Tetrahedron 109 (2022) 132683

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Photodisulfidation of alkenes with linear disulfides: Reaction scope and kinetics

Joshua T. Kamps [a, 1], Shafer M. Soars [a, 1], Nichloas J. Bongiardina [b], Benjamin D. Fairbanks [c], Christopher N. Bowman [c, *]

[a] Department of Chemistry, University of Colorado- Boulder, Boulder, CO, 80303, United States
[b] Material Science and Engineering Program, University of Colorado, Boulder, CO, 80309, United States
[c] Department of Chemical and Biological Engineering, University of Colorado- Boulder, Boulder, CO, 80303, United States

ARTICLE INFO

Article history:
Received 31 October 2021
Received in revised form
3 February 2022
Accepted 7 February 2022
Available online 12 February 2022

ABSTRACT

Thiol-ene and thiol-yne photomediated conjugations have received substantial attention in research and in practice. Herein is presented the photodisulfidation of alkenes based on the radical-mediated 1:1 reaction of a disulfide and a vinyl ether, which provides an additional route for the formation of the types of sulfides seen in thiol-ene and thiol-yne polymers. Although similar linkages are formed, this approach starting with disulfides is expected to have benefits over the thiol-ene and thiol-yne reactions including extended shelf life of disulfides compared to thiols, reduced shrinkage stress, and increased refractive index of the resulting materials. It was determined that vinyl ethers were the only alkenes capable of undergoing photodisulfidation under ambient conditions and in reasonable timescales. The reaction between vinyl ethers and disulfides performed well in a variety of solvents providing modest to excellent yields (100% for bis(1-methylacetate) disulfide (DSMA)/triethyleneglycol divinylether (TEGDVE)) for numerous disulfide substrates evaluated. It was determined that the mechanism of the photodisulfidation reaction involves an auto-propagating cycle of thiyl radicals which add into either end of a vinyl ether to form thio-ether and thio-acetal linkages in the final product. Finally, although the reaction rate is slower than that of the thiol-ene reaction, the photodisulfidation reaction proceeds relatively rapidly under the explored conditions.

