

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

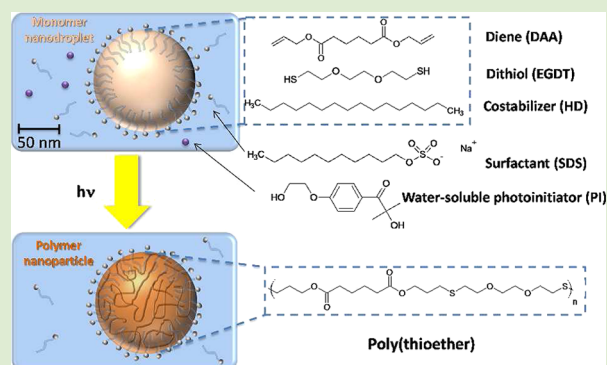
Florent Jasinski,[†] Emeline Lobry,[†] Bassam Tarablsi,[†] Abraham Chemtob,^{*,†} Céline Croutxé-Barghorn,[†] Didier Le Nouen,[‡] and Adrien Criqui[§]

[†]Laboratory of Photochemistry and Macromolecular Engineering, ENSCMu and [‡]Laboratoire de Chimie Organique et Bioorganique, ENSCMu, University of Haute-Alsace, 3 bis rue Alfred Werner, 68093 Mulhouse Cedex, France

[§]Mäder Research - MÄDER GROUP, 130 rue de la Mer Rouge, 68200 Mulhouse, France

S Supporting Information

ABSTRACT: Historically, the synthesis of aqueous polymer dispersions has focused on radical chain-growth polymerization of low-cost acrylate or styrene emulsions. Herein, we demonstrate the potential of UV-initiated thiol–ene step-growth radical polymerization, departing from a nontransparent difunctional monomer miniemulsion based on ethylene glycol dithiol and diallyl adipate. Performed without solvent and at ambient conditions, the photopolymerization process is energy-effective, environmentally friendly, and ultrafast, leading to full monomer consumption in 2 s, upon irradiating a miniemulsion contained in a 1 mm thick quartz cell microreactor. The resultant linear poly(thioether ester) particles have an average diameter of 130 nm. After water evaporation, they yield a clear elastomeric film combining chemical resistance and high degree of crystallinity (55%).



Over the past decade, light-driven thiol–ene chemistry has widely expressed its potential in macromolecular synthesis,^{1,2} mainly as an efficient tool for polymer functionalization³ and cross-linking (polymer network,⁴ dendrimer,⁵ hyperbranched polymer⁶). Yet, the unique attributes of thiol–ene reaction—including benign conditions, fast rates, oxygen and functional group tolerance, no byproducts, and little or no radical photoinitiator—might also be inspiring to other areas of polymer chemistry, such as emulsion polymerization processes. These heterogeneous polymerizations, leading primarily to aqueous polymer dispersions, are widely and historically dominated by radical chain-growth polymerization.⁷ There are very few attempts at producing latex via an alternative radical step-growth photopolymerization. In fact, the review of the literature shows photoinduced thiol–ene chemistry more as a way to functionalize^{8–12} or cross-link^{13–15} polymer particles already formed. Very recently, several reticulated microparticles were nevertheless synthesized under UV light in water through suspension polymerization^{16–18} as well as microfluidic devices.¹⁹

However, most commercial emulsion polymers exhibit a nanosize, ranging usually between 100 and 250 nm, and need a limited cross-linking density for subsequent processing. In the typical latex applications such as coatings, adhesives, binders for paints, and nonwoven fabrics, the water is evaporated, and film formation requires indeed a sufficient degree of polymer particle deformability. There are several reasons why thiol–ene

photopolymerization may be highly amenable to the efficient synthesis of latexes with film-forming ability:

(i) The polymerization of difunctional alkene and thiol monomers yields linear chains, with very little possibility of branching.

(ii) Propagation and chain transfer reactions governing polymer growth have high kinetic constants (typically 10^5 – 10^6 L mol⁻¹ s⁻¹) for a wide range of thiol–ene monomers. This versatility may be crucial to devising a fast process, addressing the limited light penetration depth in a turbid dispersed medium.

(iii) A new range of polysulfide nanoparticles could be accessed. As a result, there exists opportunities to expand latex use toward nanotechnology,²⁰ biomaterials,²¹ high-energy absorbing materials,²² and electro-optic devices.²³ Such applications are currently unattainable with conventional chain-growth systems like acrylic or vinyl acetate dispersions.

