

# In-situ study of network creation in polymers during polymerization initiated by light

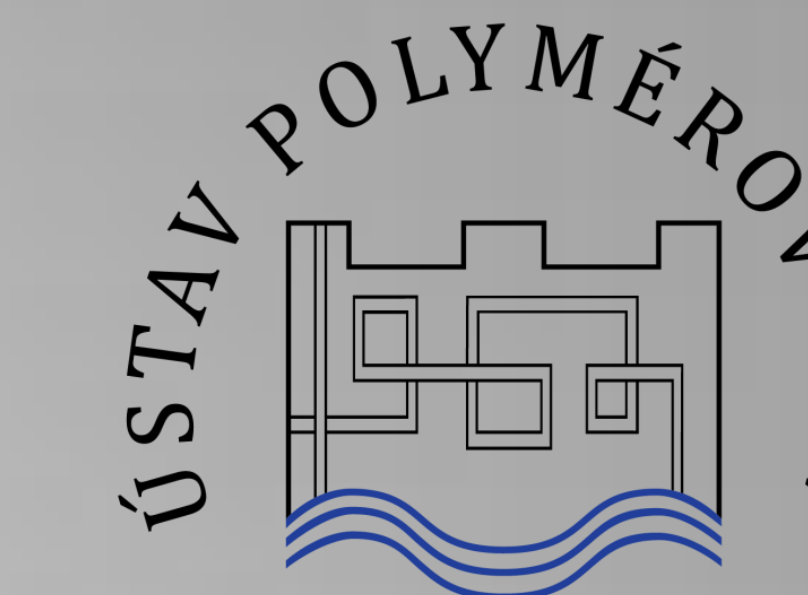
Ondrej Šauša<sup>1,2,\*</sup>, Helena Švajdlenková<sup>3</sup>

<sup>1</sup>Institute of Physics SAS, Dúbravská cesta 9, 845 11 Bratislava, Slovak Republic

<sup>2</sup>Department of Nuclear Chemistry, Faculty of Natural Sciences, Comenius University, Mlynska Dolina, Ilkovicova 6, 84215 Bratislava, Slovak Republic

<sup>3</sup>Polymer Institute SAS, Dúbravská cesta 9, 845 41 Bratislava, Slovak Republic

\*email: ondrej.sausa@savba.sk



**Fig. 1** The configuration of the aluminium chamber with the light source (LED, 405 nm, 0,27 mW cm<sup>-2</sup>, in the middle of chamber)

## INTRODUCTION

Photopolymerization is an excellent technique for the rapid formation (< 5 s) of highly crosslinked networks, which have found use in a wide variety of applications. Such as fast processes are impossible to monitor in-situ using PALS. However, if the reaction can be interrupted (in the case of conventional light-initiated polymerization), then PALS will make it possible to monitor the course of the reaction and characterize the various stages of polymer network formation even for rapid processes.

An example is intermittent photopolymerization, where after a short light pulse, which supplies energy to generate radicals and triggers a crosslinking reaction, the stage of crosslinking is measured in the dark using an o-Ps probe. By setting a low-light intensity, it is possible to slow down the reaction so that intermittent illumination lasting a few seconds achieves multiple and repeated gradual crosslinking of the polymer until the stage of complete curing.

