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Cuong Minh Quoc Le, Gautier Schrodj, Ibrahima Ndao, Brahim Bessif, Barbara Heck, et al.. Semi-Crystalline Poly(thioether) Prepared by Visible-Light-Induced Organocatalyzed Thiol-ene Polymerization in Emulsion. *Macromolecular Rapid Communications*, 2021, pp.2100740. 10.1002/marc.202100740 . hal-03575201

HAL Id: hal-03575201

<https://hal.science/hal-03575201v1>

Submitted on 15 Feb 2022

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Semi-crystalline poly(thioether) prepared by visible-light-induced organocatalyzed thiol-ene polymerization in emulsion

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Keywords: photocatalysis, visible-light, emulsion polymerization, semicrystalline polymer

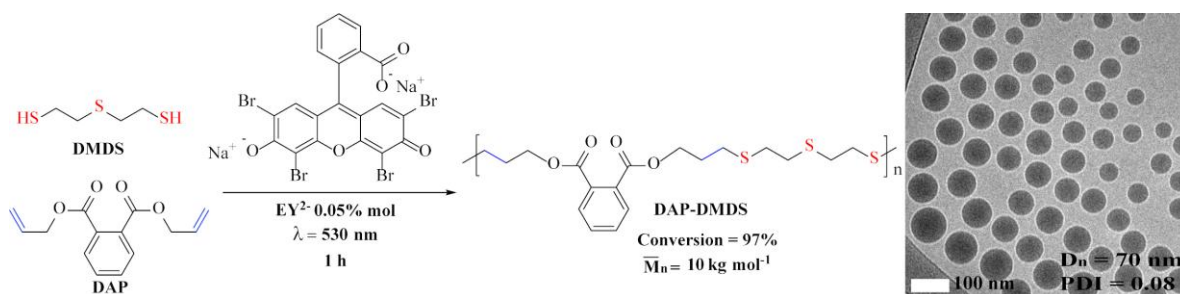
Abstract

A photocatalytic thiol-ene aqueous emulsion polymerization under visible-light is described to prepare linear semicrystalline latexes using 2,2'-dimercaptodiethyl sulfide as dithiol and various dienes. The procedure involves low irradiance (3 mW cm^{-2}), LED irradiation source, eosin-Y disodium as organocatalyst, low catalyst loading ($< 0.05\% \text{ mol}$) and short reaction time scales ($< 1 \text{ h}$). The resulting latexes has molecular weights of about 10 kg mol^{-1} , average diameters of 100 nm and a linear structure consisting only of thioether repeating units. Electron-transfer reaction from a thiol to the triplet excited state of the photocatalyst is suggested as the primary step of the mechanism (type I), whereas oxidation by singlet oxygen generated by energy transfer has a negligible effect (type II). Only polymers prepared with aliphatic dienes such as diallyl adipate or di(ethylene glycol) divinyl ether exhibit a high crystallization tendency as revealed by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction. Ordering and crystallization are driven by molecular packing of poly(thioether) chains combining structural regularity, compactness and flexibility.

