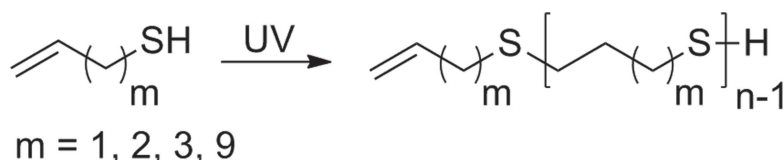


Polythioethers by Thiol-Ene Click Polyaddition of α,ω -Alkylene Thiols

Frank Deubel, Victor Bretzler, Richard Holzner, Tobias Helbich, Oskar Nuyken, Bernhard Rieger,* Rainer Jordan*

The straightforward synthesis of a series of poly(thioether)s by photoinduced thiol-ene click polyaddition of α,ω -alkylene thiols is reported. It is found that linear and telechelic poly(thioether)s can be directly obtained from α,ω -alkylene thiols with, for example, alkyl chain length of $m = 1, 2, 3$, and 9. The reaction proceeds without additives such as (radical) initiators or metal compounds and can simply be carried out by UV-irradiation of the bulk monomer or monomer solution. Ex situ kinetic studies reveal that the reaction proceeds by a typical a step-growth polyaddition mechanism. As the homologue series of poly(thioether)s are now synthetically accessible, new direct pathways to tailored poly(alkyl sulfide)s and poly(alkyl sulfone)s are now possible.



1. Introduction

The addition of a thiol to a nonactivated carbon-carbon double bond known as the thiol-ene click reaction, recently developed into a widely used reaction in synthetic chemistry. Its simplicity, selectivity, and efficiency make the thiol-ene click reaction ideally suited for quantitative polymer analog reactions, surface functionalization, and synthesis of bioorganic hybrids.^[1–3] Even though, this reaction is known for over 100 years,^[4] the thiol-ene click reaction only recently received much attention for polymer network synthesis, polymer functionalization, dendrimer synthesis, and modification of three-dimensional objects as it can be induced by light, is metal-free, and orthogonal to various other ligation reactions.^[5,6]

However, the synthesis of linear aliphatic poly(thioether)s has received considerably less attention,

although they are intriguing materials for a wide variety of applications such as polymer electrolytes for lithium ion batteries,^[7] as sealants or adhesives,^[8,9] metal chelating polymers,^[10] or oxidation-sensitive polymers for medical applications.^[11–13] This is because polythioethers of reasonably high molar mass are very difficult to obtain by thiol-ene polymerization from dithiols and dienes (AA and BB monomers),^[14–22] or from dibromoalkanes with dimercaptoalkanes and their alkali metal salts.^[7,23–25] The alternative route, the living ionic ring-opening polymerization of sulfur-containing heterocycles (e.g., thiethanes), circumvents the problems of AA-BB polyaddition reactions but suffers from reactivity problems and side reactions for rings larger than three.^[11]

A direct route to polythioethers is the photoinduced polyaddition of α,ω -alkylene thiols, as first described in the late 1920s by Braun and Murjahn^[26] and Barun and Plate^[27] Much later, Oswald et al.^[28] used allylic sulfides, and in a series of papers Nuyken et al.^[29] and Nuyken and Hofinger^[30–34] studied the polyaddition of styrenic thiols. Based on a first report by Kharash et al.,^[35] Morgan et al.,^[36] and Bowman and co-workers^[37–39] investigated the photocopolymerization of thiols with different comonomers and confirmed the step-growth mechanism. They also pointed out several unique advantages of the thiol-ene photopolymerization being photoinitiator/catalyst free, oxygen tolerant, and specifically suited for

F. Deubel,^[+] V. Bretzler,^[+] R. Holzner, T. Helbich,
Prof. O. Nuyken, Prof. B. Rieger
Technische Universität München, Lichtenbergstr. 4, 85747
Garching, Germany
E-mail: rieger@tum.de

Prof. R. Jordan
Technische Universität Dresden, Mommsenstr. 4,
01069 Dresden, Germany
E-mail: rainer.jordan@tu-dresden.de

^[+]These authors contributed equally.