### The aim of our work

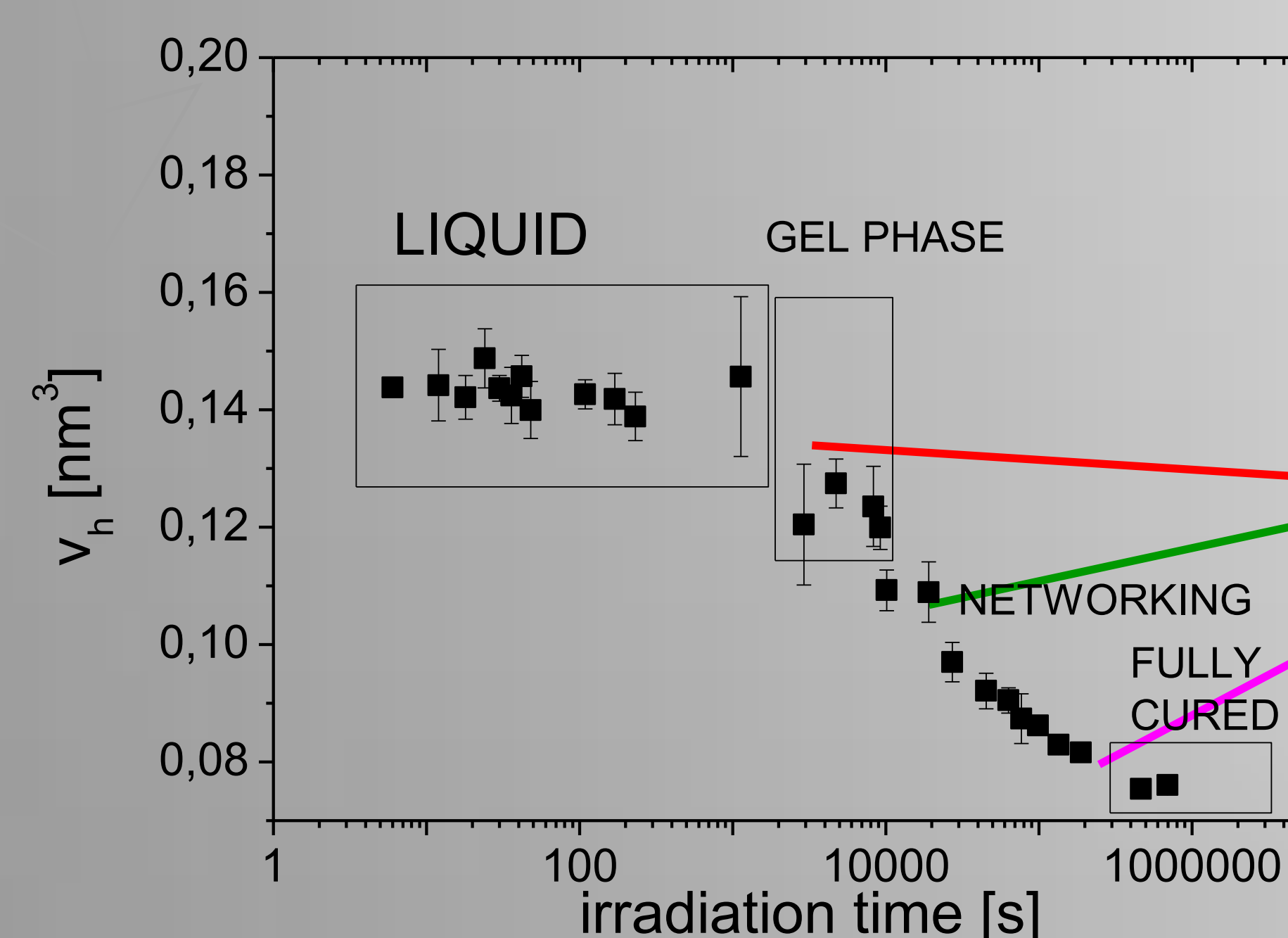
- to determine the free-volume characteristics of different stages of crosslinking of the examined sample as well as the reaction kinetics