The radical addition of a thiol S-H bond across an alkene is one of the archetypal “click” reactions. Its high significance in macromolecular synthesis and biochemistry mainly resides in the high efficiency of the carbon-sulfur bond-forming reaction and a broad functional group tolerance. Generally, the radical thiol-ene reaction is initiated by thermal^[1] or photochemical means.^[2] The decomposition of a radical (photo)initiator yields some primary radicals that abstract a hydrogen radical from thiols to form thiyl radicals. These latter species then initiate the typical thiol-ene polymerization that consists of alternating radical propagation and chain transfer reactions. Since the pioneering work of Yoon in 2013,^[3] a number of redox photocatalysts are also known to mediate visible-light radical thiol-ene reactions. The main class of compounds includes transition metal complexes (Ru(bpz)₃(PF₆)₂,^[3] Ru-(bpy)₃Cl₂,^[4] Ir(ppy)₃^[5]), metal oxide particles (TiO₂,^[6] BiO₂^[7]), as well as various organic photocatalysts (acridinium derivatives,^[8] eosin-Y,^[5, 9] *N*-hydroxyphthalimide,^[10] phenyl-glyoxylic acid^[11]). With very few exceptions,^[4] the mechanism is considered to involve the direct photooxidation of thiol by the electronically excited catalyst to generate a thiyl radical cation R-SH⁺. Its subsequent deprotonation generates a thiyl radical, which is then involved in the classical thiol-ene reaction cycle as described previously. Most photocatalytic chromophores typically absorb at longer wavelengths than radical photoinitiators, and therefore avoid undesirable photochemical reactions of functionalized molecules. Additionally, a photoredox catalysis proceeds in principle by a radical chain process mechanism involving some catalyst-regenerating turnover steps, which help minimizing the amount of catalyst used. Although many studies concluded the ease of accomplishing a thiol-ene reaction with relatively high yields (70–90%) and a minimum of side reactions, they also reported that long irradiation times (1–24 h), high catalyst loadings (1-10% mol) or high irradiances were required. The studies of Yoon are an exception to this generalization.^[3-4] These limitations explain that photocatalytic thiol-ene polymerization is used to much lesser extent than the corresponding small molecule reaction. From the practical viewpoint of obtaining high yields of a high-molecular-weight product, such thiol-ene step polymerizations must be run with a stoichiometric ratio of bifunctional ene and thiol monomers in order to obtain very high conversions (> 98-99%). The synthesis of low molecular weight telechelic poly(thioether)s was described using *fac*-Ir(ppy)₃^[12] and 4-(diphenylamino)benzaldehyde as photocatalyst.^[13] Higher molecular weights and reaction rates were attained by Boyer^[14] and Konkolewicz^[15] through a different reaction mechanism

involving an additional redox mediator, an amine or alkyl halide respectively, which circumvents the slow rate of direct photooxidation of thiol with the photocatalyst.^[16]

To further expand the visible-light mediated photocatalytic thiol-ene polymerization, we describe herein an industrially relevant emulsion polymerization process to prepare linear poly(thioether) latexes in water using eosin-Y disodium (EY^{2-}) as photocatalyst, and leading after precipitation to semicrystalline polymers.^[9d, 17] We have been successful in designing a process that operates with accessible LED irradiation sources at low irradiance ($< 5 \text{ mW cm}^{-2}$) and low catalyst loadings ($< 0.1\% \text{ mol}$). It also features short reaction time scales ($< 1 \text{ h}$), high selectivity and the possibility of using a wide range of monomers. All these characteristics are in agreement with the criteria defined by Bowman for a “photoclick” reaction.^[18] Additionally, the process description is accompanied by a detailed mechanistic investigation.



Scheme 1. Photocatalytic thiol-ene emulsion polymerization. Cryo-TEM image of latex derived from DMDS and DAP.

Our investigations began by examining the radical thiol-ene polymerization of an emulsion based on 2,2'-dimercaptodiethyl sulfide (DMDS) and diallyl phthalate (DAP) (**Scheme 1**). A macroemulsion was prepared by mixing the mixture of thiol-ene monomers (10% w) with an aqueous phase containing sodium dodecyl sulfate (SDS) as surfactant (13.5 mM), EY^{2-} as photocatalyst (0.29 mM in water, 0.05% mol/monomers) and a pH = 8 phosphate buffer (0.01 M). The resulting emulsion was irradiated for one hour under the irradiation of a green light (530 nm, $I = 3 \text{ mW cm}^{-2}$). A stable colloidal latex suspension was obtained (see a photo in **Figure S1** of supporting information), displaying a high monomer conversion ($> 97\%$), a moderate number-average molecular weight ($\overline{M}_n = 10 \text{ kg mol}^{-1}$) and a number-average diameter D_n of 70 nm (cryo-TEM data) (Scheme 1). All the experimental data including were summarized in **Table 1** (entry **1**) (see complete experimental data and apparent absorbance in Figure S1 of SI). ^1H NMR analysis established that linear polymer