(iv) While a thiol–ene step-growth mechanism strongly differs from a radical chain-growth process—thiyl radical instead of carbon-centered radical propagates across the ene group—the active species remain free radicals. Water is thus tolerated and can continue to play its role of inexpensive and environmentally friendly solvent. By contrast, conventional

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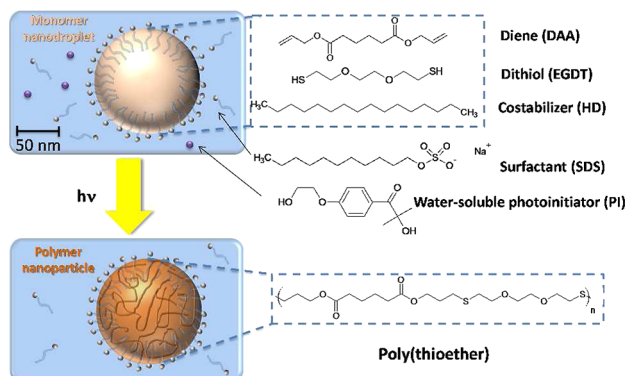
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step-growth polymers' synthesis is not radically mediated and involves water-sensitive precursors (polyurethane) or water byproduct (polyester) leading to equilibrium processes. Although their implementation in aqueous dispersed medium has proven to be feasible,^{24,25} peculiar conditions are required to avoid poor yields and low molecular weights.

We report herein the first preparation of poly(thioether ester) latex nanoparticles using miniemulsion thiol–ene photopolymerization. Our synthesis was performed in water, at ambient temperature, and without the use of any organic solvent. While conventional chain radical photopolymerization of acrylate^{26–28} and styrene miniemulsions²⁹ have been recently reported, an effective transposition to a step-growth mechanism involving dithiol–diene nanodroplets is unprecedented. The relevance of miniemulsion polymerization relies on a nucleation prevalently localized in the monomer nanodroplets.^{30,31} In principle, the absence of mass transfer through the aqueous phase is a key feature to maintain a 1:1 ratio of thiol and ene monomers within the droplet for achievement of full conversion and high molecular weights. In addition, miniemulsions are significantly smaller (50–500 nm) and less polydisperse than classical macroemulsions (0.1–20 μm). The result is a less scattering emulsion in order to overcome the constraints associated with uniform through-cure in a thick turbid medium.³²

As shown in Scheme 1, the synthesis begins with a miniemulsion involving a stoichiometric amount of thiol and

Scheme 1. Schematic Representation of a Thiol–Ene Miniemulsion Photopolymerization of Stoichiometric EGDT and DAA, with a Hydroxyacetophenone-Type Photoinitiator Dissolved in the Aqueous Phase^a



^a[HD] = 4 wt %, [SDS] = 3.5 wt %, C_{monomer} = 20 wt %, irradiation with a Hg–Xe lamp during 5 min, $I = 685 \text{ mW cm}^{-2}$. Costabilizer and surfactant concentrations are given with respect to the monomer phase.

ene monomers: ethylene glycol dithiol (EGDT, 1.78 g) and diallyl adipate (DAA, 2.22 g) known to avoid homopolymerization (i.e., chain growth).³³ Both compounds behave as AA and BB monomers where A and B represent coreactive alkene and thiol functional groups. As both monomers are difunctional, sequential chain transfer/propagation leads to the formation of a linear polymer. Hexadecane (HD, 0.2 g) was added to the monomer mixture as costabilizer to hinder or slow the mass exchange between the different oil droplets (Ostwald ripening). The resultant organic phase was emulsified by sonication with an aqueous phase of distilled water (16 g) containing sodium dodecyl sulfate as surfactant (SDS, 0.14 g) and a water-soluble

α -hydroxyketone type I photoinitiator (PI, 15 mg). The thiol–ene miniemulsions (20 wt % organic phase content) displayed an average droplet diameter of 150 nm as evidenced by dynamic light scattering (DLS), while being photolabile and colloidally stable during several hours. Experimental details of synthesis and characterization methods are available in the Supporting Information (SI).

