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Mechanistic Kinetic Modeling of Thiol–Michael Addition Photopolymerizations via Photocaged “Superbase” Generators: An Analytical Approach

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Abstract

A kinetic mechanism and the accompanying mathematical framework are presented for base-mediated thiol–Michael photopolymerization kinetics involving a photobase generator. Here, model kinetic predictions demonstrate excellent agreement with a representative experimental system composed of 2-(2-nitrophenyl)propyloxycarbonyl-1,1,3,3-tetramethylguanidine (NPPOC-TMG) as a photobase generator that is used to initiate thiol–vinyl sulfone Michael addition reactions and polymerizations. Modeling equations derived from a basic mechanistic scheme indicate overall polymerization rates that follow a pseudo-first-order kinetic process in the base and coreactant concentrations, controlled by the ratio of the propagation to chain-transfer kinetic parameters (k_p/k_{CT}) which is dictated by the rate-limiting step and controls the time necessary to reach gelation. Gelation occurs earlier as the k_p/k_{CT} ratio reaches a critical value, wherefrom gel times become nearly independent of k_p/k_{CT} . The theoretical approach allowed determining the effect of induction time on the reaction kinetics due to initial acid–base neutralization for the photogenerated base caused by the presence of protic contaminants. Such inhibition kinetics may be challenging for reaction systems that require high curing rates but are relevant for chemical systems that need to remain kinetically dormant until activated although at the ultimate cost of lower polymerization rates. The pure step-growth character of this living polymerization and the exhibited kinetics provide unique potential for extended dark-cure reactions and uniform material properties. The general kinetic model is applicable to photobase initiators where photolysis follows a unimolecular cleavage process releasing a strong base catalyst without cogeneration of intermediate radical species.

Graphical abstract

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ASSOCIATED CONTENT

Supporting Information

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Experimental kinetic data, methodology, and derivation of analytical equations (PDF)

The authors declare no competing financial interest.

INTRODUCTION

Owing to the widespread commercial availability of free-radical photoinitiators, photocuring of multifunctional thiol–ene monomers offers a robust technique for the rapid fabrication of highly cross-linked networks by irradiating photosensitive molecules with high energy light, typically in the spectral ultraviolet (UV) band.¹ Thiol–ene photopolymerizations generally proceed via a step- or mixed-mode step/chain-growth radical mechanism, depending on the specific ene selected, and exhibit reaction kinetics strongly dependent on the electronic density of the ene (electron-rich vs electron-poor) as well as thiol/ene structures.^{2–5} These intrinsic features clearly dictate the “click” character of thiol–ene reactions. Nevertheless, thiol–vinyl addition reactions are not limited exclusively to radical-mediated processes as they can also proceed via a thiol–Michael mechanism, which involves anionic centers as reactive intermediates. For instance, the base- or nucleophile-catalyzed thiol–Michael addition reaction proceeds exclusively via a two-step anionic pathway, thus without any possibility for competing homopropagation of the vinyl group, which is often an undesirable side reaction in stoichiometric thiol–ene photopolymerizations, particularly for acrylates. Interestingly, despite the different catalysts and mechanisms, the product of both the ideal radical-mediated thiol–ene and anion-mediated thiol–Michael reactions is the very same β -thioether coupled product (C–S bond).⁶

The major difference between base and nucleophile catalysts resides in the initiation process related with the production of thiolate anions (RS^-) resulting from deprotonation of a thiol (Michael donor). Strong base catalysts, such as tertiary amines, pick up the hydrogen atom directly from the thiol, whereas in the case of nucleophile catalysts, such as phosphines and primary (or secondary) amines, an intermediary zwitterionic enolate species is formed instead via nucleophilic attack to an electron-deficient vinyl (Michael acceptor), which in turn deprotonates the thiol ascribed to the strong basic character of zwitterions.^{7–9} In this case, substitution of the base catalyst by a strong nucleophile allows the initiation kinetics to be virtually independent of the thiol’s pK_a , resulting in superior reaction rates at extremely low catalyst loadings, when contrasted to amine-based catalysts.⁶