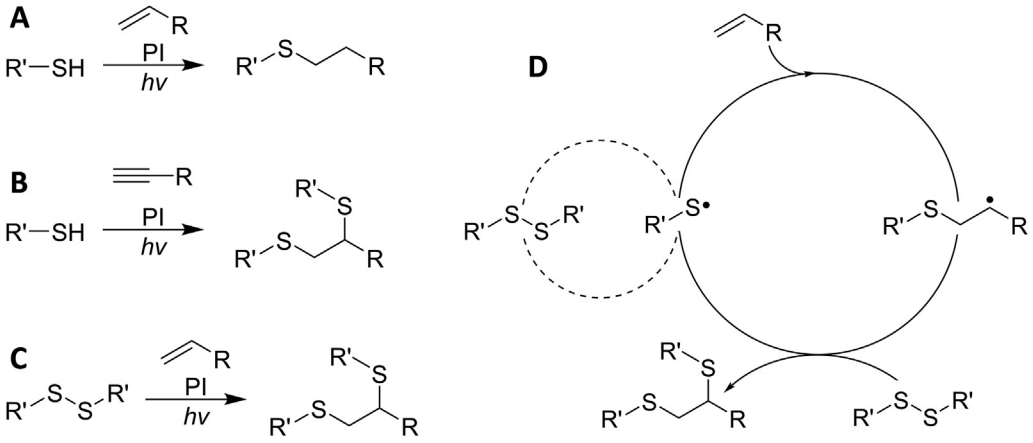
1. Introduction

The disulfidation of alkenes is a useful method for incorporating high ratios of sulfur to carbon in organic products. Sulfur based chemistries have been extensively explored in hydrogels and other polymer network formulations, rubber vulcanization, and ligation strategies [1,2]. Specifically, reactions involving thiol-X chemistries, including thiol-ene, thiol-yne, thiol-halide, and thiol-Michael reactions, have found use in materials applications for their chemoselectivity, click-like behavior, high atom efficiency, ability to react under mild conditions, and in their ability to form optical materials with high refractive indices (Scheme 1A, 1B) [3]. Thiol-X chemistries, however, often suffer from low shelf life stability due to spontaneous initiation, and have malodorous smells. In contrast, disulfides can be synthesized readily from essentially any thiol, are stable at ambient conditions and have more tolerable smells than thiols, while still being able to form similar linkages to thiol-X chemistries via a radical-mediated pathway (Scheme 1C, 1D). Additionally, the disulfide-ene reaction incorporates two sulfur atoms per carbon-carbon double bond from a single disulfide and may therefore be not only more efficient but also may result in materials with an even higher refractive index and reduced polymerization-induced shrinkage stress [4,5]. Moreover, the nearly quantitative yields, 100% atom economy, low energy input, negligible byproducts, and fast reaction rates observed in model studies portend utility in the broader organic synthesis field. This work is expected to expand the toolkit of radical-mediated photoreactions and find significant use as well in the development of novel materials, particularly in the optics field.

There are several methods previously reported that successfully catalyze the disulfidation of alkenes, including with catalysts such as I_2, and ruthenium or gallium complexes [6–10]. While these

* Corresponding author.
E-mail address: christopher.bowman@colorado.edu (C.N. Bowman).
[1] Indicates significant contributions from both authors.

https://doi.org/10.1016/j.tet.2022.132683
0040-4020/



Scheme 1. A) The radical-initiated thiol-ene reaction. B) The radical-initiated thiol-yne reaction. C) This work aims to develop and understand the radical-initiated disulfide-ene reaction. D) Radical-initiated autopropagation cycle of the photodisulfidation of alkenes wherein alternating thiyl propagation across carbon-carbon double bonds and chain transfer to disulfides results in the formation of thioether and thioacetal (for vinyl ethers) linkages.

catalytic methods are sufficient for small molecule applications, the need for solvent and diffusion of the catalyst makes these reactions less suitable for bulk material formulation via polymerization, where spatial and temporal control over the reaction is desired [11]. Work has also been done using free-radical methods to convert elemental sulfur (S_8) and other polysulfides into a variety of interesting materials using inverse vulcanization processes [12–14]. Limited work has also been done using UV irradiation to initiate thiyl radical mediated disulfidation of alkenes, notably between cyclic disulfides such as 1,2-dithiolane and 1,2-dithiane, but adequate substrate scopes and kinetics have yet to be explored for linear disulfides [15–20]. The combination of ease of synthesis for disulfides and spatio-temporal control over the reaction present a significant improvement over previously reported synthetic means for disulfidation. Herein, the photodisulfidation of alkenes using linear disulfides under ambient conditions, along with their reaction kinetics, are reported to identify suitable reaction conditions and disulfide and alkene monomers for use in photopolymerization reactions.

2. Results and discussion

The model reaction for the photo-disulfidation reaction was carried out between the disulfide DSMA and the divinyl ether TEGDVE with diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) as the photoinitiator. The reaction was performed at a stoichiometrically balanced ratio between disulfide and alkene (i.e. one disuflide per alkene) and irradiated with 405 nm light for 5 min (Scheme 3).

NMR data of the reaction (Fig. S3) show complete disappearance of the vinyl protons and appearance of a peak at ~4.8 ppm corresponding to the thioacetal linkage formed from reaction with the internal carbon of the original vinyl ether.

A solvent screen was performed to determine if there would be effects on the rate and final conversion of the reaction in various solvents (Fig. 1).

The reaction proceeded the fastest in $CDCl_3$ ($m = -1.99$ mol L^{-1} min^{-1}) and Acetone-D_6 ($m = -2.54$ mol L^{-1} min^{-1}), and at approximately the same rate in DMSO, MeOD and acetonitrile (slopes of conversion vs. time of 1.7 mol L^{-1} min^{-1}, 1.7 mol L^{-1} min^{-1}, and 1.5 mol L^{-1} min^{-1}, respectively). The differences in reaction rate did not correlate with either the relative polarities [23] or the class of solvent (i.e. protic versus aprotic) (Fig. S2). For these reasons it is likely that solvent effects have a negligible role in the observed rates of photo-disulfidation.