chains were formed, composed almost exclusively of thioether repeating units ($\text{CH}_2\text{-CH}_2\text{-S}$). Only a small fraction of disulfide bonds was detected (2-3%). No sulfone or sulfoxide group was observed, ruling out the possibility of over-photooxidation reactions of the thioether units.^[5] Two control experiments were performed which proved that in the absence of catalyst or light no monomer conversion occurred (entries 2-3), supporting the photolateness of the thiol-ene monomer mixture and the initiating role played by the excited photocatalyst. Other dyes (rose Bengal, acridine yellow, entries 4-5) were tried but found less effective than EY^{2-} . Because photoredox systems are known to be pH-sensitive, the effect of pH was also studied in the range 5-8. Lower and higher pH values were avoided to limit photocatalyst decomposition and undesirable thiol-Michael reactions. We observed that a pH of 8 yielded the highest conversions and molecular weights (entries 6-8). In the course of a more exhaustive survey of the role played by molecular oxygen ($^3\text{O}_2$), we found that the reaction can be conducted either in the presence of air, or under rigorously degassed conditions (entry 9).

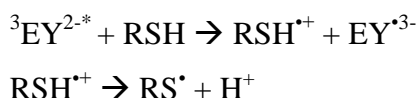
Table 1. Effect of various experimental parameters on the photocatalyzed thiol-ene emulsion polymerization of DAP-DMDS.

Entry	Irradiation ^a	pH	Catalyst	Ene conversion ^b [%]	\overline{M}_n^c [g mol ⁻¹] / Đ
1	Green light	8	EY^{2-}	97	10600 / 3.1
2	Green light	8	No	0	-
3	No light	8	EY^{2-}	0	-
4	Green light	8	Rose Bengal	67 ± 14	-
5	Blue light	Not controlled	Acridine yellow	>96	7100 / 2.5
6	Green light	5.5	EY^{2-}	94	6940 / 2.3
7	Green light	7.2	EY^{2-}	>96	9910 / 2.7
8	Green light	7.4	EY^{2-}	>96	9070 / 2.8
9	Green light Under N ₂	8	EY^{2-}	96	4200 / 2.0

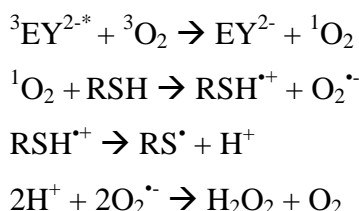
^a Green light: LED, 530 nm, I = 3 mW cm⁻²; blue light: LED, 472 nm, I = 3 mW cm⁻². ^b Yields determined by ¹H NMR spectroscopy in CDCl₃. ^c Molecular weights determined by SEC in THF.

In the case of eosin photosensitization, two competitive mechanisms can take place: (i) the first one involves the proton-coupled electron-transfer reaction from a thiol to generate a thiyl radical as described previously (type I mechanism); (ii) the second one is the oxidation of the thiol by singlet oxygen ($^1\text{O}_2$) (type II mechanism). This latter reactive oxygen species can result from an energy transfer from $^3\text{EY}^{2-*}$ to $^3\text{O}_2$.

(i) **Type I mechanism:**



(ii) **Type II mechanism:**



To gain better insight into the primary mechanisms, the polymerization kinetics of a DAP-DMDS emulsion was compared in air and under nitrogen. As shown in **Figure 1A**, the reaction rate in the presence of air was approximate twice as fast as under nitrogen, resulting in significantly higher molecular weights (particle size and polymer structure were found to be similar). Similarly, an acceleration of a thiol-alkyne reaction was noted by Allegrezza et al. but by using the organometallic photocatalyst $\text{Ir}(\text{ppy})_3$.^[19] To substantiate whether singlet oxygen might contribute, the same experiment was performed in the presence of air and sodium azide (4.3% mol) acting as singlet oxygen quencher. Under these conditions, no significant effect on monomer conversion was observed (**Figure S2** in SI).^[20] Our conclusion is that the type I mechanism prevails, but that molecular oxygen is likely to be involved in a reaction regenerating the photocatalyst, resulting in increased rates of the reaction due to a higher EY^{2-} concentration (*vide infra*).^[21] In support of the minor role of reactive oxygen species, a fully converted latex illuminated in the presence of 0.5% mol of EY^{2-} for 14 h did not yield sulfoxide or sulfone as oxidation products (**Figure S3** in SI). Finally, **Figure 1B** shows a “light/dark” experiment in which the progress of the polymerization was examined for alternating periods of irradiation and darkness. Clearly, monomer conversion required constant irradiation and conversion ceased during the periods of darkness. As widely