## EXPERIMENTAL

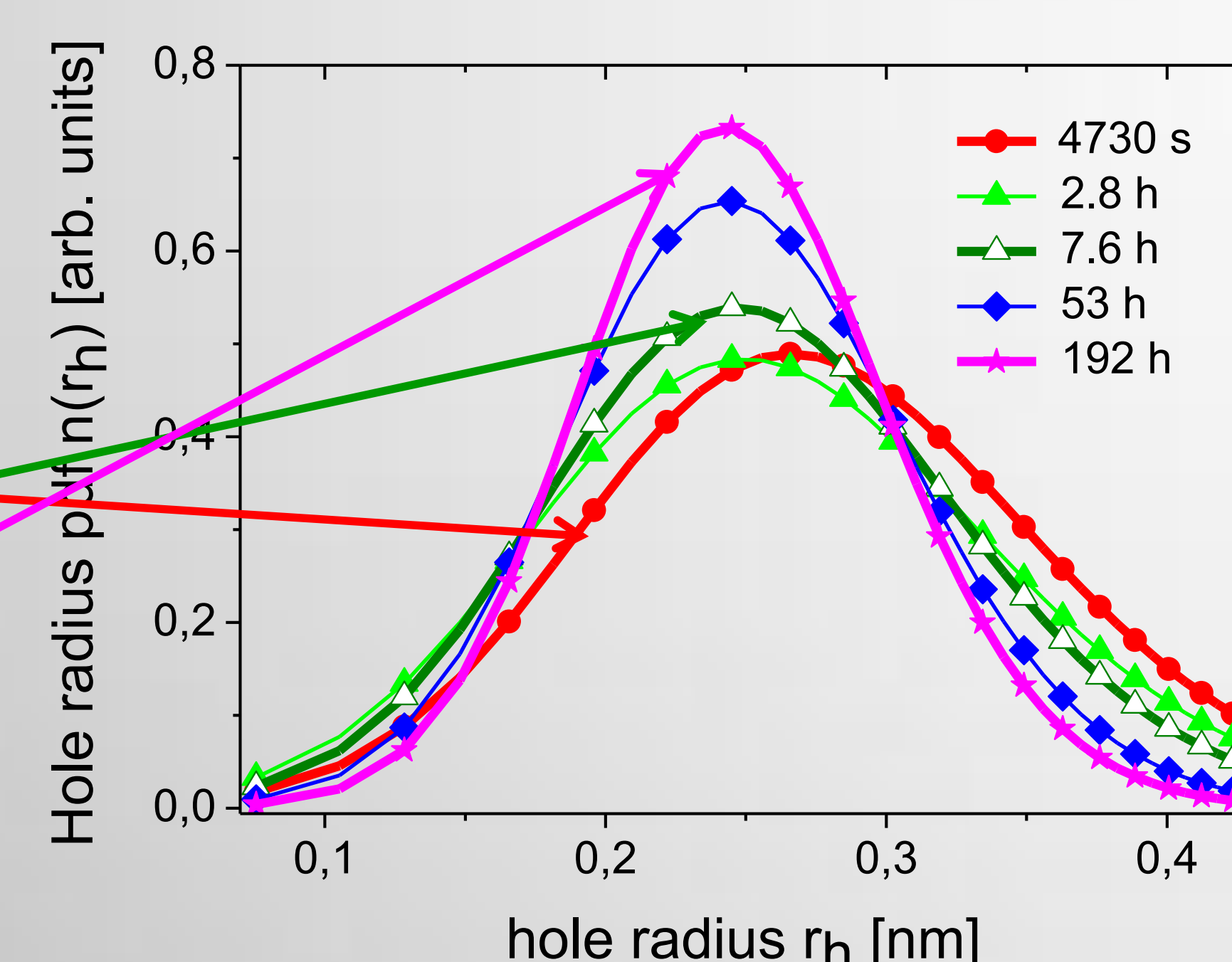
- commercial mixture of three types of acrylates in SPOT LV [1]
- configuration of Al chamber with the sample and light source is in Fig. 1, sandwich configuration of sample-positron source,
- the individual degrees of crosslinking achieved were characterized by o-Ps lifetime spectra in "dark" intervals after light impulse defined or in the later and slower stages of the reaction directly during lighting (continuous mode of illumination)
- LT program

## RESULTS AND DISCUSSION

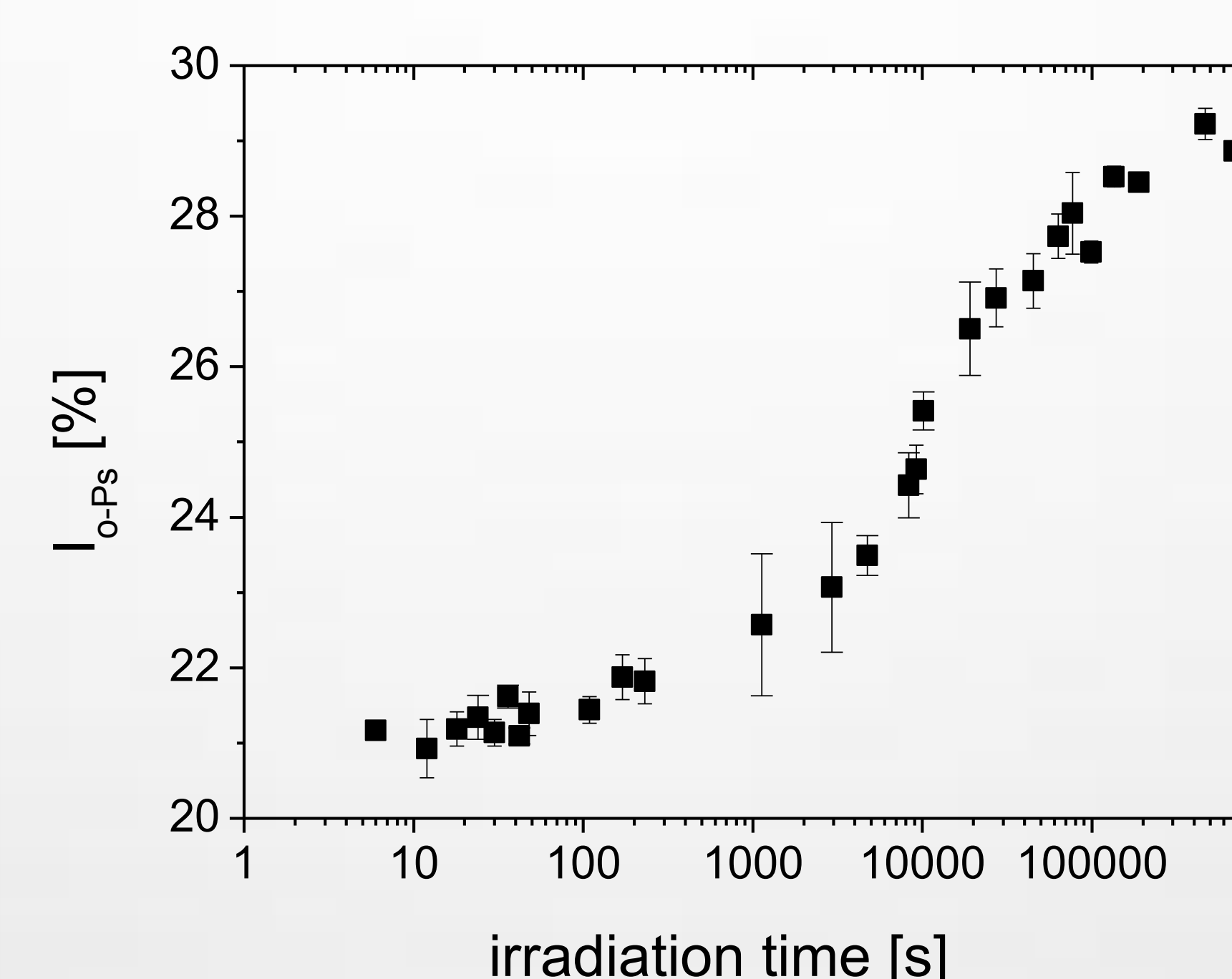
The both evolutions of microstructural shrinkage (Fig. 2) and free volume distributions (Fig. 3) for different stages of the investigated system were found: from liquid monomers, through the gel stage to the cured polymer.



