of the particles in the sample has been proven.