As it follows a pure step-growth mechanism, polymerization via a thiol–Michael addition process results in (nearly) ideal homogeneous network structures, reduced volume shrinkage, and shrinkage stress development due to delayed gelation, as well as high functional group conversions leading to potentially limited amount of elutable material when

multifunctional monomers are reacted.^{9–12} For this reason, this particular thiol–X “click” reaction, namely the thiol–vinyl sulfone Michael addition reaction, is becoming attractive in the context of the formation of high modulus, high T_g materials for applications such as coatings, dental restorative materials, shape memory materials, and composites.^{13,14} In addition to the unique potential for long-term dark-cure capability, the reaction is also insensitive to inhibition by oxygen and is readily performed in benign/mild reaction conditions. Despite these benefits, the lack of efficient photoinitiation systems has limited the applicability of thiol–Michael addition reactions toward creation of cross-linked polymers that could provide spatiotemporal control over the course of the reaction (cure-on-demand), while simultaneously benefiting from the unique attributes of step-growth polymers.

The most favorable approach to initiate thiol–Michael addition photopolymerizations relies on the photochemical generation of superbase catalysts such as tertiary amines, guanidine, or bicyclic amidine bases by means of light irradiation, often ultraviolet (UV), in a manner similar to well-accepted photoacid generators (PAG's) established within the fields of cationic UV-curing and microlithography technologies.^{15,16} *O*-Nitrobenzyl carbamate derivatives, *O*-acyloximes, quaternary ammonium salts (QA-salts),¹⁷ and cobalt(III) amine complexes^{18,19} have all been reported to be useful photobase generators (PBG's) for a variety of anionic photopolymerization chemistries not involving electron-deficient vinyls.

For instance, Allonas and co-workers²⁰ have reported the development of new type of highly efficient PBG's in the form of QA-salts of phenylglyoxylic acid (PA) that liberate strong bases upon exposure to UV-light. The photoreleased bases were cyclohexylamine (CHA), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and 1,1,3,3-tetramethylguanidine (TMG). The catalytic power of these bases was successfully tested in the cross-linking of an epoxide resin, without the need for postexposure baking, in the presence and absence of ethylene glycol di(3-mercaptopropionate) (GDMP) as hydrogen-donating agent. Addition of this dithiol to all photocatalyst systems led to an effective enhancement of the polymerization performance due to formation of a highly reactive nucleophilic thiolate anion upon the base-mediated thiol deprotonation reaction. In a previous report,²¹ the same authors demonstrated the applicability of a strong photobase generator composed of tetramethylguanidine–phenylglyoxylate as an ion pair to the UV-induced photopolymerization of epoxidized hydrogenated bisphenol A and thiol–isocyanate resins. The release of a highly basic TMG molecule led to complete homopolymerization of the epoxide monomer resin as well as the rapid formation of a polythiourethane polymer network.

In an early study, Hanson et al.²² have utilized the same concept in photoresist and polymer curing applications using QA-salt PBG's involving trimethylbenzhydrylammonium or trimethylfluorenylammonium iodides and triethylamine (TEA) reporting encouraging results. Photochemical dissociation of *N,N,N*-trimethylbenzhydrylammonium iodide, quaternary ammonium carboxylic acid, and quaternary ammonium borates have also been reported to generate tertiary amines.¹⁵ Other thermally stable QA salts bearing onium moieties derived *N*-methylpiperidine or DABCO and an *N,N*-dimethyl-dithiocarbamate

anion also proved useful PBGs in photoinitiated thermal insolubilization of epoxides based on poly-(glycidyl methacrylate).¹⁵

Recently, Sun et al.²³ have reported bicyclic guanidinium tetraphenylborate as a novel PBG to yield 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a superbase catalyst. Although the tetraphenylborate moiety represents an attractive chromophore, the quantum yield ($\phi_{254} = 0.18$) is not very high. Ketoprofen derivatives, in alternative, offer many advantages such as high quantum yield ($\phi_{313} = 0.75$) but suffer from poor absorption above 300 nm. In response to these limitations, Arimitsu and Endo have in a recent communication²⁴ designed several novel PBG's based on xanthone acetic acid ($\phi_{350} = 0.64$) combined with a series of strong base catalysts, including TBD, which also underwent photodecarboxylation reactions with satisfactory quantum yield (TBD, $\phi_{350} = 0.38$). A novel anionic thiol–epoxy UV-curing system based on each PBG was developed without the conventional requirement for post-thermal treatment while affording film materials with excellent transparency and essentially no volume shrinkage. More details regarding photolabile base generators can be found in the papers by Dietliker^{16,25} and Shirai.¹⁷