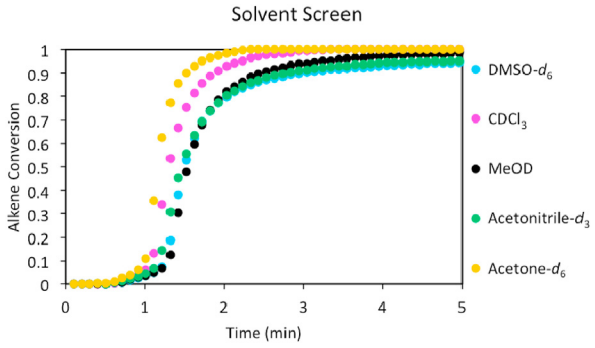
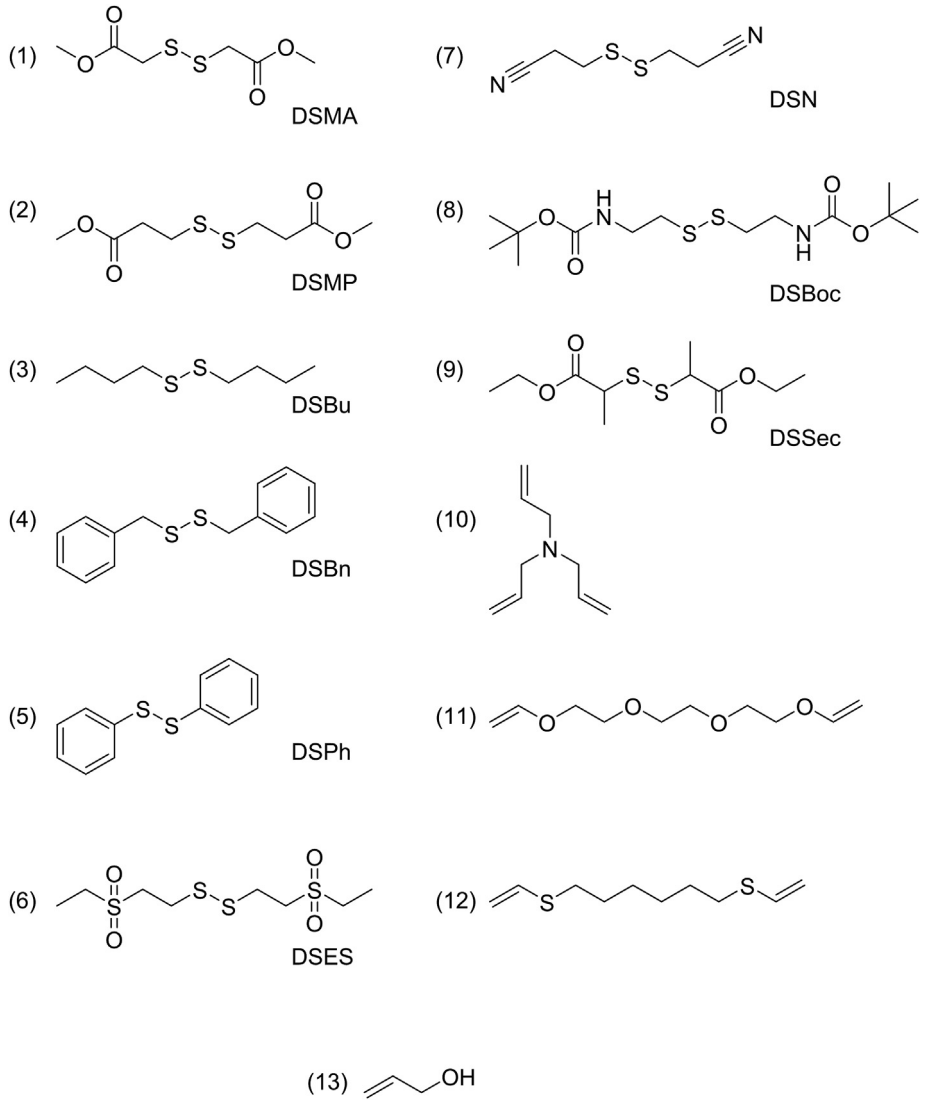


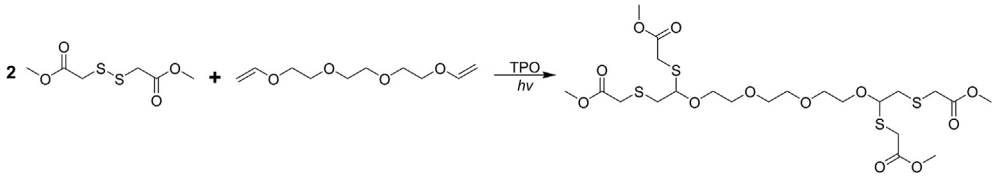
Fig. 1. Alkene conversion of TEGDVE with DSMA in various solvents as monitored by ATR-IR. Samples were formulated with an initial stoichiometric ratio of 1:1 disulfide:ene at a concentration of 2 M disulfide, and 1 M TEGDVE (2 M alkene), with 3 wt% TPO and were continuously irradiated beginning at 0.5 min with 10 mW/cm^2 of 405 nm light.

