Electronic Supplementary Information

In situ investigation of the kinetics and microstructure

during photopolymerization by positron annihilation

technique and NIR-photorheology

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1. Sample-source assembly

In Fig. S1 the aluminium chamber with the light source (LED with light guide) at the top of chamber and a round space (diameter of 15 mm, thickness of 3 mm) in the centre for the sample is shown. The light is absorbed in the sample directly from the source and the reflection of light from the glossy inner walls of the aluminium chamber. The measured average lifetimes reflect microstructural changes of the crosslinking sample in the whole volume at such arrangement.



FIGURE S1. The configuration of the aluminium chamber with the light source. The direct and reflected absorptions of the light are marked by arrows.

The sandwich assembly placed between the two detectors contains two parts of the same sample, the ²²Na source and the light guides as is plotted in Fig. S2. The intensity of light in both chambers was identical. The dark shield was used for this assembly and placed between the detectors of the PALS spectrometer.



FIGURE S2. The sketch of sandwich geometry. A detectors, B aluminium chambers, S sample, L lightguides, C ²²Na positron source, D dark shield.

2. Ortho-positronium lifetime distribution for the different stages of curing process

The LT routine allows to evaluate from the time spectrum not only the discrete lifetime values with their relative intensities but also the lifetime distribution for i component $\alpha_i(\tau)d\tau = \alpha_i(\lambda)\lambda^2 d\tau$, which is described by logarithmic Gaussian.¹ Here, the annihilation rate is $\lambda = 1/\tau$. The routine outputs are the mean lifetime τ and the standard deviation σ , from which the radius distribution $n(r_h)$ (probability density function, pdf) or hole-volume pdf $g(V_h) = n(r_h)/4\pi r_h^2$ can be determined.²



FIGURE S3. The hole radius distribution for different stages of network formation.

The liquid state is excluded from the Fig. S3 due to the bubble effect at the creation of Ps that it is explained in the main text. In this case, the distribution shows significantly distorted values not reflecting real intermolecular distances. It should be noted that this is a fairly simplified approach for the evaluation of the free volume size based on a simple model of spherical holes with many other simplifications.

3. The onset of the decrease of microstructural free volume $V_{\rm h}$ determined as gel point via PALS

In Fig. S4, the intersection point of two linear dependences of microstructural free volume Vh at which the reaction runs fast, can be defined as the onset of microstructural shrinkage and the gel point. Two points with large error bars around 1000 s were not included into the response. The gel point is determined at 2357 ± 11 s.



FIGURE S4. The intersection point of two fitting lines corresponds to the onset of microstructural shrinkage and the gel point.

4. Double bond conversion via NIR

Fig. S5 shows the evolution of double bond conversion at different stages of the reaction obtained from NIR measurements. The evolution of the acrylate double bond signal at $\sim 6200 \text{ cm}^{-1}$ was integrated and used to evaluate the respective double bond conversion during the photopolymerization.



FIGURE S5. The storage (...) and loss modulus (–) as well as double bond conversion DBC (\blacktriangle) as a function of the irradiation time for the photopolymerization of SPOT LV.

References:

- 1 J. Kansy, Nucl. Instrum. Meth. A, 1996, **374**, 235-244.
- 2 L. A. Utracki, A. M. Jamieson, Polymer Physics: From Suspensions to Nanocomposites and Beyond, Wiley, Hoboken, NJ, USA **2010**.