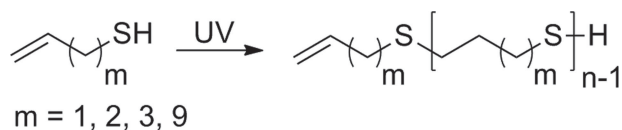


Figure 1. Reaction of α,ω -alkylene thiols to poly(thioether)s by photoinduced thiol-ene polyaddition.

the production of coatings. Surprisingly, and to the best of our knowledge, no work has been reported so far that describes the simplest route to poly(thioether)s from α,ω -alkylene thiols.

Here, we report the straightforward and facile synthesis of a set of poly(thioether)s by photoinduced thiol-ene click polyaddition of α,ω -alkylene thiols for the first time. We found that linear and telechelic poly(thioether)s can be directly obtained from α,ω -alkylene thiols with, for example, alkyl chain length of $m = 1, 2, 3$, and 9 (Figure 1). The melting temperatures of the resulting poly(thioether)s were found to be a direct function of m . Analog to the thiol-ene copolymerization, the thiol-ene polyaddition proceeds without additional (radical) initiators or metal compounds and can simply be carried out in solution under UV-irradiation ($\lambda_{\text{max.}} = 350$ nm with a spectral range of 300–400 nm). The general reaction scheme is outlined in Figure 1.

2. Results and Discussion

A set of four α,ω -alkylene thiols were selected for the thiol-ene click polyaddition. While prop-2-ene thiol (allyl thiol) is commercially available, the other monomers as listed in Table 1 could be readily prepared in high yields and with high purity according to the literature.^[40,41] Monomers were stored in the dark at -20 °C and did not show any sign of decomposition (weeks). Prop-2-ene thiol has been freshly distilled prior to use in polymerization reactions. The polymerization was carried out in a 2 M solution under vigorous stirring at room temperature and constant

irradiation with UV light for 24 h. Analog to the previous results from Oswald, chloroform was found to be the most suitable solvent. Although, in benzene, the polyaddition reaction proceeds, but only low-molar-mass products were obtained, in pentane, oligomeric products already precipitated, polymerization of allylic thiols in chloroform yielded polymer products in all cases.^[28] Table 1 summarizes the results of the reactions for all monomers used so far.

Polymer purification by precipitation in methanol was straightforward, and in all cases, odor free and colorless polymers were obtained. ¹H-NMR spectroscopy of the obtained polymers unambiguously confirmed the formation of the desired poly(thioether)s and revealed a very high-monomer conversion as judged from the signal intensity of olefinic protons at 5.1 and 5.8 ppm (Supporting Information). Gel permeation chromatography (GPC) gave dispersity values around 2 or lower and molar masses from 3.7–7.3 kg mol⁻¹. Oswald et al.^[28] reported the synthesis of poly(propylene sulfide) with $\bar{M}_w = 0.5$ to a maximum of 5 kg mol⁻¹. In this work, significantly higher molar mass could be realized by longer irradiation times (48 h) as well as irradiation of bulk monomer. As listed in Table 1, this resulted in, for example, poly(butylene sulfide) with $n = 180$ ($\bar{M}_w = 16$ kg mol⁻¹, $\bar{D} = 1.9$). However, although ¹H and ¹³C NMR spectra of poly(undecylenesulfide) indicate formation of disulfides (Figure S7 and S8, Supporting Information), the obtained polymer shows a high degree of polymerization (Table 1). Thus, it is suggested that disulfides, if formed during polymerization reaction, can be cleaved by UV irradiation or by reaction with other present radicals^[42,43] and consequently do not impede a step growth polymerization mechanism. Another explanation for the origin of disulfide bonds could be their formation after-polymer precipitation under oxidative air atmosphere by oxidation of thiols.^[44]

In Figure 2, the development of the molar mass and dispersity with the irradiation time is shown for a 6 M solution of prop-2-ene thiol in chloroform, as analyzed by GPC. The observation that the reaction proceeds more slowly

Table 1. Molar mass average, dispersity and conversion for poly(thioether)s prepared from α,ω -alkylene thiols by UV irradiation in chloroform (2 M) for 24 h or bulk monomer for 48 h (*).

