Supporting Information


Micromolding Surface-Initiated Polymerization: A Versatile Route for Fabrication of Coatings with Microscale Surface Features of Tunable Height

Carlos A. Escobar, Tyler J. Cooksey, Matthew P. Spellings, and G. Kane Jennings*
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Table S1. Summary of the atomic force microscopy characterization results for the structures shown in Figure 2e and 4c.

<table>
<thead>
<tr>
<th></th>
<th>DFEA</th>
<th></th>
<th>Klarite®</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Master</td>
<td>Mold</td>
<td>Film</td>
<td>Master</td>
</tr>
<tr>
<td>Height [µm]</td>
<td>1.86 ± 0.03</td>
<td>1.73 ± 0.02</td>
<td>1.05 ± 0.02</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td>Width [µm]</td>
<td>4.05 ± 0.09</td>
<td>4.06 ± 0.13</td>
<td>4.16 ± 0.14</td>
<td>1.80 ± 0.02</td>
</tr>
<tr>
<td>Pitcha) [µm]</td>
<td>4.57 ± 0.09</td>
<td>4.45 ± 0.08</td>
<td>4.66 ± 0.12</td>
<td>2.30 ± 0.03</td>
</tr>
</tbody>
</table>

a) Pitch refers to the distance between peaks of the features.

The disparity in base width between the film and mold for the Klarite® case may be explained as a consequence of the incomplete monomer conversion, mechanical distortion of the high-relief features on the mold by the applied load, and insufficient containment of the monomer within the mold given that it does not exhibit an enclosed (recessed) surface topography.

Derivation of Equation (1)

At \( t = 0 \) we have: \( C_M = C_{M0}, C_I = C_{I0}, \) and \( C_{Pi} = 0 \)

where \( C_M \) and \( C_I \) represent the monomer and initiator concentrations at a given time, \( t \), respectively. \( C_{M0} \) and \( C_{I0} \) represent initial monomer and initiator concentrations, respectively, and \( C_{Pi} \) represents the concentration of monomer that has been polymerized (on a repeat unit basis).

Stoichiometry:

\[
C_M + C_{Pi} = C_{M0} \tag{S1}
\]

As monomer reacts, polymer forms:

\[
\frac{dC_M}{dt} = \frac{dC_{Pi}}{dt} \tag{S2}
\]

The rate of change for these variables is defined as:

\[
\frac{dC_M}{dt} = -k_p C_I C_M \tag{S3}
\]

assuming a first order propagation in terms of both monomer and initiator, and
\[ \frac{dC_I}{dt} = -k_I C_I \] (S4)

which assumes a first order termination reaction.

\[ \frac{dC_{pL}}{dt} = k_p C_I C_M \] (S5)

From (S4):

\[ \frac{dC_I}{C_I} = k_I dt \] (S6)

Integration of (S6) yields:

\[ C_I = C_{I0} e^{(-k_I t)} \] (S7)

Substituting (S7) in (S3) and rearranging:

\[ \frac{dC_M}{C_M} = -k_p C_{I0} e^{(-k_I t)} dt \] (S8)

where,

\[ k_p C_{I0} = K \] (S9)

Integration of (S6) using u-substitution yields:

\[ C_M = C_{M0} e^{\left\lfloor \frac{K_{I0}}{K} \right\rfloor e^{(-k_I t)}} \] (S10)

Substituting (S10) into the conversion (\( \chi \)) equation (Equation 1 of the main text) yields:

\[ \chi = 1 - \frac{C_M}{C_{M0}} = 1 - e^{\left\lfloor \frac{K_{I0}}{K} \right\rfloor e^{(-k_I t)}} \]