It was hypothesized that electron-withdrawing substituents near the disulfide bond would increase the rate and final conversion of the photodisulfidation reaction. To address this hypothesis a variety of disulfides were synthesized, including some made from thiols similar to those frequently used in radical thiol-ene couplings (Scheme 2). Reactions between these disulfides and TEGDVE were analyzed via FT-IR to explore the differences in their reaction rates and overall conversion (Fig. 2). Some of the synthesized disulfides were solids at room temperature or immiscible with TEGDVE, precluding neat reactions. To analyze the reactivity of these starting materials and to maintain consistent starting concentrations across reactions, all samples were dissolved in DMSO-D_6 at a concentration of 1 M for both disulfide and alkene.

Electron-withdrawing substituents near the disulfide bond generally increase the rate of reaction and final conversion of the alkene. This trend is best seen in the differences in reaction rate (determined by the slope of conversion in the linear regime, following exposure, but prior to the plateau of conversion) between DSMA ($m = -1.47$ mol L^{-1} min^{-1}), DSES ($m = -0.83$ mol L^{-1} min^{-1}), DSN ($m = -0.43$ mol L^{-1} min^{-1}), and DSMP ($m = -0.30$ mol L^{-1} min^{-1}). DSMA, which has a carbonyl on the beta carbon of the disulfide bond and is thus the least distance away from the disulfide, had the fastest reaction. DSES, DSN, and DSMP each have their electron withdrawing substituents the same



Scheme 2. Materials used: (1) bis(1-methylacetate) disulfide (DSMA), (2) bis(1-methylpropionate) disulfide (DSMP), (3) dibutyl disulfide (DSBu), (4) dibenzyl disulfide (DSBn), (5) diphenyl disulfide (DSPh), (6) bis(1-ethyl ethylsulfone) disuflide (DSES), (7) bis(1-ethyl-2-cyano) disulfide (DSN), (8) bis(1-ethyl tertbutylcarbonate) disulfide (DStBC), (9) bis(2-methylpropionate) disulfide (DSsec), (10) triallyl amine, (11) triethylene glycol divinyl ether (TEGDVE), (12) 1,6-hexanedivinylsulfide, and (13) allyl alcohol.



Scheme 3. Model reaction between DSMA and TEGDVE with 3 wt% TPO, irradiated at 405 nm, 10 mW/cm^2.

distance from the disulfide bond (gamma carbon). Therefore, their rates of reaction align with the relative strength of their electron withdrawing substituents: sulfone > nitrile > carbonyl. The rest of the disulfides investigated also follow this trend, with the slowest derivative being DSPh ($m = 0.0$ mol L^{-1} min^{-1}). A notable exception to this trend is the secondary disulfide (DSsec, $m = -0.15$ mol L^{-1} min^{-1}) in which the carbonyl is still in the beta position, but the rate is greatly decreased due to the methyl group adjacent to the disulfide, suggesting a steric effect on the photodisulfidaton reaction. A summary of the disulfides and their corresponding reaction rates are included in the supplemental information (Fig. S3). In addition, attempts were made to correlate the observed reaction rates with calculated bond dissociation energies of the disulfides but no apparent trend could be discerned.