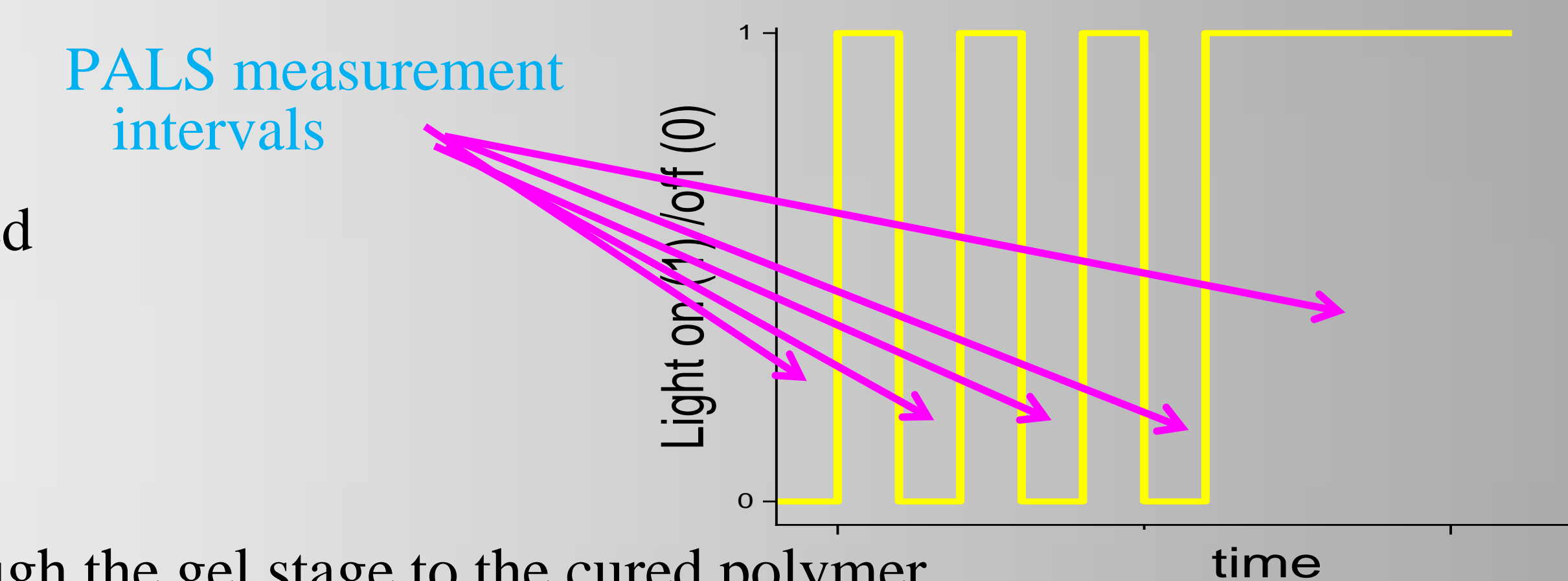
**Fig. 2** Microstructural shrinkage versus irradiation time during photopolymerization of SPOT LV.



