Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information (ESI)

Continuous-flow synthesis of polymer nanoparticles in a microreactor via miniemulsion photopolymerization

Emeline Lobry,[a] Florent Jasinski,[a] Marta Penconi,[b] Abraham Chemtob,*[a] Céline Croutxé-Barghorn,[a] Esther Oliveros,[b] André M. Braun,[c] Adrien Criqui[d]

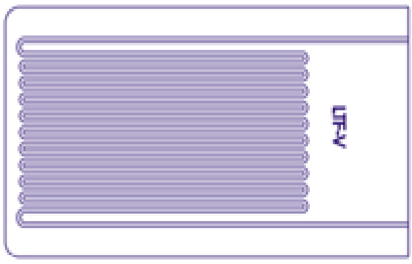
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

1. Materials

Technical grade monomers and costabilizers were all obtained from Sigma-Aldrich and used without further purification: methyl methacrylate (**1**), butyl acrylate (**2**), acrylic acid (**3**), diallyl adipate (**4**), ethylene glycol dithiol (**5**), octadecyl acrylate (OA) and hexadecane (HD). For the preparation of the miniemulsion's aqueous phase, distilled water and sodium dodecyl sulfate (Aldrich) were employed as received. 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone (I2959) is a water-soluble type I radical photoinitiator kindly donated by BASF Specialty Chemicals.

2. General techniques

The microreactor (Mr Lab Series – LTF-V) was supplied by Little Things Factory GmbH (Figure S1). It is a classical single-lane microreactor made of borosilicate glass, with channels of 1 mm internal diameter and a total volume of 1.7 mL. Unlike quartz, borosilicate exhibits a strong absorption below 300 nm, thus preventing the self-initiation of acrylate or thiol-ene monomers. The microreactor and the syringe pump (KD Scientific) were connected with ETFE tubing. UV Irradiation was provided by a compact system UV 236 (dimension: 470 x 280 x 100 mm) purchased from Waldmann SA, and including two fluorescent tubes (UV6, 36 W) placed above the microreactor by about 8 cm (Figure S2). These lamps used originally for phototherapy applications cover a broad continuous spectrum spanning essentially from 280 to 360 nm (see emission spectrum in Figure S2) with an total irradiance of approximately 3 mW cm^{-2} measured by radiometry (Sola check from Solatell). Compared to conventional Hg arc lamps, this UV source is distinguished by its very low heat development and low power consumption.



