

Supporting Information (SI)

Light-Mediated Thiol-Ene Polymerization in Miniemulsion: a Fast Route to Semicrystalline Polysulfide Nanoparticles

Florent Jasinski^a, Emeline Lobry^a, Bassam Tarablsi^a, Abraham Chemtob^{a}, Céline Croutxé-
Barghorn^a, Didier Le Nouen^b, Adrien Criqui^c*

^aLaboratory of Photochemistry and Macromolecular Engineering, ENSCMu, University of
Haute-Alsace, 3 bis rue Alfred Werner 68093 Mulhouse Cedex, France

^bLaboratoire de Chimie Organique et Bioorganique, ENSCMu, University of Haute-Alsace, 3
bis rue Alfred Werner, 68093 Mulhouse Cedex, France

^cMäder Research - MÄDER GROUP, 130 rue de la Mer Rouge, 68200 Mulhouse, France

*Corresponding author: E-mail: abraham.chemtob@uha.fr; Tel: +33 3 8933 5030; Fax: +33 3

8933 5034

Materials

Ethylene glycol dithiol (EGDT) and diallyl adipate (DAA) were purchased from TCI Chemicals without further purification. Hexadecane (HD, Aldrich) was employed as costabilizer. Sodium dodecyl sulfate (SDS, Aldrich) was used as surfactant. Dimethylsulfoxide (DMSO, Aldrich) was used as solvent in solution photopolymerization. Irgacure 2959, (1-[4-(2-Hydroxyéthoxy)-phényl]-2-hydroxy-2-méthyl-1-propane-1-one, I2959, BASF) was used as radical photoinitiator.

Preparation of thiol-ene miniemulsions

4 g of monomer based on a thiol-ene mixture (EGDT: 1.78 g / DAA: 2.22 g, 1:1 mol) was mixed with 0.16 g of HD to form the organic phase. Separately, an aqueous phase was prepared by dissolving 0.14 g of SDS and 80 mg of I 2959 in 16 g of distilled water; the surfactant concentration was 3.5 wt % with respect to monomer, the photoinitiator concentration was 2 wt % with respect to the monomer. Both phases were mixed together and magnetically stirred during 10 minutes at 600 rpm. The resulting coarse dispersion was then emulsified under sonification (Branson Sonifier 450 W/L) for 5 minutes at 90 % amplitude while maintaining the stirring.

Photopolymerization in a spectroscopic cell (micro-photoreactor)

In a typical procedure, the photopolymerization of the thiol-ene miniemulsion was carried out in a capped quartz rectangular cell (1 mm thick, 340 μ L volume) without nitrogen bubbling and stirring. Irradiation was applied with the polychromatic light of a medium-pressure Hg-Xe arc lamp (Hamamatsu L8252, 200 W) coupled to a flexible light-guide. The lamp is backed by a semi-elliptical mirror or reflector to focus radiation and minimize irradiance loss. In this study, a 365 nm reflector was used, enhancing the reflection of the mentioned wavelength. The end of the optical guide was placed at a distance of 4.2 cm from the sample and directed at an incident angle of 90° onto the sample window. In the spectral region between 250 and 600 nm, the light irradiance I was 685 mW cm⁻². This irradiation set-up was used for the kinetic analysis of the polymerization by real-time Fourier transform IR spectroscopy (RT-FTIR)

Photopolymerization in annular batch photoreactor (macro-photoreactor)

The annular photoreactor (UV-Consulting Peschl) shown in Figure S3 is composed of three parts. First, a standard medium-pressure Hg arc lamp (Heraeus Noblelight TQ 150, arc length: 4.4 cm) emits a series of rays from 250 nm to 600 nm. This lamp is housed in a fused borosilicate sleeve showing an excellent transmittance for wavelength beyond 300 nm, which is essential to photoinitiator excitation. Because of the heat liberation during lamp processing, an external cooling jacket surrounds the sleeve vessel in order to hold the photoreactor contents at a temperature between 20 and 25 °C throughout the polymerization reaction. Third, a borosilicate cylindrical section (outer annulus) is then installed around the sleeve to accommodate and irradiate 150 mL of monomer miniemulsion when the reactor is full. The distance between the two annular sections (external sleeve wall and inner reactor wall) is 9 mm and defines the optical path length. Magnetic stirring of the miniemulsion is maintained throughout the polymerization. Samples were drawn during polymerization to determine the conversion (FTIR spectroscopy).

Characterization methods

Dynamic light scattering (DLS)

Droplet and particles diameters, respectively labeled as D_d and D_p , were determined through DLS using a Zetasizer Nano ZS (Malvern Instrument). Typically, the monomer miniemulsion or the resultant latex was diluted 125 times in filtered and distilled water before measurement.