Several useful strategies have been developed toward the formation of cross-linked polymers directly from the anionic thiol–Michael addition pathway, yet offer only partial solutions. For example, temporal control of the polymerization kinetics at the onset has been accomplished via a time-clock (delay) mechanism by judiciously reacting an electron-deficient vinyl, a nucleophile, and an acid, providing predictable induction times relevant for the development of thiol–Michael networks without sacrificing the progress of the polymerization, once initiated.²⁶ Another advancement involves a visible-light base generating system based on isopropylthioxanthone/triazabicyclodecene tetraphenylborate (ITX/TBD-HBPh₄), an ionic complex, supplemented with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a radical inhibitor.²⁷ This hybrid photoinitiation system was shown to suppress the vinyl radical homopropagation pathway and provided full stoichiometric conversion of both thiol/vinyl functional groups, thus offering a viable chemical route toward low-energy visible-light-initiated Michael-type network-forming systems.

Although most photobase generators found in the literature show effective applicability in epoxy, thiol–epoxy, and thiol–isocyanate photopolymerizations, they have limited potential for implementation in thiol–Michael addition systems. This result is mainly attributed to the production of intermediary radical species during the photoinduced dissociation process leading to the development of a competitive vinyl homopropagation route to which thiol–Michael additions are greatly sensitive. Particular cases are photobase generators coexisting in the form of ionic complexes (e.g., QA salts with borate ions), which also suffer from poor solubility in nonpolar or low polarity thiol–Michael comonomer systems, and some covalently linked photobases (e.g., carbamates, *O*-carbamoyloximes, *O*-acyloximes and α -aminoketone).^{17,21} Therefore, designing photobase generators that do not produce any intermediate radicals during photoinitiation would be greatly advantageous within the context of base-catalyzed thiol–Michael photopolymerizations.

One strategy is the covalent attachment of bases to photolabile protecting groups of the 2-nitrobenzyl or coumarin types.^{28–30} Xi et al.²⁸ demonstrated that a covalently linked

photolabile primary amine catalyst, namely 2-(2-nitrophenyl)-propyloxycarbonyl (NPPOC)-hexylamine, efficiently triggers the thiol–acrylate Michael addition via a nucleophile-initiated pathway upon exposure to UV-irradiation. In the photolysis step, release of hexylamine allowed for yields greater than 90% of the β -thioether adduct when simple thiols of the propionate/glycolate-ester types and 2-mercaptoethanol were reacted with methyl acrylate after 1 h of illumination and a photocatalyst loading of just 5 mol %. The same photobase demonstrated successful applicability in the formation of thiol–Michael networks by photopolymerizing tetrathiols and diacrylate comonomers. Along the lines with this previous work, Xi et al.²⁹ further developed a new range of more potent thiol–Michael photobase catalysts, including 6-nitroveratroyloxycarbonyl (NVOC)-amine and NPPOC-amine compounds, and demonstrated the same spatiotemporal control concept onto the fabrication of dual stage thiol–Michael networks as well as surface photopatterning. More recently, Zhang and coworkers³⁰ synthesized a coumarin-coupled TMG photobase generator for visible-light (400–500 nm) curing applications demonstrating equimolar conversion of thiol/vinyl functional groups by reacting pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) with divinyl sulfone (DVS), which also produced homogeneous thiol–Michael polymer networks. The photobase developed was also proven effective toward a thiol–epoxy step-growth photopolymerization system using stoichiometric formulations of the same tetrafunctional thiol and bisphenol A diglycidyl ether accompanied by visible-light irradiation.

