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## Electronic Supplementary Information

# Dual-cure photochemical/thermal polymerization of acrylates: a photoassisted process at low light intensity

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#### **Content:**

- 1. Reproducibility
- 2. CRM measurements of thermal system with different TBH amounts

### 1. Reproducibility

Depth profiles were measured by CRM at different reaction times (from 1 to 30 h) using a different monomer batch. Results are shown in Figure S1. A very similar behaviour as already observed in Figure 7 can be noticed: in the first 500  $\mu$ m of the sample, the polymerization is not complete after 45 min of reaction time with a conversion around 62 % and a 40  $\mu$ m inhibited layer. A pronounced characteristic peak of conversion can be clearly seen. After 1:30 h, a highly efficient polymerization with conversion around 95 % was achieved.

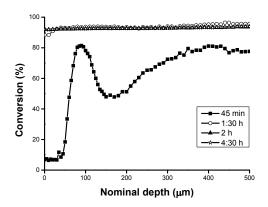


Figure S1 - Depth conversion profile of the polymer (E270/SR306; 0.2 wt % Co<sup>II</sup>; 0.5 wt % TBH) at different curing time.

#### 2. CRM measurements of thermal system with different TBH amounts

Figure 3, Figure 4 and Figure 5 show the CRM depth profiles obtained with the thermal system while varying the amount of TBH: 0.2, 0.5 and 2 wt % respectively.

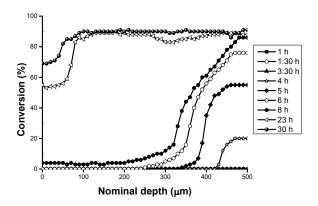


Figure 3 - Depth conversion profile of the polymer (E270/SR306; 0.2 wt %  $Co^{II}$ ; 0.2 wt % TBH) at different curing time.

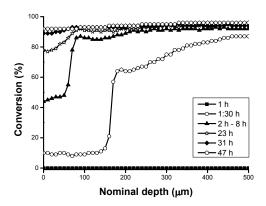


Figure 4 - Depth conversion profile of the polymer (E270/SR306; 0.2 wt % CoII; 0.5 wt % TBH) at different curing time.

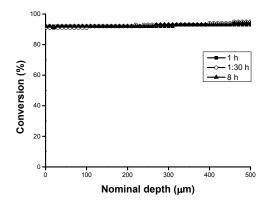


Figure 5 - Depth conversion profile of the polymer (E270/SR306; 0.2 wt % Co<sup>II</sup>; 2 wt % TBH) at different curing time.