Real-time Fourier transform infrared spectroscopy (RT-FTIR)

Ene conversion was followed *in-situ* by RT-FTIR. In these rapid scan experiments, a near IR probe beam and a UV exciting beam irradiated simultaneously the spectroscopic cell containing the miniemulsion.

The NIR region ($\lambda = 970\text{-}1940\text{ nm}$) is well-suited to thick samples ($1000\text{ }\mu\text{m}$) and can accommodate the high water concentrations of monomer miniemulsions without detector saturation. In this spectral range, the alkene monomers exhibited a band at 4484 cm^{-1} which is assumed to be a combination of two C-H stretching bands.¹ The band is isolated enough from the other vibrational overtones of water so that it can be used for quantitative purposes. Thus, polymerization kinetics were followed in situ using RT-FTIR by calculating the integrated absorbance of this band and monitoring its decrease during irradiation.

Size exclusion chromatography (SEC)

Molecular weights were determined by gel permeation chromatography (GPC). The GPC column was calibrated with polystyrene standards, implying that all the molecular weight values (M_n) will be considered as polystyrene equivalent.

Nuclear magnetic resonance (NMR)

^1H (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were obtained respectively in CDCl_3 and $\text{DMSO-}d_6$ on a Bruker Avance 400 at 295 K using tetramethylsilane (TMS) as internal standard.

Differential scanning calorimetry (DSC)

For the DSC experiments (DSC Q200, TA Instruments) performed under nitrogen atmosphere (50 mL/min), 8 mg of polysulfide film was placed in an aluminium hermetic pans and heated at $10\text{ }^\circ\text{C min}^{-1}$.

Thermal gravimetric analysis (TGA)

TGA analysis (TGA Q500 from TA Instruments) was carried out under nitrogen atmosphere (20 mL/.min). 9 mg of polysulfide film was placed in an open aluminium pan and heated from ambient conditions to $1000\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C min}^{-1}$.

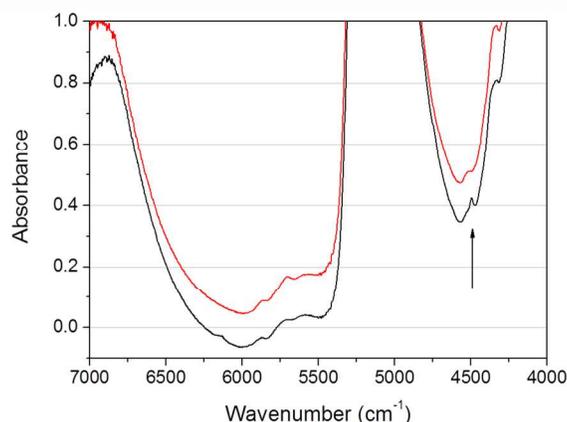


Figure S1. IR spectra in the near IR region ($4000 - 7000 \text{ cm}^{-1}$) of the DAA-EGDT miniemulsion before (black) and after 5 min irradiation (red). The “ene” absorption peak at 4484 cm^{-1} is marked by the arrow. Its area rapidly decreases during photopolymerization indicating that the thiol-ene reaction is occurring. Irradiation with a Hg-Xe lamp, $I = 685 \text{ mW cm}^{-2}$. $C_{\text{monomer}} = 20 \text{ wt } \%$, $D_d = 150 \text{ nm}$, cell thickness= 1 mm.