Poly(thioether)	Monomer	\bar{M}_n^a [kg mol ⁻¹]	\bar{M}_w^a [kg mol ⁻¹]	n^b	\bar{D}^c	Conversion ^d [%]
Poly(propylene sulfide)	Prop-2-ene thiol	2.3	5.5	74	2.37	99
Poly(butylene sulfide)	But-3-ene thiol	2.9	3.7	42	1.27	98
		8.5*	16.1*	183*	1.90*	100*
Poly(pentylene sulfide)	Pent-4-ene thiol	2.5	3.7	36	1.48	97
Poly(undecylene sulfide)	Undec-10-ene thiol	4.4	7.3	39	1.65	98

^aNumber average (\bar{M}_n) and weight average (\bar{M}_w) molar mass as determined by gel permeation chromatography; ^bDegree of polymerization; ^cDispersity, $\bar{D} = \bar{M}_w/\bar{M}_n$; ^dCalculated by Carothers' equation: $c = 1-1/n$.

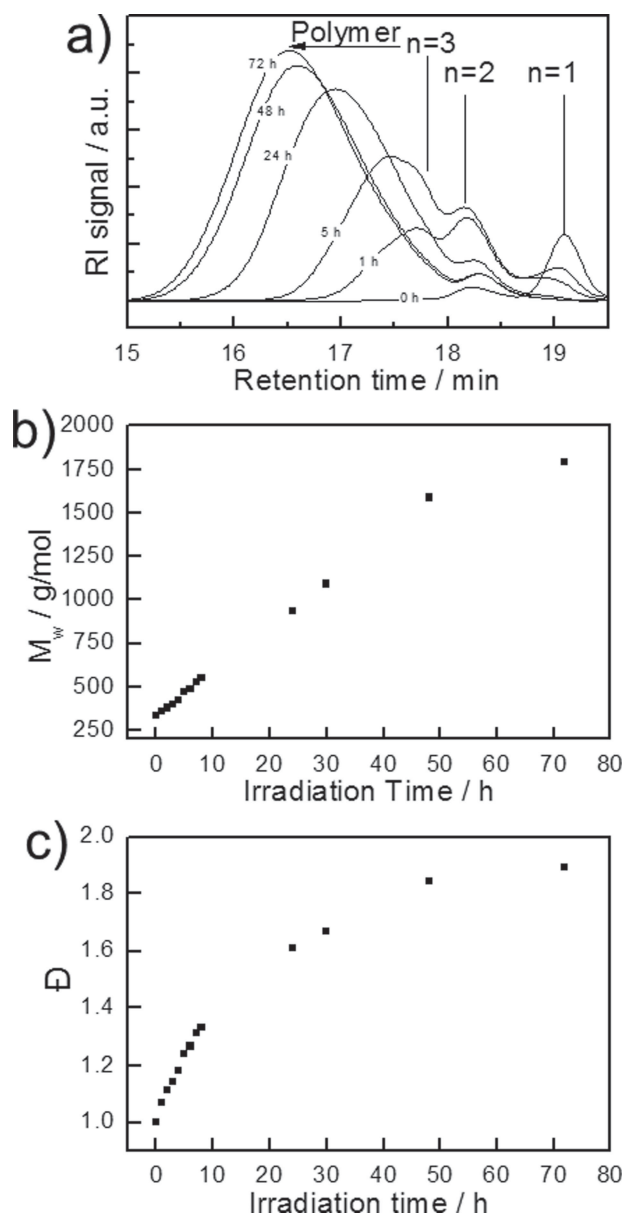


Figure 2. a) GPC traces of aliquots of a 6 M solution of prop-2-ene thiol in chloroform under constant UV irradiation sampled at indicated times. b) Development of the weight average molar mass (\bar{M}_w) and c) dispersity (\mathcal{D}) with the irradiation time.

than one would expect from results depicted in Table 1 might be attributed to the increased monomer concentration. The viscosity of the reaction mixture increases significantly when a concentration of 6 M is used compared to 2 M. The observation that the molar mass is leveling off at around 2 kg mol⁻¹ might be a result of trace amounts of oxygen that enter reaction vessel when aliquots necessary for GPC measurements are taken.