Due to its rapid rate of reaction and quantitative conversion, DSMA was chosen as the model disulfide for subsequent experiments designed to explore the influence of various alkenes on the photodisulfidation reaction. Neat samples of DSMA and alkenes (10–13) with stoichiometric ratios of disulfide to alkene and 3 wt% TPO were continuously irradiated at 405 nm. Under ambient

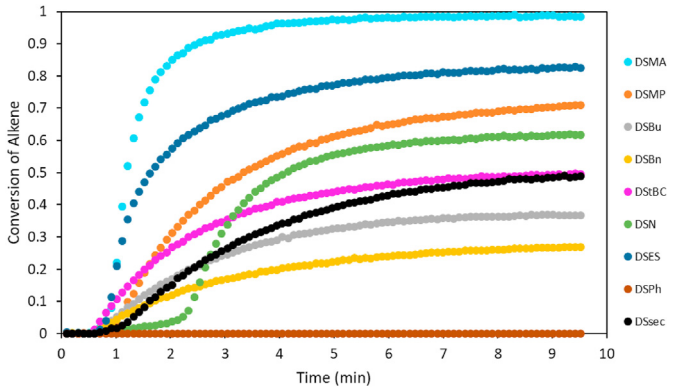


Fig. 2. Conversion of TEGDVE with various disulfides (1–9) in 1 M DMSO-D_6. Samples were formulated with a 1:1 ratio of disulfide to alkene, 3 wt% TPO and were continuously irradiated from 30s at 405 nm, 10 mW/cm^2. Final conversions were validated with ^{1}H NMR.

conditions the only alkene that had appreciable conversion was the vinyl ether, while the vinyl sulfide (12) and allyl-enes (10, 13) showed no appreciable conversions.

Finally, the kinetics and mechanism of the photodisulfidation reaction were explored. Neat samples of four representative disulfides and TEGDVE were combined stoichiometrically with 3 wt % TPO, and irradiated with 405 nm light for 10 min (Fig. 3). DSMA had both the fastest rate ($m = -3.00$ mol L^{-1} min^{-1}) and overall conversion of the disulfides tested, as was expected from the substrate scope experiments presented in Fig. 2. Additionally, compared to the same reaction performed at 1 M, the rate approximately doubles, further demonstrating the potential use of this reaction in bulk material formulation and polymerization. When irradiation was paused during the reaction, conversion of TEGDVE stopped almost immediately and very little additional conversion was seen until irradiation resumed likely due to the rapid radical-radical termination reaction (Fig. S1). DSMA was thus chosen as the model disulfide for our investigation into the kinetics and mechanism of the photodisulfidation reaction.

Samples of TEGDVE and DSMA were formulated at various concentrations of both alkene and disulfide, and their conversions and rates were measured with FT-IR (Fig. 4). The presumed rate law follows the proposed, analogous thiol-ene mechanism and thus leads to an expression for reaction rate functionally identical to that established for thiol-ene. Therefore, a generalized rate expression for the disulfide-ene reaction is presumed to be $r = k[\mathrm{S-S}]^a[E]^{1-a}$,

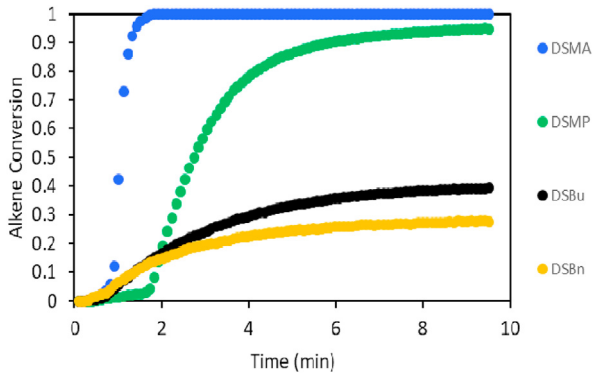


Fig. 3. Conversion of neat samples of TEGDVE with various disulfides (1–9). Samples were formulated with a 1:1 ratio of disulfide to alkene, 3 wt% TPO and were continuously irradiated from 30s at 405 nm, 10 mW/cm^2. Final conversions were validated with ^{1}H NMR.