discussed in the literature,^[22] this result does not mean that a chain radical process did not occur but rather illustrates the short life times of thiyl and carbon-centered radicals. In our case, the fast reactions and low catalyst loadings can be reconciled with a chain radical process.

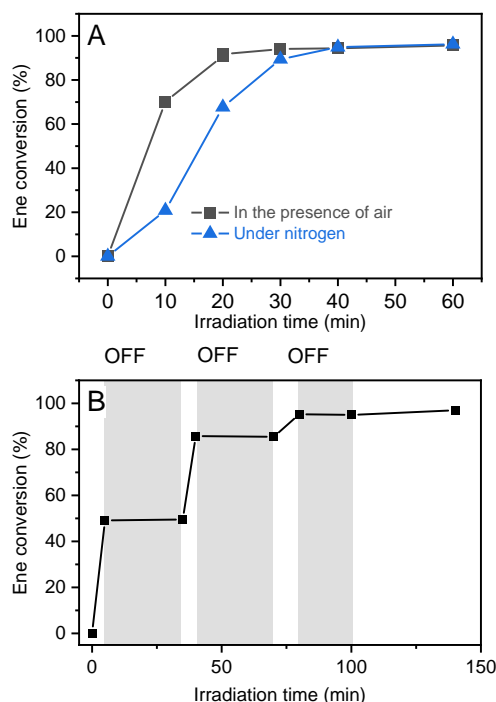


Figure 1: (A) Conversion-time plot for photocatalyzed thiol-ene emulsion polymerization of DAP-DMDS under air or nitrogen atmosphere. (B) Light/dark experiments for polymerization performed under air.

A number of evidences supported the electron-transfer from a thiol upon electronic excitation of EY^{2-} (type I mechanism). According to the Rehm-Weller equation, the free energy change for an electron-transfer from thiol to ${}^3[EY^{2-}]^*$ is favorable ($\Delta G_{et} = -0.52$ V vs SCE). Quenching of ${}^3EY^{2-*}$ in the presence of DMDS was also proved by fluorescence emission experiments in which increasing amounts of dithiol were added to an aqueous solution of EY^{2-} (**Figure 2A**). An interaction rate constant was determined by measuring the rate of fluorescence decay F_0/F at 537 nm from a Stern-Volmer plots ($F_0/F = 1 + K_{SV}[DMDS]$, $R^2 = 0.994$, and $K_{SV} = 1.44 \times 10^3$ M).^[23] The linearity of the Stern-Volmer plot is consistent with a dynamic quenching process. In order to gain more insight into the quenching mechanism and to investigate the possible formation of a ground-state charge transfer complex, the effect of thiol concentration on the UV-Vis spectra of a binary EY^{2-} /DMDS solution in water was also analyzed. Addition of increasing amounts of DMDS caused a slight

increase of the spectrum intensity (**Figure 2B**), which agrees with the formation of a weak eosin/DMDS complex in water. Such complex is important because it can increase the electronic density of the excited state of EY^{2-} and favors its reductive quenching by a thiol to generate the thiyl radical cation, but only upon irradiation.^[24]