Polymerization was performed at ambient temperature in a spectroscopic quartz cell (thickness: 1 mm, volume: 0.34 mL, no stirring) acting as a photochemical microreactor. Illumination was provided by the polychromatic light of a medium pressure mercury–xenon arc lamp (λ : 250–600 nm, irradiance = I : 685 mW cm^{-2}) focused on the sample through a flexible light guide. Photopolymerization kinetics were monitored directly in this compact vessel throughout irradiation using real-time Fourier transform infrared (RT-FTIR) spectroscopy. Of high interest is that the near-IR region was able to accommodate high water concentrations without saturating. A well-resolved band specific to the terminal ene groups of DAA at 4484 cm^{-1} was exploited³⁴ to assess the polymerization progress (FTIR spectra are provided in Figure S1 of SI). Despite radiation shielding due to scattering, the conversion–time curve (Figure 1) showed a very rapid consumption of the

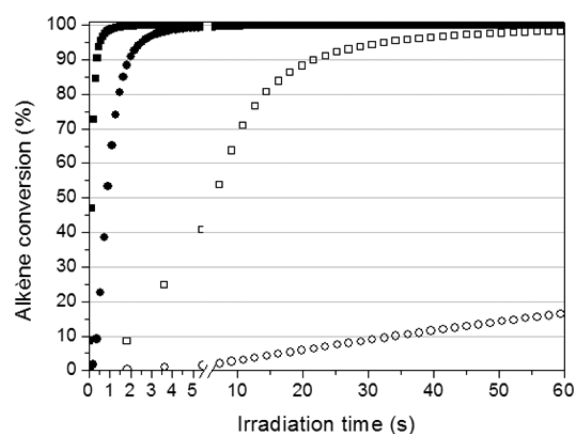


Figure 1. Ene conversion–time profiles determined by RT-FTIR for EGDT–DAA thiol–ene photopolymerization in miniemulsion irradiated without filter (square, $I = 685 \text{ mW cm}^{-2}$) and with a long pass filter $\lambda > 300 \text{ nm}$ (circle, $I = 588 \text{ mW cm}^{-2}$). Full and open symbols are, respectively, for miniemulsions without or with PI (2 wt %). $C_{\text{monomer}} = 20 \text{ wt } \%$, $D_d = 150 \text{ nm}$, cell thickness = 1 mm.

alkene functions completed in less than 2 s. Confirmation of full dithiol conversion was also provided by gravimetric measurements after polymerization. This result supports that the hydrophilicity of EGDT does not prevent particle entry to achieve a quantitative thiol–ene polymerization. Noteworthy also is the presence of an elliptical reflector in the irradiation device that prevented any significant increase of temperature, thus eliminating any thermal contribution to polymerization. Another outstanding characteristic is that the polymerization rate in miniemulsion was even higher than in clear bulk or solution (DMSO) systems (Figure S2 of SI). However, when a cutoff filter blocking wavelengths below 300 nm was added ($I = 588 \text{ mW cm}^{-2}$), the miniemulsion polymerization was slower, and 4 s was necessary to reach completion. Finally, the low bond dissociation energy of the S–H group enabled us to conduct initiatorless photopolymerizations.³⁵ As expected, more sluggish rates were obtained under these conditions,

but a full consumption was achieved after 1 min of UV exposure (Figure 1). In contrast, no conversion took place without photoinitiator under a filtered UV light ($\lambda > 300$ nm), highlighting the importance of short excitation wavelengths in the self-initiation mechanism.

In terms of colloidal characterization, Figure 2 shows two monomodal size distributions somewhat similar for the initial

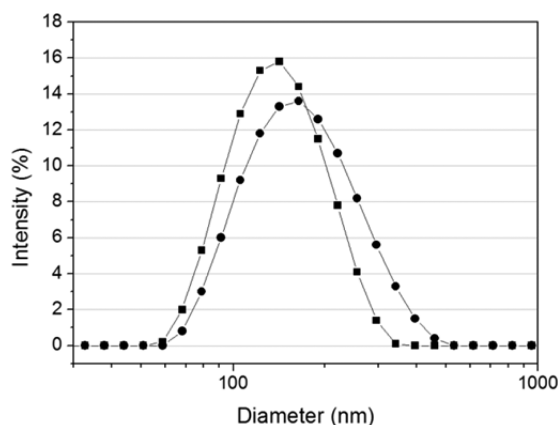


Figure 2. Droplet and particle size distribution (DLS data) for EGDT-DAA thiol-ene miniemulsion before (●) and after (■) irradiation.