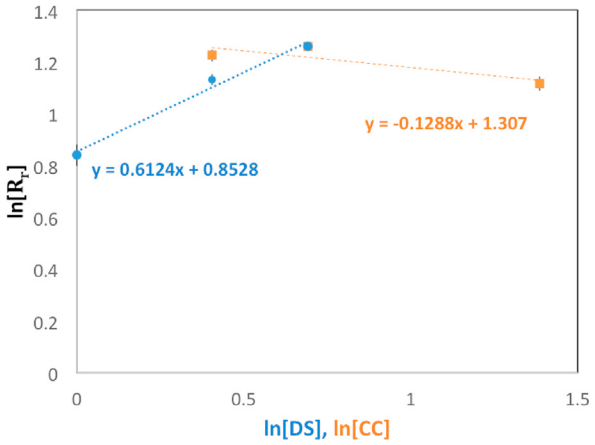


Fig. 4. Log-log plot of initial reaction rate versus initial concentration of disulfide (blue line, at 2.0 M alkene) and alkene (orange line, at 2.0 M disulfide). Samples were formulated with 0.086 M TPO, using ethyleneglycol diacetate (EGDA) as a diluent, and were continuously irradiated from 30s at 405 nm, 10 mW/cm^2. Conversion was measured using FT-IR The respective reaction orders are given by the slope of the lines of best fit.

where [S–S] and [E] are the concentrations of disulfide and alkene, respectively. Regression analysis shown in Fig. 4 shows a strong rate dependence with respect to the disulfide concentration ($a = 0.61\pm0.08$) and a near zero order reaction with respect to the alkene ($b = -0.12\pm0.07$) indicating that the rate-limiting step in the disulfide-ene reaction is the chain transfer step where the carbon-centered radical reacts with a disulfide to form the dithioether and a new thiyl radical. While these values do not align precisely as expected for a first order reaction, we attribute these discrepancies to inherent uncertainties of these measurements and sensitivities of the subsequent calculations, though we cannot rule out contributions from side reactions. The overall trend, however, is consistent with our prior results and suggests a much stronger effect on the rate of reaction from changes in the disulfide concentration compared to changes in the alkene concentration.

For thiol-ene reactions that are chain transfer limited, the radical that is formed from the addition step is somewhat stable, and therefore slower to abstract a thiol hydrogen [21]. The proposed mechanism of the disulfide-ene reaction (Scheme 1D) closely follows that of the thiol-ene reaction with an overall product resembling that of the thiol-yne reaction (SI Fig. 4), and it is expected that the formation of a new thiyl radical from the disulfide is now responsible for the slower reaction rate at this step (Scheme 1D) [22]. This retardation relative to thiol-ene couplings may be attributed to steric effects from the disulfide bond compared to the sulfur-hydrogen bond, which considerably hinders chain transfer to disulfides.

Additional evidence that the disulfide-ene reaction is chain transfer limited is seen in the trend for rate and final conversion of the disulfides used in this study (Fig. 2). Electron withdrawing groups near the disulfide bond destabilize the already electron-deficient thiyl radical that is formed in the chain transfer step (Scheme 1D). The less stable this resulting radical is, the faster it reacts in the propagation step. A balance therefore exists for the stability of this radical in both its ability to initially form, and its subsequent reaction. If the thiyl radical is too unstable, the chain transfer to the next disulfide will not proceed sufficiently fast, but if it is too stable, then the propagation to the alkene after that step will be hindered instead.

Similar radical stability arguments may help explain the observed difference in reactivity of disulfides between vinyl ethers

and allyl amine and allyl alcohol. The radical formed from vinyl ethers is more stable than the radical formed from allyl amine or allyl alcohol due to stabilization from the adjacent oxygen lone pairs. Since the chain transfer step for the disulfide-ene reaction is slower in comparison to that of the thiol-ene, this more persistent radical from the vinyl ether is necessary to observe product formation under these conditions. The shorter-lived allyl radical, in comparison, may undergo other radical pathways before chain transfer occurs. Since no obvious side products were observed with NMR, it is expected that reversion back to the original thiyl radical and alkene dominates this process.

3. Conclusions

The photodisulfidation of alkenes was explored in both substrate scope and kinetics. Using low amounts (2–3%) of photoinitiator and low light intensities (10 mW/cm^2), rapid conversion of vinyl ethers and electron deficient disulfides was demonstrated up to near quantitative conversions of alkene, and with no appreciable solvent effect. While many disulfides were useable in this reaction, only vinyl ethers showed appreciable conversions under the conditions tested, prompting further studies into expanding the alkene scope of this reaction. NMR and mass spectrometry data confirm the appearance of thioacetal and thioether peaks, and overall mass corresponding to the proposed product for this reaction. The photodisulfidation reaction rate was found to depend primarily on disulfide concentration, indicating that the reaction is chain-transfer limited. The photodisulfidation of alkenes provides an efficient route to accessing compounds with high sulfur content. Further development of this reaction, and exploration into its use for photopolymerizations will allow development of novel materials that are expected to have a variety of desirable applications.