GPC analysis of freshly distilled prop-2-ene thiol already revealed the existence of monomers along with

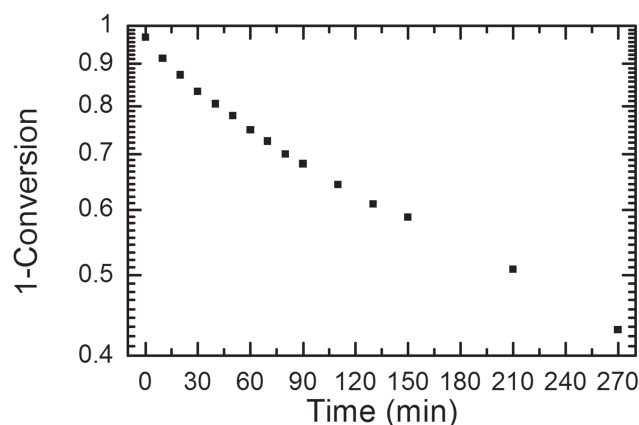


Figure 3. Ex situ NMR kinetics of double bond conversion over time for the photoinduced thiol-ene click polyaddition of prop-2-ene thiol solution in chloroform (2 M).

a small fraction of dimers. This was corroborated by ¹H NMR spectroscopy; approximately, 3.2 mol% dimer was determined (Figure 2a). After UV irradiation for 1 h, mostly dimers (CH₂ = C₂H₃-S-C₃H₆-SH) and trimers, are formed, similar to the findings of Oswald et al.^[28] After 5 h, oligomers were already detectable, and with ongoing polymerization time, higher molar mass poly(propylene sulfide) was formed with a typical development of \bar{M}_w and \mathcal{D} with the reaction time (Figure 2b,c). Analog investigations for the other monomers were not possible since the photopolymerization proceeded too fast for the sampling procedure. For pent-4-ene thiol, after 10 min of UV irradiation, the conversion of double bonds was already >90%, as determined by ¹H NMR spectroscopy. So far, all results indicate a conversion of α,ω -alkylene thiols via a photoinduced polyaddition reaction. This was further investigated by ex situ kinetic measurements in which we determined the double bond conversion with time, as determined by ¹H NMR spectroscopy (Figure 3).

The conversion of one function of the AB monomer system (here the olefin function) nicely follows the typical trend for a step-growth reaction. A similar double bond conversion was found by Cramer and Bowman^[39] for the photopolymerization of dithiols and dienes monitored by real-time Fourier transform infrared (FTIR) spectroscopy. Moreover, GPC investigation of a reaction mixture aliquot at 40% conversion (after 150 min reaction time) revealed an average molar mass of 150 g mol⁻¹, which most probably corresponds to a dimer ($M_{\text{theor.}} = 148.29$ g mol⁻¹). Neither ¹H NMR spectroscopy nor GPC analytical data gave hints for the formation of significant amounts of cyclic thioethers.^[45] Even excessive dilution of the reaction mixture did not result in detectable traces of compounds from ring formation as judged by ¹H NMR spectroscopy. In a solution of but-3-ene thiol diluted in benzene, no signals attributed to tetrahydrothiophene (thiolane) at chemical

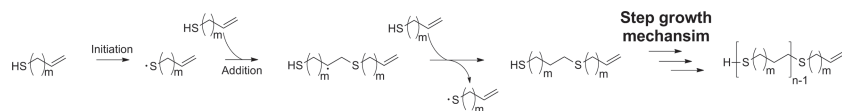


Figure 4. Proposed reaction mechanism for the photoinduced thiol-ene polyaddition of α,ω -alkylene thiols leading to linear poly(thioether)s.

shifts of 2.53 and 1.55 ppm could be detected. A solution of pent-4-ene thiol in benzene also showed no signals that could be assigned to the sulfur-containing heterocycle, thiane, expectable at 2.29 ppm. Although formation of cyclic monomers was not observed by ^1H NMR spectroscopy, formation of macrocycles cannot be excluded and are in fact likely for polyaddition or polycondensation reactions. However, it has to be mentioned that in our case, analysis by, for example, mass spectrometry cannot distinguish between linear and cyclic products as their sum formula are identical.

So far, all results indicate a step-growth polyaddition mechanism of the α,ω -alkylene thiols, which is conveniently induced by UV irradiation. Based on our results and in agreement with earlier studies by Bowman et al.,^[38] and Cramer and Bowman,^[39] we propose a mechanism for the photoinduced thiol-ene click reaction as depicted in Figure 4.

Furthermore, we investigated first properties of the novel poly(thioether)s such as the melting temperature as a function of the main chain methylene group number (number of CH_2 units = $m+2$). Differential scanning calorimetry (DSC) was performed with the poly(thioether)s of methylene segment lengths, $m = 1, 2, 3,$ and 9 . The results are summarized in Figure 5. The DSC data show that higher m lead to a systematic increase of the melting temperatures.