monomer miniemulsion ($D_d = 150$ nm) and the final poly(thioether ester) latex ($D_p = 130$ nm). To give a deeper insight into the nucleation process, the ratio of the final latex particles number to the initial monomer droplets number was also estimated. Its value of 1.4 supports a dominant droplet nucleation but also the fact that new particles could be generated in the aqueous phase (by homogeneous nucleation) most likely because of the high water solubility of EGDT (15 g L^{-1} at 25 °C). However, the latter does not seem to hinder the reaction course, demonstrating that monomer molecules can readily diffuse through the aqueous phase into the reactive sites. Finally, to prove the feasibility of scaling-up the approach, a similar thiol-ene photopolymerization was carried out in a 150 mL immersion-type photoreactor at room temperature (depicted in Figure S3 of SI, 150 W medium pressure Hg lamp). Despite different irradiation conditions ($I = 62$ mW cm^{-2}), a full conversion was reached in less than 10 min without significant variation in the final particle size, which is a very promising result.

The polysulfide latex formed a clear elastomeric film after water evaporation, which cannot be dissolved in most conventional solvents at ambient temperature. Accordingly, dynamic scanning calorimetry (DSC) analysis (Figure S4 in SI) revealed, in addition to a glass transition temperature (T_g) at -63 °C, a semicrystalline behavior reflected by an endothermic melting peak at 18 °C (T_m) and an exothermic recrystallization peak at 6 °C (degree of crystallinity = 55%). There were no differences in T_g , T_m , and even particle size when changing irradiance, or with a filtered light. An additional thermogravimetric analysis showed that the polymer was stable thermally up to 180–200 °C under nitrogen (Figure S5 in SI). However, the most striking point is crystallinity, accounting for the film insolubility and indicating that no significant amount of branching is present. The driving forces for the ordering and crystallization of polymer chains are linearity, structural regularity, and the presence of intermolecular attractive forces involving thioether and ester functional groups. Note that very

few chain-growth polymer dispersions form films with a high content of crystalline regions. Vinylidene chloride copolymer latexes, for instance, employed as barrier coatings for packaging materials, are a notable exception. Although the low melting point of our polysulfide polymer limits its utility (and prevents electron microscopy characterization), we think that significant chain stiffening could be induced by other thiol-ene building blocks with aromatic or amide bridging units. This could pave the way to a range of polysulfide resins or coatings satisfying the industrial requirements of chemical resistance, impermeability, and extended service life. These aspects of structure-property relationships will be examined in greater details in the future. Here, only the impact of crystallinity on the poly(thioether ester) latex hydrolytic stability was assessed. The dilution at different concentrations in $H^+Cl^-(aq)$ (pH = 2) or $Na^+OH^-(aq)$ (pH = 12) did not cause any variation of turbidity (UV-vis spectroscopy) or particle size distribution (DLS) during more than 1 month. Despite the presence of numerous ester functions in the polymer backbone, the particles did not show any sign of dissolution or colloidal destabilization in acidic and basic environment. This result supports crystallinity as an efficient barrier to water penetration inside the particles. By comparison, the literature reports a number of amorphous thioether ester-based polymers as films³⁶ or particles³⁷ which are much more susceptible to hydrolysis despite their cross-linked structure. The progressive cleavage of esters in biocompatible polyester nanoparticles is a well-established method for the controlled release of drugs.

The final poly(thioether ester) structure was also investigated by nuclear magnetic resonance (NMR). The 1H NMR spectra of the two monomers and the polymer are shown in Figure 3 (the ^{13}C NMR spectrum is also provided in Figure S6 of SI). Unlike precursors, the polymer was not easily soluble in $CDCl_3$, but a solid gel formed after 24 h enabling an NMR characterization. The typical thiol proton resonances of EGDT (H_{6b} at 1.65 ppm) and ethylenic proton signals of DAA (H_{4a} and H_{5a} at, respectively, 5.25 and 5.90 ppm) completely vanished upon polymerization, suggesting a complete thiol-ene reaction. The formation of multiple $-C-S-$ thioether bonds was also accompanied by the onset of two new resonances assigned to aliphatic protons (H_{4c} and H_{5c} at 2.72 and 1.91 ppm, respectively) arising from the cascade of thiol additions to $C=C$ bonds. In addition, the small fraction of (amorphous) chains that could be dissolved in THF was characterized by size exclusion chromatography (SEC). The molecular weights were determined against polystyrene standards and ranged between 14 and 23 kDa with polydispersity index of 2.5.