4. Experimental section

Methyl thioglycolate, benzyl mercaptan, acrylonitrile, triethylenegylcol divinyl ether were purchased from TCI chemicals, and methyl-3-mercaptopropionate, 1-butanethiol, thiophenol, ethyl vinyl sulfone, cysteamine, ethyl-2-mercaptopropionate, triallylamine, 1,6-hexanedithiol were purchased from Sigma-Aldrich. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), a near-UV active photoinitiator was obtained from Sigma-Aldrich.

^{1}*H-NMR* and ^{13}*C-NMR* spectra were recorded on a Bruker 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ). The δ scale was referenced to the residual proton content of various deuterated solvents, indicated in the respective measurement.

Attenuated total reflection infrared spectroscopy (ATR-IR): Reaction kinetics were analyzed using a ATR-IR spectrometer (Nicolet iS50 FTIR spectrometer with Smart iTR ATR accessory, diamond plate). Irradiation was accomplished using an ActicureHg (Xe) lamp (EXFO) with a 405 nm bandgap filter. The light intensity used was 10 mW/cm^2. The real time functional group conversion of the alkene was measured by the IR peak area decreasing at 1580 cm^{-1}-1650cm^{-1} and was calculated as the ratio of real-time peak area to the peak area of the unirradiated spectra.

5. Synthesis of disulfides

The disulfides used in this study were synthesized from their respective thiols with the following general procedure: To a solution of thiol (1 equiv) in EtOH (0.3 M) was added NaI (0.01equiv) and 30% H_2O_2 (1 equiv). The mixture was allowed to stir at room temperature for 18 h, after which the reaction was quenched by addition of sodium thiosulfate (aq.) (~15 mL) until no further color change was observed. The mixture was concentrated to remove EtOH, and then the aqueous mixture was extracted with EtOAc (150 mL, 3X). The organic layer was then washed with H_2O, and brine (1X), dried with Na_2SO_4, and the solvent was removed under reduced pressure to give the disulfide products (1–9). Disulfides that required further purification were purified using column chromatography with EtOAc/Hexanes solvent systems ranging from 10 to 60% EtOAc (See Supporting Information).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors gratefully acknowledge DARPA (DARPA grant: W911NF1920024) and the National Science Foundation (NSF grant: CHE 1808484) for funding this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2022.132683.