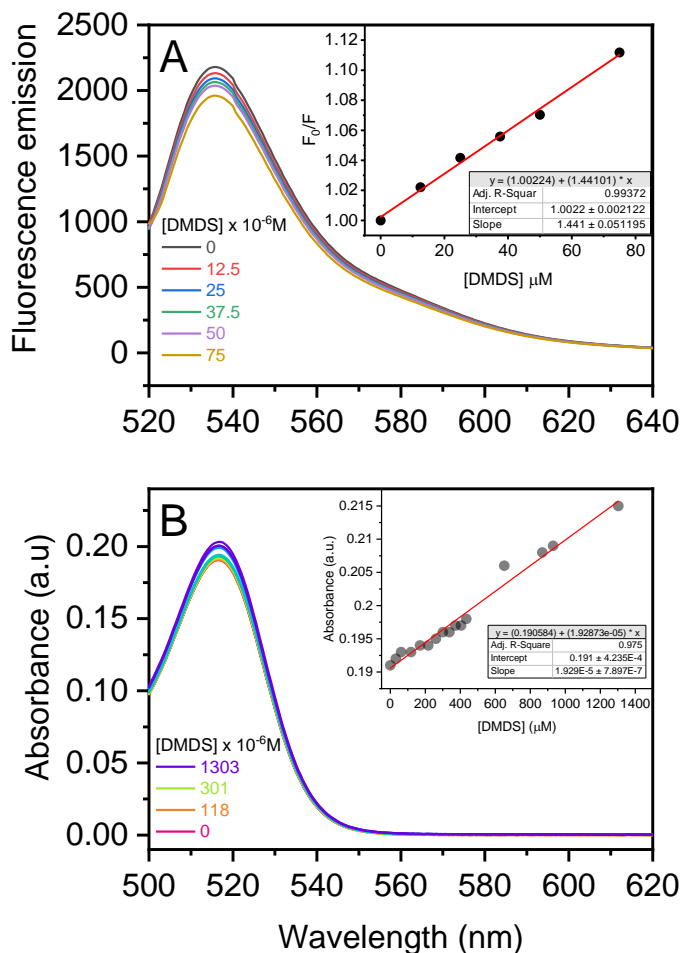
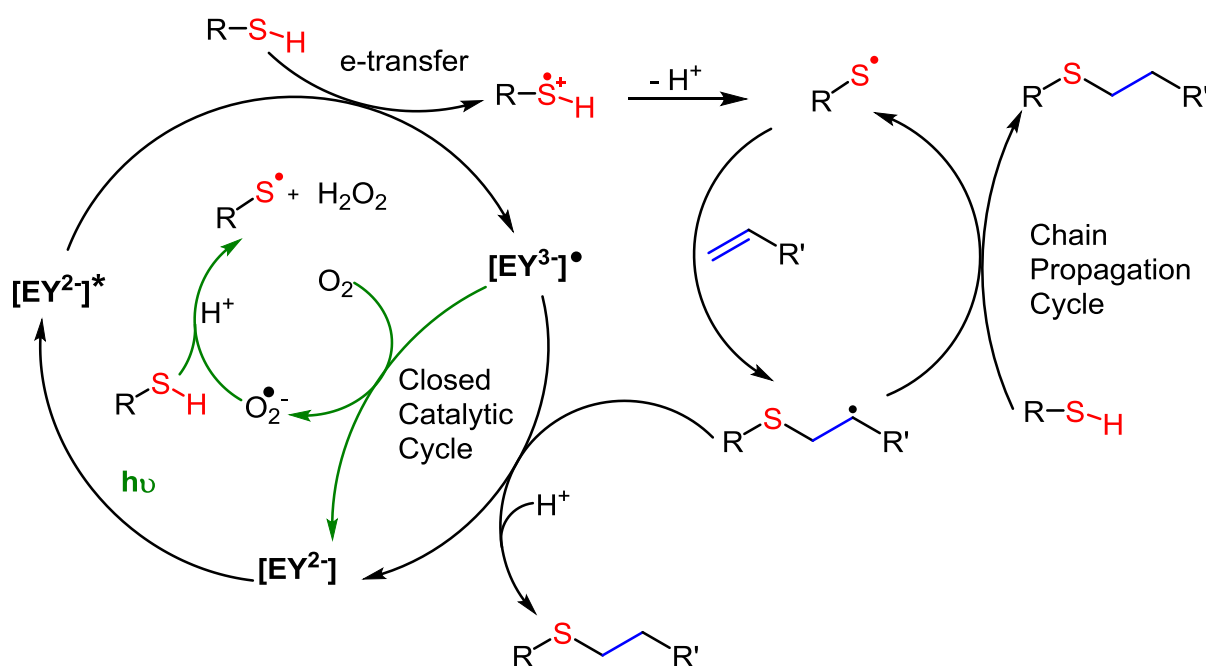


