Supporting information

Microstructural study of different thick dimetacrylate-based samples using different amount of photoinitiator

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1. **The time dependence of the local free volume of samples described by the Boltzmann function.**

   Figs. S1 – S2 display the time dependence of the local free volume size V_h for two different thick 2M samples with two different contents of PI. The experimental time dependence of the local free volume changes (V_h) during photopolymerization was fitted by the Boltzmann sigmoid function given as

   $$V_h(t) = V_{h,2} + \frac{V_{h,1} - V_{h,2}}{1 + e^{\left[(t - t_{ip})/dt\right]}}$$

   (1)

   where t and dt is the reaction time and the time constant, respectively. $V_{h,1}$ and $V_{h,2}$ are the initial liquid and final cured state of the local free volume, respectively and t_{ip} is a center of sigmoid or the time which corresponds to inflection point of sigmoidal curve. Fitting the time evolution of the local free volume sizes (V_h) with eq. 1 provides following important parameters: the time of reaction at the inflex point (t_{ip}) which corresponds to $V_{h,ip}$ and the maximum of 1st derivation (R_{max}). The inflection point also indicates the time when the reaction has the fastest progress. Other important parameter is the full width at half of maximum (FWHM) of 1st derivative curve of sigmoid function which characterizes the time region of obvious local free-volume

changes in the sample. The main time region of obvious local free-volume changes, characterized by FWHM, reflects a continuous change of microstructure during crosslinking. Finally, $V_{h,2}$ parameter corresponds to the local free-volume size of the final cured sample. The 2M samples with 0.5mol% of PI exhibit more reduced $V_{h,2}$ compared to the 2M samples with 0.1mol % of PI (Figs. S1-S2).
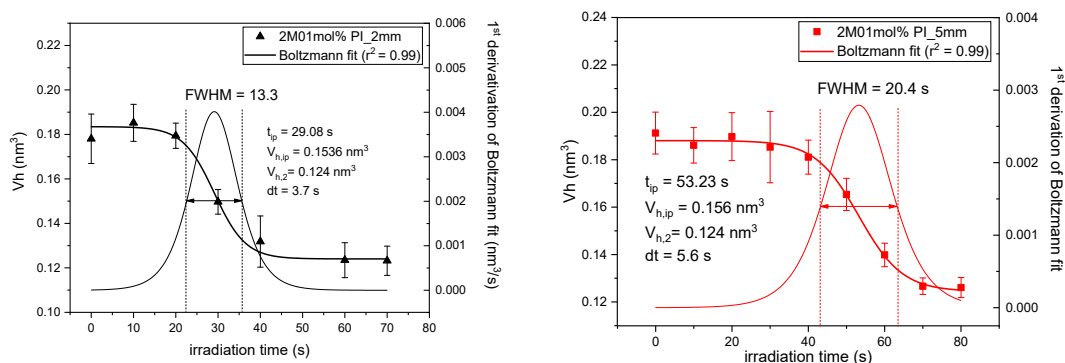

Fig.S1 The time dependence of the local free volume V_h for the 2 mm and 5 mm thick 2M sample with 0.1mol % of PI described by the Boltzmann function and its first derivation.
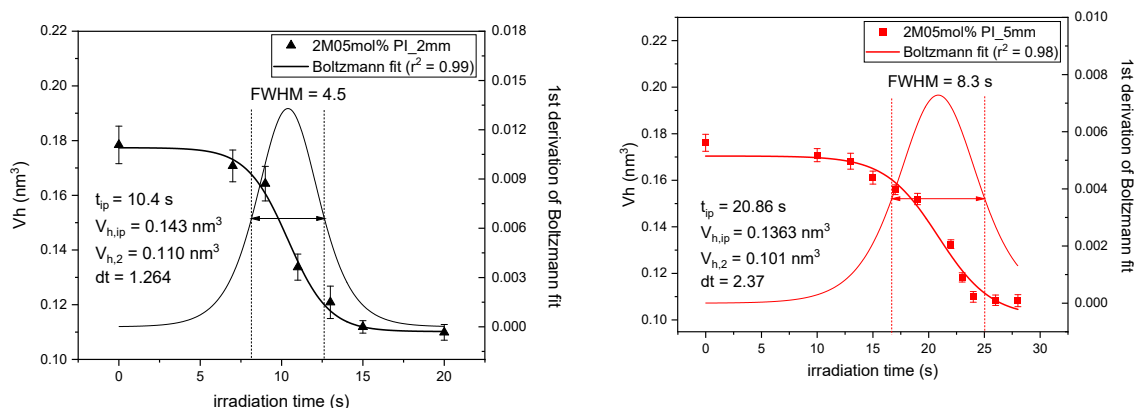

Fig.S2 The time dependence of the local free volume V_h for the 2 mm and 5 mm thick 2M sample with 0.5mol % of PI described by the Boltzmann function and its first derivation.

2. NIR – regions of double bonds and the 1st overtone of NH groups

Figure S3 shows the absorption band of double bonds (6172.3 cm^{-1}) and the region of NH groups (6500.21 – 6901.24 cm^{-1}) selected at the fitting procedure for a serie of the cured 2M samples.
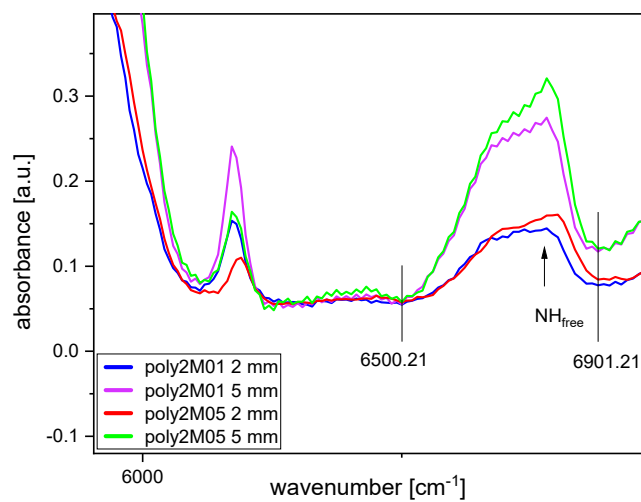
Fig. S3 The absorption regions of double bonds and 1st overtone of NH groups for the cured 2 mm and 5 mm thick poly2M samples with 0.1 and 0.5 mol% of PI.