Although it would be desirable the development of stable photocaged nucleophiles (amine or phosphine initiators) as efficient triggers for thiol–Michael photopolymerizations,⁹ the strategy involving photolabile superbases generators (PBG's) provides, to date, the best method to initiate the reaction in a controlled manner. PBG's, such as 2-(2-nitrophenyl)propyloxycarbonyl-1,1,3,3-tetramethylguanidine (NPPOC-TMG) and coumarin-TMG, have also shown to exhibit very low basicity when the base is under protection and remain relatively stable within formulated monomer mixtures, but once photocleaved led to a dramatic increase in basicity of the released organobase, allowing the reaction to proceed in a living fashion even at extremely low amounts of the free TMG.^{29,30}

The base-catalyzed Michael addition reaction has been extensively studied for decades;^{31,32} however, none of the kinetic studies available in the literature appear to involve a detailed examination or modeling of the reaction kinetics and mechanism using a superbases photogenerator as the initiation system. Given the promising new achievements in the development of photocaged amines^{28–30} as efficient catalyst precursors for thiol–Michael additions, here is reported for the first time a novel physicochemical model proposed for this reaction involving a photobase UV-initiator, e.g., NPPOC-TMG. Modeling equations are developed using the established two-step reaction mechanism for the catalytic cycle coupled with photoinitiation kinetics, and reasonable predictions are made with respect to the overall kinetic behavior prior to the onset of gelation, under a variety of circumstances. Analytical methodologies for measuring the kinetic parameters are also presented. We are confident that this comprehensive kinetic study will enhance upon the understanding of the fundamental phenomena, driving mechanisms and primary factors affecting thiol–Michael photopolymerizations establishing limits and aid at providing useful guidelines for future research in the field.

THEORETICAL MODEL DEVELOPMENT

Kinetic Mechanism

The proposed multistep mechanism for the photoinduced thiol–Michael reaction is detailed in Scheme 1. Thiol–Michael additions are known to proceed exclusively via a sequential two-step anionic mechanism that propagates by chain transfer, which means a competitive propagation/chain-transfer process must occur, with one of the elementary reaction steps often becoming rate-limiting. This catalytic cycle mirrors that of the conventional thiol–ene radical mechanism involving single-substituted electron-rich olefins and norbornenes but excludes occurrence of self- and cross-termination reactions by bimolecular (re)combination of the intermediate species.

Steps 1 and 2 are initiation steps whereas steps 3 and 4 are coupled via reactive intermediates corresponding to the anionic propagation cycle. Step 1 accounts for the photochemical cleavage of a photolabile base generator (PB), such as NPPOC-TMG (used herein as reference model photoinitiator), whereupon UV-light excitation releases a strong Lewis base B (1,1,3,3-tetramethylguanidine/TMG, $pK_a \sim 13.6^a$)³³ serving as precatalyst for the reaction. An efficiency factor f , in the range of $0 < f < 1$, is included in the model since immediately after photolysis formation of base is accompanied by decarboxylation of a TMG-based complex intermediate. An efficient visible-light-sensitive coumarin-coupled TMG photobase generator has been recently developed following a similar decarboxylation process following photocleavage.^{28–30} Step 2 determines the extent of thiolate anion (RS^-) production resulting from reversible thiol (RSH) deprotonation promoted by the base, along with generation of a conjugated acid (HB^+). The thiolate anion is generally considered a potent nucleophile which efficiently adds across the electron-deficient β -carbon of an electrophilic vinyl (e.g., (meth)acrylate, (meth)acrylamide, vinyl sulfone, maleimide, unsaturated ketones, nitroalkenes, carboxylic- and cyano-olefins, etc.)³⁴ to produce a reactive carbon-centered anion intermediate (RC^-) at the α -position (step 3). This carbanion, being an exceptionally strong base, can either deprotonate the conjugated acid regenerating the initial base catalyst (step 5) or dehydrogenate another thiol that renews the thiolate anion (step 4) to yield, in both cases, a neutral thioether (β -C–S) addition product (P) with anti-Markovnikov orientation.^{9,35} Cumulative research has found that the reaction kinetics and final yield of the β -thioether product are strongly dependent on the concentration and basicity of the base catalyst, the acidity/ pK_a of the thiol, steric bulk accessibility of the thiol structure, and the chemical character (strength) of the electron-withdrawing group (EWG) that activates the double bond.^{6,9} In the occasion of a bimolecular termination mechanism caused by preferential reaction of the released base with trace protic contaminants (designated here in the general form of a monoprotic HA species) that may be present initially in the reaction medium (e.g., water, acids or protic solvents),³⁶ the original mechanism proposed in Scheme 1 will be affected by an “acid–base” neutralization reaction (step 6), which limits the availability of base catalyst for step 2:

^aRelative to the conjugated acid (tetramethylguanidinium ion, HTMG⁺). A pK_a value of 23.3 relative to HTMG⁺ has also been reported in CH₃CN solvent.⁵⁵

where k_t^+ and k_t^- denote second-order rate constants for the forward and reverse reactions of the chemical equilibrium, respectively, and A^- will be designated an inactive anionic species.