Figure 2: (A) Steady state fluorescence quenching of EY^{2-} (10^{-7} M) in non-degassed water in the presence of different concentrations of DMDS ($0-7.5 \times 10^{-5}$ M). (B) UV-vis spectroscopy of EY^{2-} (2×10^{-6} M) after addition of DMDS ($0-1.3 \times 10^{-3}$ M).

Based on these previous results, the following mechanism can be proposed (**Scheme 2**). A thiyl radical cation RSH^{++} may be generated by photooxidation of thiol with $[EY^{2-}]^*$. A subsequent proton-transfer step affords the chain-propagating thiyl radical RS^\bullet involved in the classical radical thiol-ene chain process with ene monomer (chain propagation cycle). To close the catalytic cycle, the photo-reduced radical trianion $EY^{\bullet 3-}$ can be oxidized to the original eosin dianion EY^{2-} by two ways: either a reaction with a carbon-centered radical to form a thioether product or a reaction with molecular oxygen to form superoxide radical anion

($\text{O}_2^{\cdot-}$). Interestingly, thiols are known to react with this latter species via a plausible mechanism of hydrogen atom abstraction giving thiyl radical and hydrogen peroxide.^[25] Regeneration of EY^{2-} and formation of thiyl radicals both originating from atmospheric oxygen might explain why an acceleration of polymerization was observed when the reaction was conducted in the presence of air. The former route proceeding in the absence of molecular oxygen is consistent with the fact that high conversions can be achieved also under nitrogen atmosphere

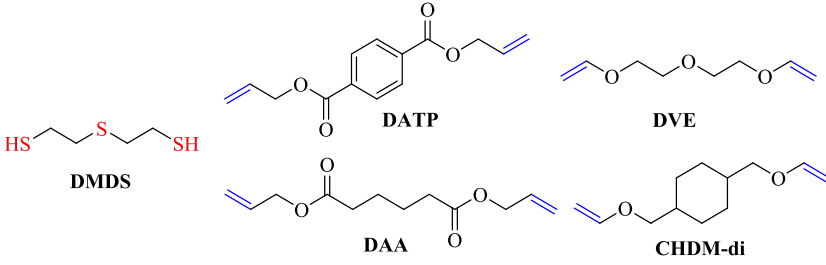


Scheme 2. Proposed mechanism of photocatalytic thiol-ene polymerization. The green arrows show reactions occurring only in presence of atmospheric oxygen.

Next, we evaluated the potential of this process for the preparation of semicrystalline polymers. Recent studies suggested that poly(thioether) linear chains, which combine secondary attractive forces and high structural regularity, can have a high a tendency for crystallization.^[26] To achieve better insight into the structure-property relationship, DMDS was polymerized with various diallyl ethers and divinyl ethers: diallyl terephthalate (DATP), diallyl adipate (DAA), di(ethylene glycol) divinyl ether (DVE), 1,4-bis[(vinyl)oxy)methyl]cyclohexane (CHDM-di), using a similar emulsion polymerization process for all of these molecules. This approach represents a simple and versatile means of

synthesizing a host of different latexes by varying the choice of the **R** and **R'** spacer groups in the dithiol (HS-**R**-SH) and the diene (H₂C=CH-**R'**-CH=CH₂). **Table 2** provides the chemical structures of the ene monomers used (DMDS is the only dithiol used, **R** = CH₂-CH₂-S-CH₂-CH₂) and some detailed characterization results including particle size, conversion and molecular weight. All latexes were made up of linear chains with the expected repeat units (-S-**R**-S-CH₂-CH₂-**R'**-CH₂-CH₂) (**Figure S4** in SI).