**Fig. 3** The hole radius distribution for different stages of network formation.

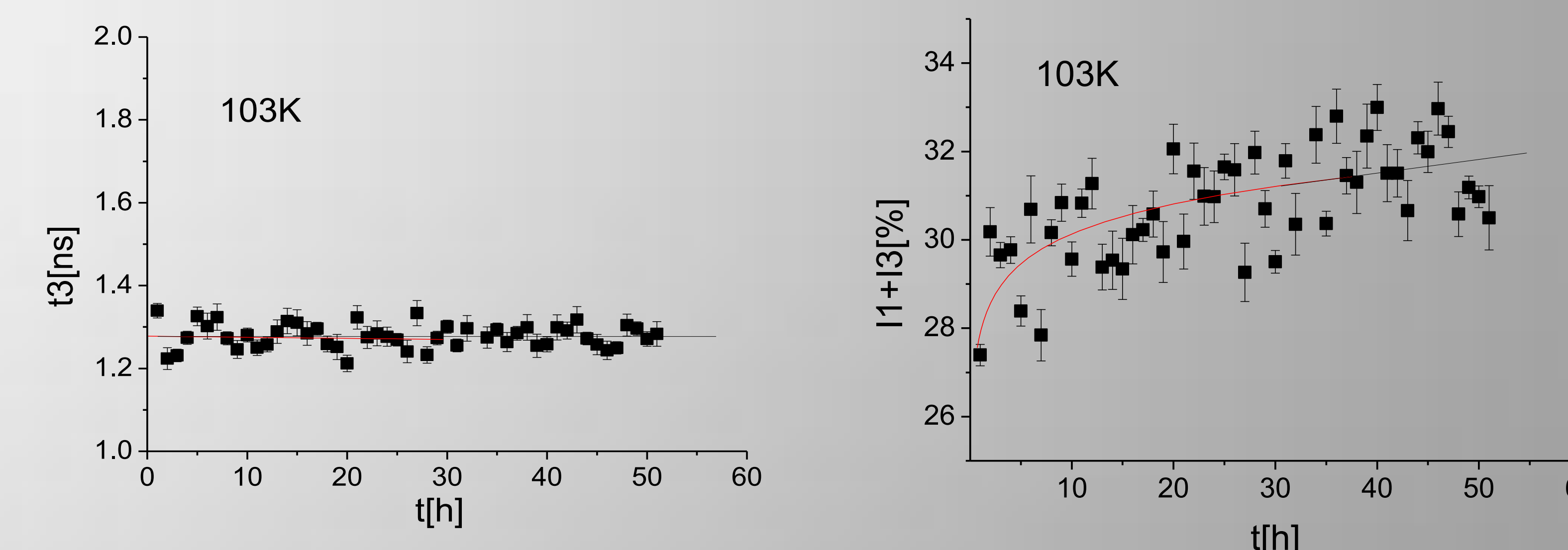


**Fig. 4** The relative o-Ps intensity during photopolymerization.



Existence of electron traps in photopolymers (Fig. 5, 103 K)

- e+ irradiation, darkness, low T, before first heating over T<sub>g</sub>
- second run after heating: I<sub>3</sub>(t)=const.
- E<sub>a</sub> of detrapping over 3eV (UV LED)-no return I<sub>3</sub> to initial state at illumination



**Fig. 5** The o-Ps lifetime and complex intensity at 103 K, the evolution in time in cured sample before heating over T<sub>g</sub>.

## CONCLUSION

- The evolution of mikroshrinkage was studied on commercial mixture SPOT LV in-situ by PALS, the intermolecular space during the curing process reduces
- in fully cured network, the hole radius distribution is the narrowest
- gel point was ascribed to the broadening of distribution and the beginning of the reduction in v<sub>h</sub> (compared from photorheology)
- The nonlinear time dependence of the relative changes in the microstructural free volumes is well described by the KWW (Kohlrausch-Williams-Watts equation)  $\Delta V / V_0 = 1 - \exp(-t/\tau)^\beta$  [1]
- existence of electron traps in photopolymers was observed

[1] H. Švajdlenková, O. Šauša, G. Peer and C. Gorsche, *RSC Adv.* **8**, 37085 (2018)

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