Initiation Kinetics

The rate of photoinitiation, R_i , in an optically thin film where the light intensity is uniform throughout is found to be

$$R_i = \left(\frac{d[B]_t}{dt} \right)_i = \xi_i [PB]_t = \xi_i [PB]_0 e^{-z_i t} \quad (1)$$

$$z_i = \frac{\ln(10) \phi_\lambda \varepsilon_\lambda \lambda}{N_{Av} h c} I_{inc} \quad (2)$$

where $[B]_t$ and $[PB]_t$ denote molar concentrations of base and photobase initiator at time t , respectively, $[PB]_0$ is the initial molarity of photobase, and z_i (in s^{-1}) is referred herein to as a lumped photochemical term, which is directly proportional to the incident light intensity (I_{inc} , in units of mW/cm^2) but independent of temperature and, hence, not an Arrhenius parameter. Note that although this photochemical term and $\xi_i = fz_i$ are not recognizable as conventional rate coefficients, they can be included in the rates of photolysis and initiation in a similar manner (under given photochemical conditions), as they retain the same units. This incorporation is necessary to model the reaction mechanism (see system of ordinary differential equations in Table 1). Equation 1 describes the evolution in base concentration over time resulting from the cleavage of photobase, allowing R_i to vary continuously as a first-order kinetic process. In the simplest case, the initiation rate is changed by varying the incident light intensity while the initiator concentration is held constant. Therefore, by exposing a photobase solution to different light intensities, individual values of $z_i = \alpha I_{inc}$ can be estimated from experiments by measuring in real-time the temporal dissociation of photobase (see Figures S1–S3 of the Supporting Information). The quantum yield of photolysis, taken in neat ethylene glycol di(3-mercaptopropionate) (GDMP) monomer, was calculated by means of eq 2 as $\phi_\lambda = 0.24 \pm 0.01$, using standard values for NPPOC-TMG at a wavelength λ of 365 nm light (efficiency: $f = 1$; molar absorptivity coefficient:²⁹ $\varepsilon_\lambda = 240 \text{ L mol}^{-1} \text{ cm}^{-1}$) and Planck's law ($E = N_{Av} h c$), with physical constants N_{Av} = Avogadro's number, h = Planck's constant, and c = speed of light in a vacuum. The quantum yield obtained is analogous to the value reported by Xi and co-workers ($\phi_{chem} = 0.15$) for the same photocaged superbase catalyst, although the authors used a different experimental setup and calculation method.²⁹ Since optically thin samples are simulated and were tested

experimentally, both the photobase concentration and UV-light irradiance are presumed to be independent of film thickness.

Reaction Kinetics

By developing material balances for all chemical species involved in the reaction mechanism (Scheme 1) with acid–base neutralization included (step 6), the individual species rates are readily expressed in terms of a system of coupled differential equations, as listed in Table 1. Molar concentrations of chemical species are represented by square brackets, and the proportionality constants (except for α_i and ξ_i) denote intrinsic rate coefficients of the elementary reactions in the mechanism, each obeying the Arrhenius relation and assumed to be conversion and mobility independent for the purpose of this model development. For practical purposes, these autonomous rate balance equations are simultaneously integrated for each species concentration as a function of time using a numerical solver, such as COPASI,^{37,38} subject to the specified initial conditions. However, to derive analytically a general mechanistic rate equation that is able to capture the principal kinetic behavior of the reaction, without considering the full complexity of the detailed mechanism, certain simplifying assumptions are necessary. For instance, while the thiol concentration is accounted for in steps 2 and 4 and the carbanion concentration appears in steps 3–5, the mechanistic model can be reduced by suppression of step 5 and supposing that every thiol participates only in the chain-transfer reaction (step 4) since only small amounts of photobase (2.0 wt %) are often used relative to the total amount of monomers, analogously to radical initiators utilized in conventional thiol–ene photopolymerizations. These two basic assumptions are supported by the prevalence of the anionic propagation cycle kinetics over initiation once a catalytic amount of thiolate anion is generated as a result of step 2. As noted, implicit in our model system definition is also the assumption that the mechanism reflects the kinetics of the curing process in its early stages, i.e., when the influence of diffusive mass transport on the kinetics is minimal³⁹ and there is negligible heat accumulation caused by the reaction exotherm combined with delivered UV-light which can lead to an accelerated increase in the reaction rate via thermal feedback. Therefore, the polymerizing sample is taken to be isothermal, and the temperature does not change as the reaction progresses. Under these ideal conditions the kinetic parameters in all model equations are assumed to remain constant throughout the reaction.