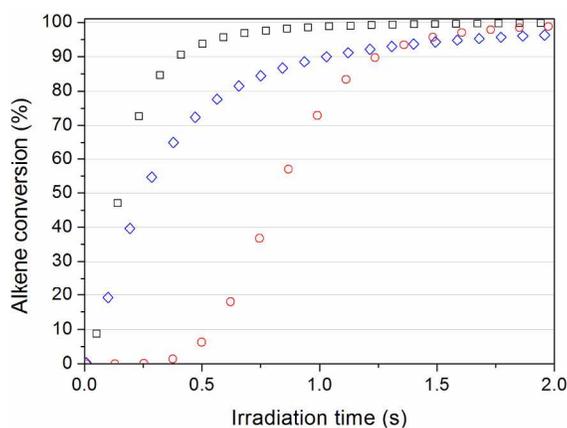


Figure S2. Conversion-times curves profiles during EGDT-DAA photopolymerization in miniemulsion ($D_d = 150 \text{ nm}$, $C_{\text{monomer}} = 20 \text{ wt } \%$, \square), DMSO solution ($C_{\text{monomer}} = 20 \text{ wt } \%$, \diamond) and in bulk (\circ). All photopolymerizations were performed in a 1 mm thick spectroscopic cells under continuous light provided by a mercury-xenon arc lamp ($\lambda = 250\text{-}600 \text{ nm}$, $I = 685 \text{ mW cm}^{-2}$). Bulk photopolymerization exhibits a distinctive inhibition time (0.5 s) probably due to the internal filtering effect arising from the higher photoinitiator concentration (5 times higher than in the other systems) and the millimeter thickness of the monomer film. Compared with miniemulsion, a more sluggish polymerizations rate was also found in DMSO solution. This may be the consequences of crystalline regions and/or the use of a poor solvent for the polymer causing both diffusion limitations. Indeed, the viscosity increased appreciably during the reaction leading to the formation of a gel after a few seconds irradiation. Obviously, the nature of organic solvent can change the polymerization by affecting the diffusion characteristics of the reaction system. However, the most outstanding characteristic is that miniemulsion yielded the fastest polymerization rate. As reported in chain-growth polymerization, this important reaction characteristic may result from compartmentalization of the propagating radicals, which reduces the rate of termination. In homogeneous polymerization, one can increase the polymerization rate only by increasing the rate of initiation.

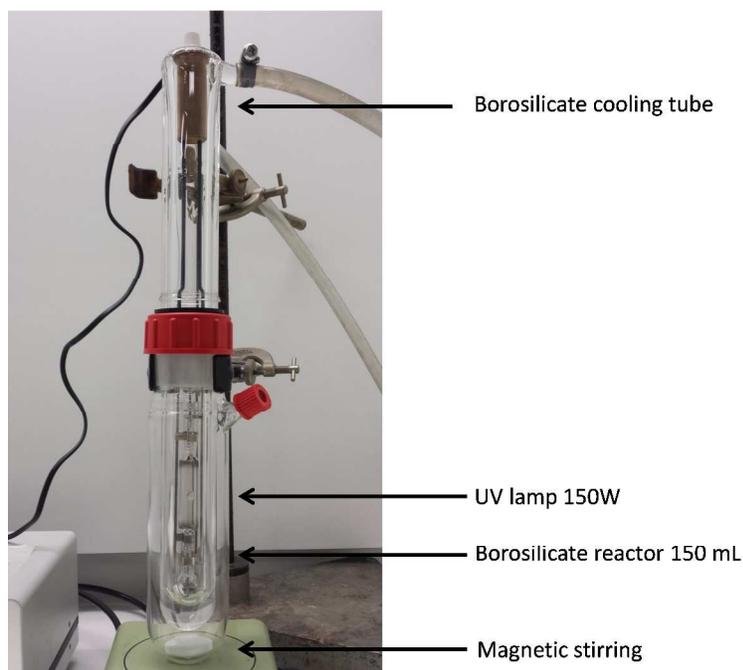


Figure S3. Image of the immersion-type photoreactor in which thiol-ene miniemulsion photopolymerization was performed. Optical path length = 9 mm, volume = 150 mL, Hg medium pressure lamp 150 W, arc length = 4.2 cm, stirring= 600 rpm. An irradiance of 62 mW cm^{-2} was measured at the surface of the borosilicate sleeve.

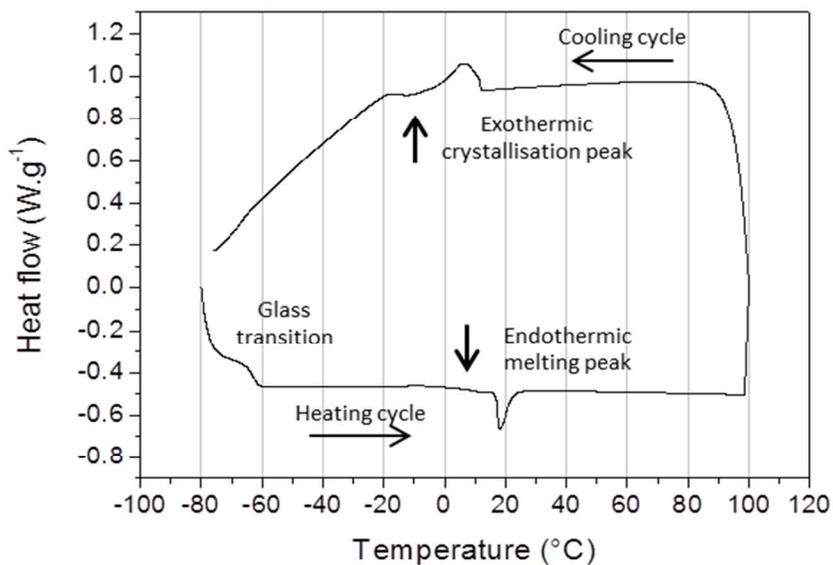


Figure S4. DSC thermogram of the poly(thioether ester). Different transitions were observed: a well-defined glass transition (endotherm) at -63°C , a sharp melting point (endotherm) at 18°C and a broader recrystallization (exotherm) at 6°C .

