pH-Sensitive Nanocapsules with Barrier Properties: Fragrance Encapsulation and Controlled Release

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Dynamic Scanning Calorimetry (DSC)
The thermal behavior of the polymeric nanocapsules was further investigated via DSC. The mobility of macromolecular chain segments is closely related to the glass transition temperature, which can also be seen as a measure for free volume and can serve as additional trigger to vary the capsule release characteristics. Most importantly a high $T_g$ of the shells serves as important prerequisite to achieve high encapsulation efficiency. Samples S1 and S5 were chosen for closer evaluation, and the respective nanocapsules were measured as dry powders after freeze-dying. Figure SI-1 shows an overlay of the DSC curves of two heating cycles in a temperature window from 25 °C to 170 °C with a heating rate of 2K/min under nitrogen flow. The first heating cycle (upper lines) gives information about the thermal behavior of polymer capsules containing the fragrance. In the second heating cycle the $\alpha$-Pinene is expected to have been completely released and evaporated, which therefore allows to determine the $T_g$ of the polymeric shell without presence of the fragrance. The most important information relevant for the discussion of thermic properties are summarized in Table SI-1.
Figure S1-1: DSC curves for the samples S1 and S5 after freeze-drying and a heating rate of 2 K/min under nitrogen flow. The upper lines represent the first heating cycle with encapsulated α-Pinene. The endothermic peaks correlate to the evaporation of the fragrance. The lines below show the data for the 2nd heating cycle and indicate the thermal behavior of the polymeric shells without any fragrance influence.

Table S1-1: Summary of important characteristic values for the samples S1 and S5, partially derived from DSC measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (est.)$^1$ [°C]</th>
<th>$\text{EE}_{\text{SC}}$ $^2$ [%]</th>
<th>$\text{EE}_{\text{GC}}$ $^3$ [%]</th>
<th>$T_{\text{onset}}$ $^4$ [°C]</th>
<th>$\Delta H$ $^5$ [J/g]</th>
<th>$T_g - T_g$ (est) $^6$ [°C]</th>
<th>$T_g - T_{\text{onset}}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>109</td>
<td>91</td>
<td>90</td>
<td>73</td>
<td>-79</td>
<td>152</td>
<td>43</td>
</tr>
<tr>
<td>S5</td>
<td>87</td>
<td>30</td>
<td>18</td>
<td>56</td>
<td>-17</td>
<td>128</td>
<td>41</td>
</tr>
</tbody>
</table>

$^1$ estimated by the Fox equation;

$^2$ encapsulation efficiency determined by solid content of freeze-dried sample;

$^3$ encapsulation efficiency determined by headspace-GC (closed capsules; pH3: 60 °C, 30 min);

$^4$ value from 1st heating cycle, corresponding to capsules after freeze drying containing the fragrance;

$^5$ value from peak in 1st heating cycle, predominantly relating to evaporation of encapsulated fragrance;

$^6$ value from 2nd heating cycle, corresponding to capsule polymer without interference of fragrance.

In the first heating cycle an endothermic peak is observed which is basically related to the evaporation of the fragrance. The peak area follows the trend for encapsulated fragrance amount and is expected to predominantly represent the enthalpy of evaporation, although
It seems obvious that significant fragrance evaporation rates can only be observed when the polymeric shell starts losing its barrier performance. Based on the assumption that the polymer chain segment mobility is of key importance within this investigation, the endothermic peak onset during the 1st heating run can be postulated to be identical with the \( T_g \) value of the capsule wall in the presence of the fragrance. The onset temperature for sample S1 was found around 73 °C and the onset temperature for sample S5 was found around 56 °C. This result signifies two important points: 1) The fragrance can partially swell the capsule shell and act as a softener, hence strongly reducing the “effective \( T_g \)” which is most relevant for high barrier performance. This phenomena was reported before for nanocapsule systems by Theisinger et al. and therefore expected. More detailed considerations are given in the main text upon the discussion of encapsulation efficiency and barrier performance. 2) The differences between EE\(_{SC}\) and EE\(_{GC}\) can be easily understood. Based on the considerations above sample S5 obtains an effective \( T_g \) below 60 °C, which are the measurement conditions for the headspace-GC investigations.