In step 2, the magnitude of the dynamic equilibrium established between the thiol and base catalyst is dictated by the difference in acidities between the thiol and the conjugate acid

$$\Delta pK_a = pK_{a(RSH)} - pK_{a(HB^+)} \quad (12)$$

assuming full dissociation of the intermediate ion-pair into free ions:^{26,40–42}

$$K_{eq} = \frac{k_f}{k_r} = \frac{[RS^-]_{eq}[HB^+]_{eq}}{[RSH]_{eq}[B]_{eq}} = 10^{\Delta pK_a} \quad (13)$$

Efficient deprotonation will thus occur when very acidic thiols (i.e., with low pK_a values) are combined with exceptionally strong bases such as TMG. Integration of eq 1 leads to the following explicit analytical solution describing the production of base

$$[B]_t = f[PB]_0(1 - e^{-z_1 t}) \quad (14a)$$

Accounting for an equilibrium constant, $K_{eq} \gg 1$ in step 2,³¹ any quantity of base that is formed from photoinitiation is thus assumed to be immediately converted into an equivalent amount of the conjugate acid (or analogously, $[RS^-]_{formed} \approx [B]_{consumed}$), so that the net balance in base concentration remains very close to zero throughout the reaction. In the event of bimolecular termination occurring for the strong base due to the presence of acidic impurities, the evolution in base concentration over the entire reaction time cannot be obtained analytically for which a solution has to be computed numerically to describe the polymerization kinetics. In both cases the concentration of base at a given reaction time will be essentially equal to the total concentration of anionic species at that time

$$[B]_t = [RS^-]_t + [RC^-]_t \quad (14b)$$

so that the law of conservation of mass is satisfied. For simplification purposes it is assumed in step 6 that the acid–base equilibrium constant $K'_{eq} \gg 1$ (i.e., $k_t^- \approx 0$), with $K'_{eq} \gg K_{eq}$.

Because of the catalytically coupled two-step reaction mechanism characterizing the anionic cycle, the elementary rates of propagation (eq 6, Table 1) and chain transfer (eq 15)

$$R_{CT} = - \frac{d[RSH]_t}{dt} = k_{CT} [RC^-]_t [RSH]_t \quad (15)$$

can be set equal to each other, and these rates are then also identical to the overall reaction rate, i.e., $R_p = R_{CT} = R_{rxn}$. However, given the strong driving forces for the forward reactions (steps 3 and 4) combined with the exceptional stability of the thiocarbanion intermediate, reflecting the high electron-withdrawing character of the vinyl substituent groups,³⁴ the contribution of the reverse reaction, i.e., the elimination reaction, to the kinetics is assumed to be negligible, i.e., $k_e (s^{-1}) \approx 0$. A general rate expression based on the mechanism (eq 16) can, thus, be obtained by solving the resulting algebraic equation with respect to $[RC^-]_t$ and by using eqs 14a, 14b, and 15:

$$R_{rxn} = \frac{k_p k_{CT} [B]_t}{k_p [C=C]_t + k_{CT} [RSH]_t} [C=C]_t [RSH]_t \quad (16)$$

where $k_{CT} = k_{CT1}$ is the chain-transfer rate constant, and $k_p = k_a - k_e [RC^-]_t \approx k_a$ denotes an effective (or net) propagation rate parameter for the reversible addition step. A closer examination of the rate expression (16) clearly establishes a link between the kinetics of the complex reaction and the intrinsic structure of the detailed mechanism: the “driving force”

of the overall reaction is represented by the numerator, while the denominator reflects a “kinetic resistance” that retards the reaction depending on which elementary step of the catalytic cycle is rate-limiting. Consequently, three particular rate-controlling cases arise depending on the relative magnitude of the two product terms in the denominator of eq 16:

i.