References

[1] D.A. Boyd, Sulfur and its role in modern materials science, Angew. Chem. Int. Ed. Engl. 55 (50) (2016) 15486–15502, https://doi.org/10.1002/anie.201604615.
[2] M.H. Stenzel, Bioconjugation using thiols: old chemistry rediscovered to connect polymers with nature's building blocks, ACS Macro Lett. 2 (1) (2013) 14–18, https://doi.org/10.1021/mz3005814.
[3] C.E. Hoyle, A.B. Lowe, C.N. Bowman, Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis, Chem. Soc. Rev. 39 (4) (2010) 1355–1387, https://doi.org/10.1039/b901979k.
[4] C.N. Bowman, C.J. Kloxin, Toward an enhanced understanding and implementation of photopolymerization reactions, AIChE J. 54 (11) (2008) 2775–2795, https://doi.org/10.1002/aic.11678.
[5] S. Ye, N.B. Cramer, I.R. Smith, K.R. Voigt, C.N. Bowman, Reaction kinetics and reduced shrinkage stress of thiol-yne-methacrylate and thiol-yne-acrylate ternary systems, Macromolecules 44 (23) (2011) 9084–9090, https://doi.org/10.1021/ma2018809.
[6] X.R. Wang, F. Chen, Iodine-catalyzed disulfidation of alkenes, Tetrahedron 67 (25) (2011) 4547–4551, https://doi.org/10.1016/j.tet.2011.04.081.
[7] S.I. Usugi, H. Yorimitsu, H. Shinokubo, K. Oshima, Disulfidation of alkynes and alkenes with gallium trichloride, Org. Lett. 6 (4) (2004) 601–603, https://doi.org/10.1021/ol036391e.
[8] M.C. Caserio, C.L. Fisher, J.K. Kim, Boron trifluoride catalyzed addition of disulfides to alkenes, J. Org. Chem. 50 (22) (1985) 4390–4393, https://doi.org/10.1021/jo00222a041.
[9] T. Kitamura, H. Taniguchi, Perkin communications, Spectroscopy 50 (30) (1991) 1607–1608.
[10] K. Matsumoto, S. Fujie, S. Suga, T. Nokami, J.I. Yoshida, Addition of ArSSAr to dienes via intramolecular C-C bond formation initiated by a catalytic amount of ArS+, Chem. Commun 36 (2009) 5448–5450, https://doi.org/10.1039/b910821a.
[11] Y. Yagci, S. Jockusch, N.J. Turro, Photoinitiated polymerization: advances, challenges, and opportunities, Macromolecules 43 (15) (2010) 6245–6260, https://doi.org/10.1021/ma1007545.
[12] Y. Zhang, R.S. Glass, K. Char, J. Pyun, Recent advances in the polymerization of elemental sulphur, inverse vulcanization and methods to obtain functional chalcogenide hybrid inorganic/organic polymers (CHIPs), Polym. Chem. 10 (30) (2019) 4078–4105, https://doi.org/10.1039/c9py00636b.
[13] J.J. Griebel, R.S. Glass, K. Char, J. Pyun, Polymerizations with elemental sulfur: a novel route to high sulfur content polymers for sustainability, energy and defense, Prog. Polym. Sci. 58 (2016) 90–125, https://doi.org/10.1016/j.progpolymsci.2016.04.003.
[14] X. Wu, J.A. Smith, S. Petcher, B. Zhang, D.J. Parker, J.M. Griffin, T. Hasell, Catalytic inverse vulcanization, Nat. Commun. 10 (1) (2019) 1–9, https://doi.org/10.1038/s41467-019-08430-8.
[15] M.E. Kuehne, R.E. Damon, Thiyl radical induced cyclizations of dienes. Cyclization of α-acoradiene, α-bulnesene, and geranyl acetate to cedrane, patchulane, and cyclogeranyl acetate products, J. Org. Chem. 42 (11) (1977) 1825–1832, https://doi.org/10.1021/jo00431a001.

[16] C. Tong, J.A.J. Wondergem, D. Heinrich, R.E. Kieltyka, Photopatternable, branched polymer hydrogels based on linear macromonomers for 3D cell culture applications, ACS Macro Lett. (2020) 882–888, https://doi.org/10.1021/acsmacrolett.0c00175.
[17] H. Tang, N.V. Tsarevsky, Lipoates as building blocks of sulfur-containing branched macromolecules, Polym. Chem. 6 (39) (2015) 6936–6945, https://doi.org/10.1039/c5py01005e.
[18] G. Gasparini, E.K. Bang, G. Molinard, D.V. Tulumello, S. Ward, S.O. Kelley, A. Roux, N. Sakai, S. Matile, Cellular uptake of substrate-initiated cell-penetrating poly(disulfide)S, J. Am. Chem. Soc. 136 (16) (2014) 6069–6074, https://doi.org/10.1021/ja501581b.
[19] J. Fang, S.H. Ye, J. Wang, T. Zhao, X. Mo, W.R. Wagner, Thiol click modification of cyclic disulfide containing biodegradable polyurethane urea elastomers, Biomacromolecules 16 (5) (2015) 1622–1633, https://doi.org/10.1021/acs.biomac.5b00192.
[20] D.W.A. Sharp, G. Haran, J.C.S. Perkin I. 34 (1967).
[21] N.B. Cramer, S.K. Reddy, A.K. O'Brien, C.N. Bowman, Thiol - ene photopolymerization mechanism and rate limiting step changes for various vinyl functional group chemistries, Macromolecules 36 (21) (2003) 7964–7969, https://doi.org/10.1021/ma034667s.
[22] B.D. Fairbanks, T.F. Scott, C.J. Kloxin, K.S. Anseth, C.N. Bowman, Thiol-yne photopolymerizations: novel mechanism, kinetics, and step-growth formation of highly cross-linked networks, Macromolecules 42 (1) (2009) 211–217, https://doi.org/10.1021/ma801903w.
[23] L.R. Snyder, Classification of the solvent properties of common liquids, J. Chromatogr. 92 (1978) 223–234.