Table 2. Characterization of latexes prepared from DMDS and various dienes



Ene	Ene conversion Conv. [%]	Z-average diameter \overline{D}_z [nm] / PDI	\overline{M}_n \overline{M}_n [g mol ⁻¹] / Đ
DAP	97	96 ± 3 / 0.18	10600 / 3.1 ^c
DATP	97 ^a	74 ± 2 / 0.18	N/D ^d
CHDM-di	N/D ^b	92 ± 3 / 0.17	7800 / 2.0 ^e
DAA	92 ^a	76 ± 3 / 0.22	8500 / 2.1 ^e
DVE	N/D ^b	226 ± 8 / 0.19	9800 / 2.2 ^e

^a Determined by ¹H-NMR in CDCl₃. ^b No reference peak is available for calculation. ^c Determined by SEC using THF eluent. ^d The polymer is neither soluble in THF nor DMF. ^e Determined by SEC using DMF eluent.

Dry and washed polymers were collected from the latexes and subjected to a number of characterization techniques to assess their ability to undergo crystallization. Unlike polymers derived from CHDM-di and DAP, those prepared with DATP, DAA and DVE were only poorly soluble at room temperature in a number of organic solvents such as acetone, ethanol, DMF, DMSO and THF, hinting indirectly at a significant fraction of less soluble crystalline domains. Crystallinity increases chemical resistance because crystalline domains can act as physical crosslinks that effectively increase secondary attractions and prevent solvation of chains. To confirm a considerable manifestation of crystalline domains in the three less

soluble polymers, a DSC analysis was performed (**Figure S5** in SI). In addition, images obtained by polarized optical microscopy on spin-coated thin films of the polymer of DVE-DMDS showed clear birefringent polygonal patterns, characteristic for coalesced crystalline spherulites (**Figure 3A** and **3B**). Interestingly, in accordance with the sequence of a first melting-, crystallization- and second melting-peak seen in the corresponding DSC heating trace (see **Figure S5E**), two distinctly different morphologies were observed. When the sample was crystallized by quenching from the melt, which is reached at a temperature of ca. 90 °C, the films showed clear signs of Maltese cross patterns of birefringence (**Figure 3A**), suggesting radial growth of multiple thin lamellar crystals which cannot be resolved individually by optical microscopy. However, when melting the sample of **Figure 3A** at ca. 64°C followed by crystallization at ca. 76°C, a distinctly different pattern of radially arranged needle-like crystalline structures could be observed in **Figure 3B**. From an analysis of corresponding XRD curves (**Figure 3C**), which also indicate that two different crystalline polymorphs are responsible for the observed two melting processes, the degree of crystallinity was estimated to be in the range of 25 – 45%. The results of XRD measurements during stepwise heating are shown in **Figure S6** (SI). It should be noted that crystallization of the polymer of DVE-DMDS was quite fast. Depending on the thermal history and crystallization temperature, the whole sample could become crystalline within seconds to hours, as could be observed in real time by optical microscopy. Fast crystallization is also indicated by the rather narrow crystallization peaks in the DSC traces (see **Figure S5** in SI), suggesting that the ease of chain packing was a driving force for ordering and crystallization of these polymer chains. Thus, profiting from structural regularity, compactness and some degree of flexibility, packing was facilitated in particular for poly(thioether) chains based on aliphatic dienes DVE ($\mathbf{R}' = \text{OCH}_2\text{CH}_2\text{OCH}_2\text{O}$) and DAA ($\mathbf{R}' = \text{CH}_2\text{OC}(\text{O})(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}_2$).^[27] Aromatic or cyclic \mathbf{R}' groups present in the other dienes (DAP or CHDM-di) are thought to lower the tendency for crystallization by preventing close packing of polymer chains.