In conclusion, thiol-ene miniemulsion photopolymerization was successfully performed providing a facile and environmentally friendly route to poly(thioether ester) nanolatex. While light attenuation represents generally a challenge for heterogeneous radical polymerization, the extremely efficient thiyl radical additions on unsaturated monomers led to a fast photopolymerization at room temperature. This suggests that such radically mediated step-growth polymerization may be amenable to the synthesis of latex in continuous flow reactors, instead of batch reactors. From the standpoint of film properties, linear thiol-ene photopolymerization imparted chain ordering which is extremely important because of its influence on chemical resistance and mechanical properties. Semicrystalline polymers are generally tougher, stiffer, and more resistant to solvent than their amorphous counterparts,

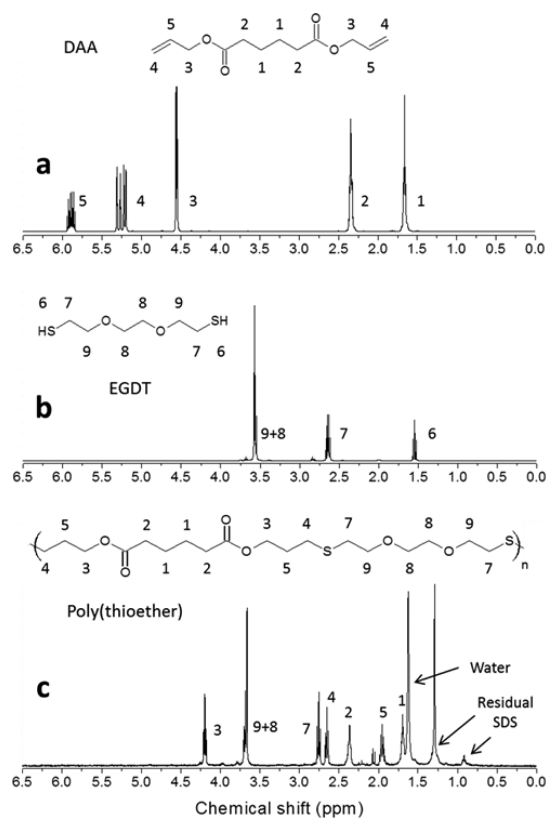


Figure 3. ¹H NMR spectra of (a) diene DAA, (b) dithiol EGDT, and (c) poly(thioether ester) formed by thiol–ene photopolymerization in miniemulsion (CDCl₃, 400 MHz). δ_{H} (in ppm): 4.16 (t, 2H, $J = 6.4$ Hz, H_{3c}), 3.65 (t, 2H, $J = 6.8$ Hz, H_{8c}), 3.62 (s, 2H, H_{9c}), 2.72 (t, 2H, $J = 6.9$ Hz, H_{7c}), 2.61 (t, 2H, $J = 7.2$ Hz, H_{4c}), 2.33 (pseudo t, 2H, H_{2c}), 1.91 (q, 2H, $J = 6.7$ Hz, H_{5c}), 1.65 (pseudo q, 2H, H_{1c}).

thereby adding value to films produced from a step-growth mechanism. In addition, a high degree of structural order would be highly desirable to enhance the utility of thiol–ene materials often compromised by too low T_g values. Other aspects of thiol–ene chemistry worth exploring are nanoparticle functionalization and monomer versatility. This latter opens the prospect of combining other dithiol and diene building blocks to obtain tailor-made properties suitable for the final film application. We contemplate that a new portfolio of polysulfide latexes could be developed in the future through thiol–ene photochemistry, competing with conventional chain-growth polymer dispersions.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization information, along with FTIR spectra (S1), conversion profiles for bulk and solution photopolymerizations (S2), photoreactor picture (S3), DSC (S4), and TGA (S5) thermograms, and ¹³C NMR spectrum of polysulfide (S6) are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: abraham.chemtob@uha.fr. Tel.: +33 3 8933 5030. Fax: +33 3 8933 5034.

Notes

The authors declare no competing financial interest.

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