

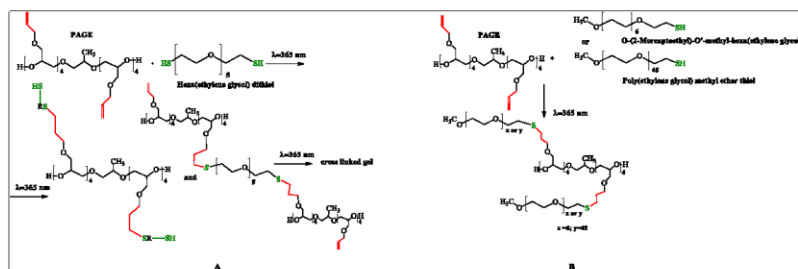
Thiol-ene coupling reaction achievement and monitoring by “*in situ*” UV-irradiation NMR spectroscopy

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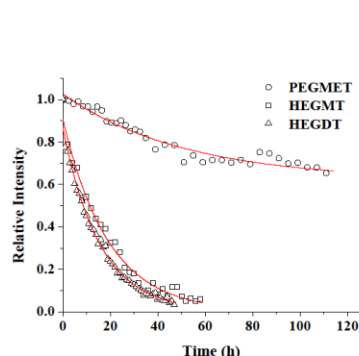
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In this study, the possibilities of a new “*in situ*” LED UV illumination NMR spectroscopic technique for performing an initiator-free thiol-ene “click” coupling reaction of an allyl-functionalized poly(allyl glycidyl ether) (PAGE) prepolymer with a number of mono- and di-oligo polyethylene glycol (PEG) thiols is demonstrated. The state-of-the-art setup constructed with LEDs as UV light sources that illuminate through optical fibers directly into an NMR testing tube at a fixed wavelength of 365 nm. The selected experimental protocol uses a series of periods of irradiation and dark periods, thus providing opportunities to conduct an effective thiol-ene “click” reaction and simultaneously study the kinetics of the photochemical reaction with the exposure time, as well as macromolecular association directly in a solution applying the whole types of NMR methods: from conventional ¹H or ¹³C NMR to diffusion NMR spectroscopy (DOSY). In addition, the molecular mass characteristics of the prepared copolymers were studied by gel-permeation chromatography (GPC).

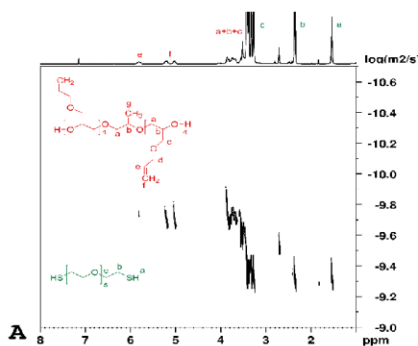


LED control unit and optical fiber to the NMR tube used for “*in situ*” UV-irradiation NMR spectroscopy

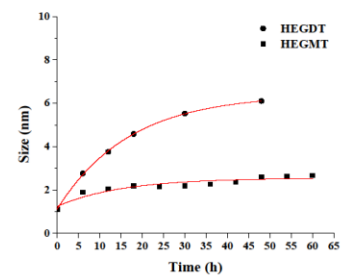
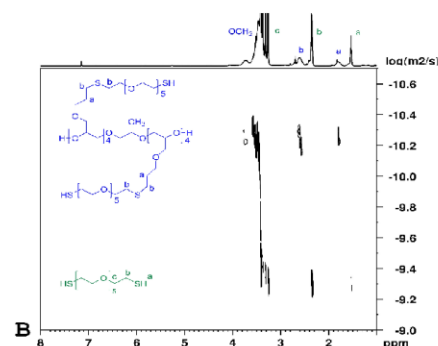
Synthesis of copolymers via thiol-ene “click” coupling reaction of PAGE and A) HEGDT ; B) HEGMT or PEGMET under “*in situ*” LED NMR irradiation at 365 nm without use of photoinitiator



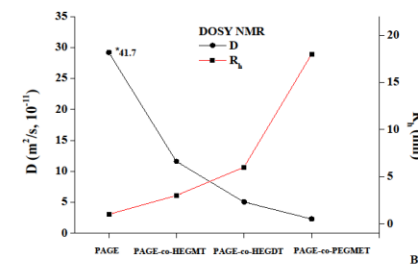
Consumption of C=C of PAGE in the course of LED UV-irradiation: A) HEGDT rate constant $1.8 \times 10^{-3} \text{ s}^{-1}$; B) HEGMT rate constant ($1.1 \times 10^{-5} \text{ s}^{-1}$), PEGMET rate constant $5.4 \times 10^{-6} \text{ s}^{-1}$



¹H DOSY NMR spectra of A) PAGE and HEGDT reaction mixture before and B) after illumination at 365 nm for 48 h at room temperature, taken in C₆D₆ (600 MHz).



A) Change in hydrodynamic radius of PAGE-co-HEGDT and PAGE-co-HEGMT based species with the exposure time at RT. B) D and R_n values of PAGE prepolymer and PAGE-co-HEGDT, PAGE-co-HEGMT and PAGE-co-PEGMET based species after thiol-ene “click” coupling reaction, in C₆D₆ at RT.



*The value is taken at 40 °C.

Sample	M _n GPC [g.mol ⁻¹]	Mw/Mn
PAGE	1300	1.08
HEGDT	-	-
HEGMT	600	1.02
PEGMET	3600 (I) 1600 (II)	1.04 1.05
PAGE-co-HEGDT	5800	1.25
PAGE-co-HEGMT	3100	1.15
PAGE-co-PEGMET	9300 (I) 4300 (II)	1.04 1.06

Characterization data of starting PAGE, HEMDT, HEGDT and PEGMET precursors and isolated copolymers

Versatile UV-irradiated NMR spectroscopy for “*in situ*” study of coupling reaction of PAGE and few oligo-/PEG (di)thiols without any photoinitiator was successfully implemented. ¹H NMR spectra and GPC traces of resulting products after LEDs UV illumination support the expected turnaround of “click” reaction and formation of pegylated (co)polymers. The reaction efficiency depends on the type of thiol (mono or dithiol) at the selected PAGE molecular weight. Upon coupling with dithiol reagent, formation of a gel-fraction in a noticeable amount was observed, suggesting occurring of cross-linking reaction, which is subject of a further study. The observed differences in the reaction rates as well as in the size of species formed (the corresponding hydrodynamic radii R_n of aggregates) as a result of the coupling process of parent PAGE prepolymers and model PEG thiols were thoroughly examined and the reaction pathway proposed.