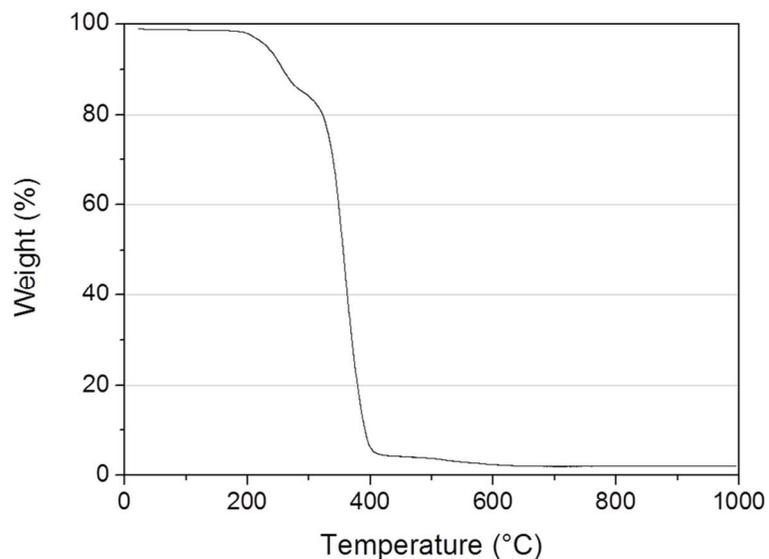


Figure S5. TGA thermogram of the poly(thioether ester) films. Two consecutive degradation reactions were observed. The first transition at 200 °C was assigned to C-S bond decomposition while that occurring at higher temperature (300 °C) may be related to C-C and C-O bonds degradation.

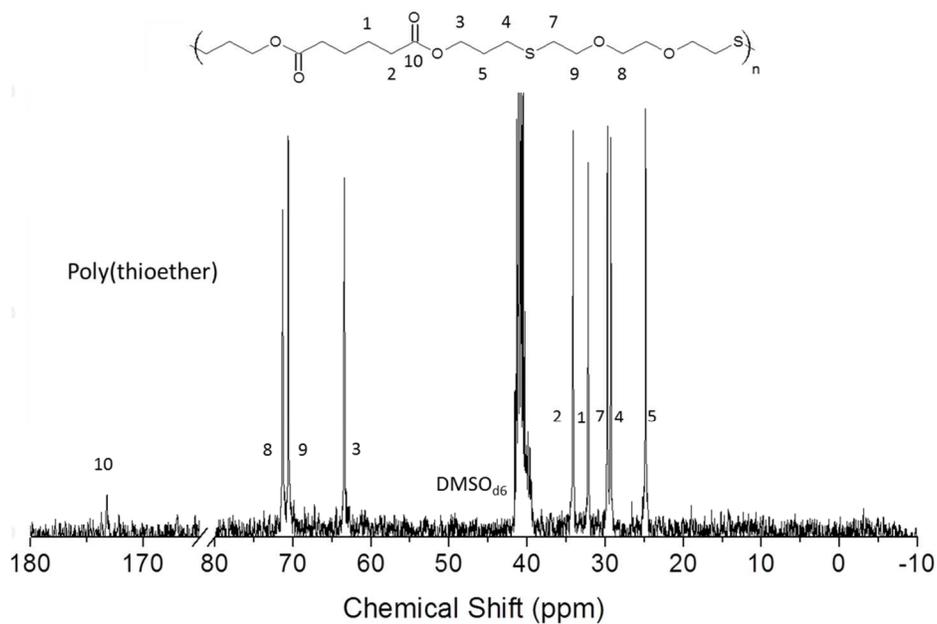


Figure S6. ^{13}C NMR spectrum of the poly(thioether ester). NMR ^{13}C (DMSO- d_6 , 400 MHz): δ_c 173.3 ppm (s, C₁₀), 71.3 ppm (t, C₈), 70.6 ppm (t, C₉), 63.4 ppm (t, C₃), 32.2 ppm (t, C₁), 29.7 ppm (t, C₇), 29.3 ppm (t, C₄), 24.8 ppm (t, C₅).