For the 2nd heating run \( T_g \) values of 152 °C and 128 °C were observed compared to the calculated \( T_g \) values of 109 °C and 87 °C for the samples S1 and S5, respectively. Please note that a significant deviation between calculated (Fox equation) and measured (DSC) \( T_g \) values can frequently be observed, which is mainly a consequence of idealized assumptions (e.g. ideal copolymerization, etc.) and imperfect correlation with real systems. Especially deviations to higher temperatures, as observed in this case, are not uncommon. Please note that the absolute deviation is of a similar magnitude (ca. 40 °C) and that within this contribution the discussion on \( T_g \) influence on the barrier performance is deliberately made only on the general trends.

**Release Kinetics**

Additional to 30 min equilibration time represented in Figure 1 in the main document, the amount of free \( \alpha \)-pinene in the headspace oven after 10 and 60 min were recorded as well. In general the free fragrance amount increases slightly at pH3 with time. Please note that measurement conditions at 60 °C can be considered as relatively harsh to the volatile and the
nanocapsule barrier walls. More significantly, at pH 9 the release kinetics are strongly
depending on the content of acidic groups. The higher the degree of acid functionalization, the
faster and the more complete the fragrance release, which supports a hydrogel-like behavior
of the polymer shell.

![Figure SI-2](image)

**Figure SI-2:** Amount of free α-pinene in the headspace of samples S8, S9, S10, S11 and S1 with increasing
MAA content from 2.5% MAA to 10% MAA for closed capsules at pH3 and for opened
capsules at pH9 after 10, 30 and 60 min equilibration time at 60 °C in the headspace oven.

Table SI-2 summarizes the relative release of α-Pinene after 10, 30 and 60 min in the
headspace oven at 60 °C for samples with varying MAA content. The results demonstrate
clearly that an increased amount of MAA accelerates the release kinetics.

**Table SI-2:** Controlled release investigation. The MAA content was varied, with small variances in $T_g$ and
particle size, but drastic changes in the release kinetics at pH9. Furthermore it can be seen
that increased MAA content leads to higher encapsulation efficiencies at pH3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MAA $^1$ [wt%]</th>
<th>$T_g$ (est.) $^2$ [°C]</th>
<th>Z-Average $^3$ [nm]</th>
<th>$EE_{SC}^4$ [%]</th>
<th>$EE_{GC}^5$ [%]</th>
<th>10 min</th>
<th>30 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>S8</td>
<td>2.5</td>
<td>102</td>
<td>170</td>
<td>77</td>
<td>70</td>
<td>0</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>S9</td>
<td>5</td>
<td>104</td>
<td>164</td>
<td>83</td>
<td>80</td>
<td>1</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>S10</td>
<td>7.5</td>
<td>107</td>
<td>172</td>
<td>88</td>
<td>85</td>
<td>19</td>
<td>48</td>
<td>69</td>
</tr>
<tr>
<td>S11</td>
<td>9</td>
<td>108</td>
<td>175</td>
<td>89</td>
<td>86</td>
<td>33</td>
<td>76</td>
<td>95</td>
</tr>
<tr>
<td>S1</td>
<td>10</td>
<td>109</td>
<td>186</td>
<td>91</td>
<td>90</td>
<td>54</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

$^1$ MAA percentage based on total weight of monomers;
$^2$ estimated by the Fox equation;
$^3$ average particle size (diameter) measured by dynamic light scattering (DLS);
$^4$ encapsulation efficiency determined by solid content of freeze-dried sample;
$^5$ encapsulation efficiency determined Headspace-GC (closed capsules; pH3; 60 °C, 30 min);
$^6$ released percentage of α-Pinene after increasing the pH to 9 determined via Headspace-GC at 60 °C in high shaking mode based
on the $EE_{GC}$ result after different time intervals.
**AFM Measurements**

AFM pictures are only shown for the closed capsules at pH3 because no difference in the morphology after fragrance release can be observed by AFM measurements. The samples were analyzed after drying, hence the swollen state of the capsules at pH 9 cannot be observed. The images show equally shaped spheres. The size distributions of the nanocapsules are in good agreement with the TEM and SEM images.

![AFM images of nanocapsules from sample S1 prepared from closed capsules at pH3 at different magnifications: left) 500 nm x 500 nm; right) 5 µm x 5 µm).](image)

**Figure SI-3:** AFM height images of nanocapsules from sample S1 prepared from closed capsules at pH3 at different magnifications: left) 500 nm x 500 nm; right) 5 µm x 5 µm).