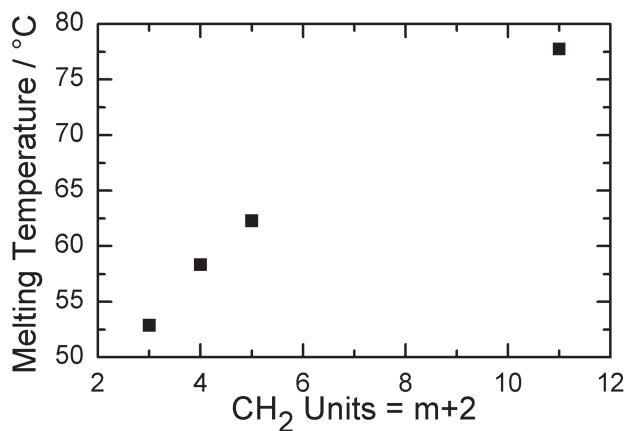


Figure 5. Melting temperature of the homologue series of poly(thioether)s as a function of the number of main chain methylene units as determined by DSC.

Disulfide formation was only observed in case of poly(undecenylene sulfide). This was not the case for all other polymers under the reaction and under standard storing conditions. As disulfides can participate in radical reactions,^[42,43] the thiol as

well as the ene - terminal functions are readily available for further functionalization of the polymer chain termini by, for example, consecutive thiol-ene click coupling reactions to form block copolymers, defined as end-functionalized polythioethers or other hybrid materials.

3. Conclusion

In summary, the synthesis of a series of aliphatic poly(thioether)s by direct photoinduced thiol-ene click polyaddition was shown for the first time. This facile and direct method now gives access to a series of linear, crystalline, and telechelic poly(thioether)s. The inherent telechelic architecture of the poly(thioether)s is ideally suited for the defined consecutive reactions for functionalization and combination with other entities such as nanoparticles, substrates, polymers using click chemistry.^[53–57] Poly(thioether)s are of high interest for the development of new materials for sealants, adhesives, high-refractive index material, and as macromolecular chelators for heavy-metal ions. Moreover, in combination with lithium, they could possibly be used as novel polyelectrolytes for polymer-based lithium batteries^[7] and may be an alternative to poly(ether)s such as poly(ethylenglycol) in biomaterial applications.^[11] As the homologue series of poly(thioether)s are now synthetically accessible, this also opens new pathways to tailored poly(alkyl sulphoxide)s and poly(alkyl sulfone)s.^[13]

4. Experimental Section

4.1. Methods

NMR spectroscopy was performed on a Bruker ARX-300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C in CDCl_3 . Chemical shifts are calibrated to the residual proton signal of the NMR solvent (CDCl_3 ; ^1H $\delta = 7.26$ ppm, ^{13}C $\delta = 77.16$ ppm). DSC was recorded on a TA-Instruments DSC-Q2000 with a heating and cooling rate of 10 K min^{-1} . GPC was performed with a Polymer Laboratories PL-GPC-50 system calibrated with PS standards. UV irradiation was performed as recently used for photopolymerization of vinyl monomers on various substrates^[46–50] in standard Duran glass vials with two UV lamps of a spectral distribution between 300 and 400 nm ($\lambda_{\text{max}} = 350$ nm, $8\text{--}10\text{ mW cm}^{-2}$) to ensure homogeneous irradiation.

4.2. Monomer Synthesis

Prop-2-ene thiol was obtained from Sigma-Aldrich (Weinheim, Germany). Other monomers were synthesized according to the literature via thiuronium bromide intermediates.^[40,41] The respective ¹H and ¹³C NMR spectra of the monomer products were in accordance with the literature reports and showed high purity.^[40,51,52]

4.3. General Polymerization Procedure

Solutions of distilled monomers in chloroform (2 M) were degassed by three freeze-thaw cycles. The solution was stirred under an argon atmosphere and irradiated for 24 h by UV light. Subsequently, the polymers were precipitated in methanol as colorless powders. Remaining monomers were removed by washing with three portions of methanol (\approx 50 mL) and dried under reduced pressure at room temperature.

For the kinetic studies of polymerization of pent-2-ene thiol, aliquots of 50 μ L were taken from the reaction mixture at indicated times. Samples were diluted in chloroform and measured instantly by GPC and ¹H NMR spectroscopy. Conversions were calculated from ¹H NMR spectra analog to the approach of Nuyken et al.^[31]

Supporting Information

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

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