Internal channel diameter	1000 µm
Volume	1.7 mL
Dimension	115×60×6 mm

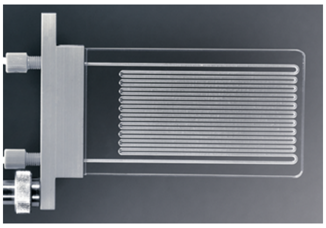


Figure S1

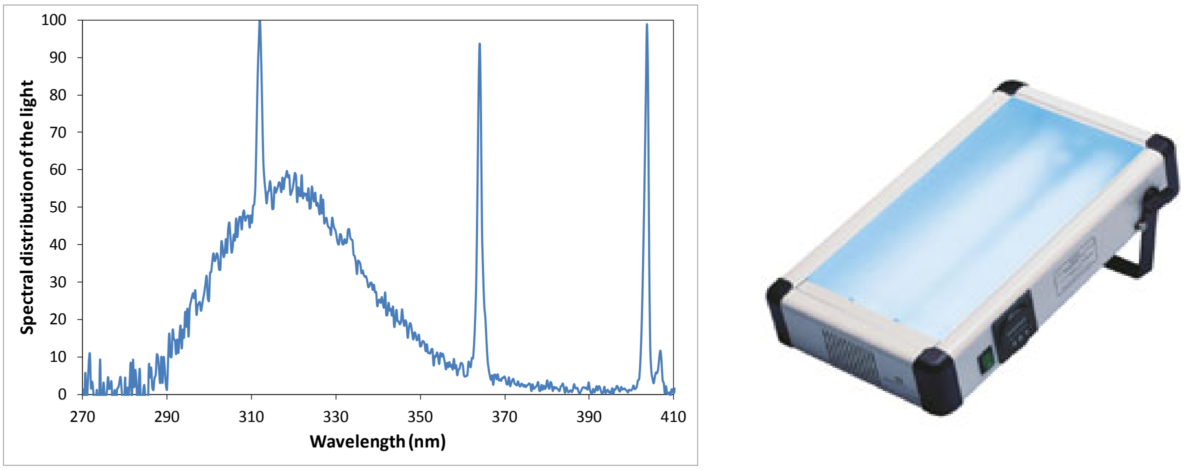


Figure S2

3. Preparation of acrylate or thiol-ene monomer miniemulsions

In a typical procedure, an organic phase was first prepared by adding OA or HD (4 wt. % with respect to the monomer phase) to the acrylate (**1**/**2**/**3**, 49.5/49.5/1 wt %) or the thiol-ene mixture (**4**/**5**, 55/45 wt %) respectively. This latter organic phase consists of an approximately 1:1 mole ratio of thiol and ene functionality. The aqueous phase was prepared separately by dissolving successively SDS (3.5 to 0.25 wt % with respect to the monomer phase) and the photoinitiator in distilled water. Both phases were mixed for 10 min using a magnetic stirrer at 600 rpm. The coarse emulsion was then homogenized for 5 min using a Branson Sonifier 450 (450 W/L) at 90 % amplitude, while maintaining the agitation. Table S1 gives the typical compositions of the two monomer miniemulsions.

Table S1 General recipe for acrylate and thiol-ene miniemulsions

	Acrylate miniemulsion		**Thiol-ene miniemulsion**	
Monomer phase	**1/2/3**	3.8 g (1.86/1.86/0.04)	**4/5**	5 g (2.75/2.25)
Costabilizer	OA	0.15 g	HD	0.20 g
Surfactant	SDS	0.009 - 0.133 g	SDS	0.175 g
Photoinitiator	I2959	0.075 g	I2959	0.100 g
Water		21.25 g		20.00 g
Solid content		15 wt %		20 wt %

4. Photopolymerization setup

The miniemulsion was loaded in a 20 mL syringe. Its content was then infused at room temperature in the microreactor under UV irradiation (UV 236) through the single inlet at a desired flowrate (7-20 mL min^{-1}, residence time: 5- 15 min). The latex product was collected from the outlet for analysis. For all tests, a stable monomer conversion was reached after 3 residence times. The reliability of the system was assessed by continuing the latex collection during at least 6 residence times (30-90 min).

For experiments above ambient temperature (35, 50 and 60 °C), the microreactor was simply immersed into a thermo-regulated bath.

5. Characterization techniques

Prior to photopolymerization, the stability of the thiol-ene and acrylate monomer miniemulsions was checked by measuring the temporal evolution of the reflectance (Turbiscan MA, Formulaction) during aging. In a typical analysis, the miniemulsions was filled in a 20 mL glass vial and analyzed 4 hours without stirring. For each instance, steady reflectance values were measured during this time, which suggests that the miniemulsions were assumed to be colloidally stable during the time required for storage (syringe) and polymerization (microreactor).

Droplet and particle diameters, respectively labelled as D_d and D_p, were determined by dynamic light scattering (DLS) with a Zetasizer Nano ZS (Malvern Instrument). Typically, monomer miniemulsions or the resultant latexes were diluted 125 times with filtered and distilled water before measurement.

Molecular weights and polymer dispersity index (PDI) were determined by size exclusion chromatography (SEC) after precipitation in methanol, filtration and dissolution of the purified polymer in THF. The SEC column was calibrated with polystyrene standards, implying that all the molecular weight values (M_n) are considered as polystyrene equivalent. Conversion rates were obtained by gravimetric measurements. A drop of a solution of resorcinol 1 mol % was added to the sample to prevent further polymerization. The sample was then dried and conversion rates determined by weighting. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 instrument, with a heating rate of 10 ºC min^{-1}. ^{1}H NMR spectra were recorded on a 400-MHz spectrometer (Brucker AC 400) using $CDCl_3$ as solvent.

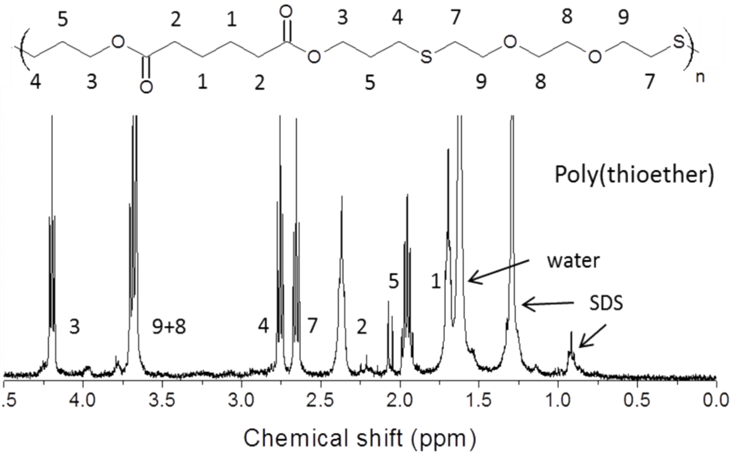


Figure S3. ^{1}H NMR spectrum of polythioether formed by thiol-ene photopolymerization in miniemulsion ($CDCl_3$, 400 MHz):