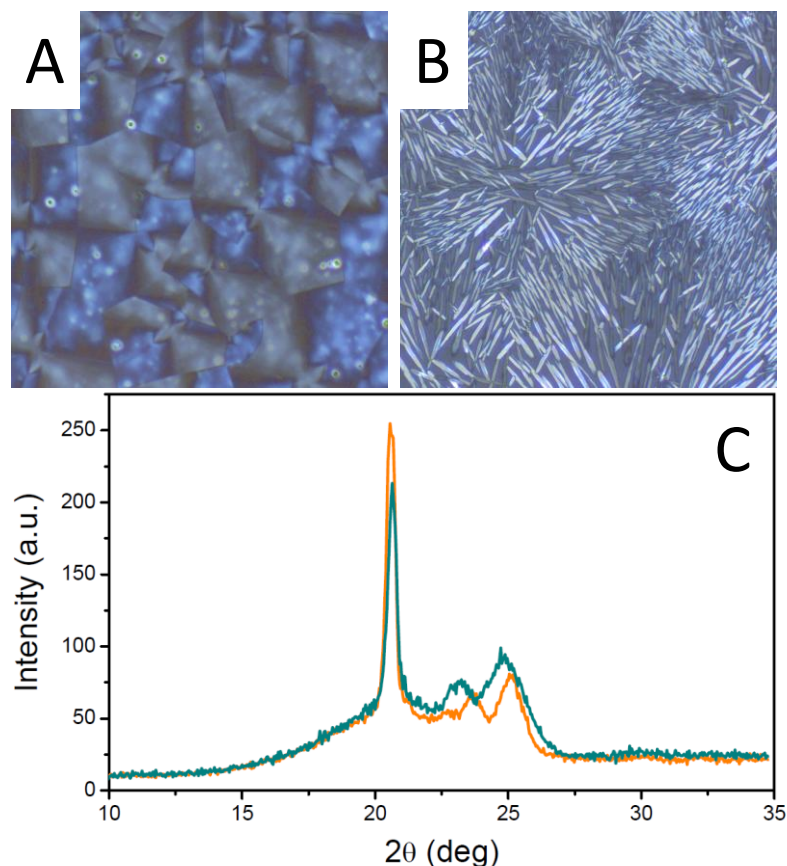


Figure 3: (A) Polarized optical microscopy images (size: $475 \times 475 \mu\text{m}^2$) of *ca.* 100 nm thick films of the polymer of DVE-DMDS crystallized rapidly at room temperature after quenching from the molten state at 100°C . (B) The sample of (A) was subsequently molten at *ca.* 64°C and further heated to *ca.* 76°C where it crystallized in a different morphology. (C) Corresponding X-ray diffraction curves of analogous samples. The curves in dark cyan and orange represent the two different crystalline states at 47°C and at 70°C , measured after 1 min and 90 min of annealing at the respective temperatures.

In conclusion, visible-light photocatalyzed thiol-ene emulsion polymerization was successfully developed using eosin disodium organic dye as photocatalyst. The process has many advantages such as low catalyst loading, absence of additive, short reaction times, low irradiance, higher reactivity under air atmosphere, and the achievement of nanolatexes of relatively high molecular weight. Using DMDS as dithiol paves the way towards achieving polymers with semicrystalline properties. Poly(thioethers) prepared with diallyl adipate or di(ethylene glycol) divinyl ether combine structural regularity, compactness and flexibility, leading to high tendency toward crystallization as proved by DSC, X-ray diffraction and polarized optical microscopy.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement n° 765341 (project photo-emulsion, MSCA-ITN-2017). The authors also thank Dr. Jean-Luc Birbaum (retired chemist from BASF Schweiz, Basel), Dr. André Braun (retired from his chair at the Department of Chemical and Process Engineering of the University of Karlsruhe) and Dr. Esther Oliveros (retired research director at the CNRS, University of Toulouse) for their valuable help in the discussion of the experimental results.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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