$$\text{if } k_p[\text{C}=\text{C}]_t \gg k_{\text{CT}}[\text{RSH}]_t \Rightarrow R_{\text{rxn}} = -\frac{d[\text{RSH}]_t}{dt} \approx k_{\text{CT}}[\text{B}]_t[\text{RSH}]_t \quad (17)$$

and the rate-limiting step is the chain-transfer reaction with the rate of the reaction exhibiting pseudo-first-order dependence only in the thiol concentration. In this case, increasing the concentration of vinyl does not alter the reaction rate too significantly since the overall kinetics is controlled by the chain-transfer rate.

ii.

$$\text{if } k_{\text{CT}}[\text{RSH}]_t \gg k_p[\text{C}=\text{C}]_t \Rightarrow R_{\text{rxn}} = -\frac{d[\text{C}=\text{C}]_t}{dt} \approx k_p[\text{B}]_t[\text{C}=\text{C}]_t \quad (18)$$

and the propagation step is rate-determining, then the overall rate depends primarily on the vinyl concentration. This behavior implies that doubling the vinyl concentration relative to the initial concentration will essentially double the reaction rate relative to its original value; however, changes in the initial thiol concentration have minimal impact on the rate in this case.

iii.

$$\text{if } k_{\text{CT}}[\text{RSH}]_t \approx k_p[\text{C}=\text{C}]_t \Rightarrow R_{\text{rxn}} = -\frac{d[x]_t}{dt} \approx \frac{k}{2}[\text{B}]_t[x]_t \quad (19)$$

and there is no rate-controlling step with both reactions exhibiting pseudo-half-order dependences on the thiol and vinyl concentrations, as they contribute equally to the net reaction rate, i.e., $[x]_t = [\text{C}=\text{C}]_t^{1/2}[\text{RSH}]_t^{1/2}$ overall, with $k = (k_p k_{\text{CT}})^{1/2}$.

In the cases presented by eqs 17 and 18, the concentration ratio of the two anionic reactive centers, $[\text{RC}^-]_t/[\text{RS}^-]_t$, is governed by the ratio of propagation-to-chain-transfer kinetic constants multiplied by the respective functional groups concentrations:

$$\frac{[\text{RC}^-]_t}{[\text{RS}^-]_t} = \frac{k_p}{k_{\text{CT}}} \frac{[\text{C}=\text{C}]_t}{[\text{RSH}]_t} \quad (20)$$

and when thiol and vinyl concentrations are equivalent, as is frequently the case in these stoichiometric reactions, the relative concentrations of the two reactive intermediates are controlled only by the ratio of the two rate parameters, k_p/k_{CT} . Noticeably, when the two reaction steps of the anionic cycle have equal magnitude (eq 19), then $[\text{RC}^-]_t = [\text{RS}^-]_t$ and $[\text{B}]_t = 2[\text{RS}^-]_t$. In all cases the concentration ratio of the two anionic intermediates is kept

constant throughout the reaction although their summed concentrations increases linearly with $[B]_t$ produced during photoinitiation reaching an end value of $f[PB]_0$. This fundamental kinetic aspect differentiates the photoinitiated thiol–Michael addition reaction from its radical thiol–ene counterpart, even though the mechanistic structure of the catalytic cycle involving the reactive intermediates is essentially the same for the two chemistries.

Equation 16 is equivalently rewritten in the following pseudo-first-order analytical form:

$$R_{\text{rxn}} = -\frac{d[x]_t}{dt} = k_{\text{kin}}[B]_t[x]_t \quad (21)$$

with

$$k_{\text{kin}} = \frac{k_p k_{\text{CT}}}{k_p + k_{\text{CT}}} \quad (\text{for } r_0 = 1, \text{ with } [x]_t = [C = C]_t^n [\text{RSH}]_t^m) \quad (22)$$

$$k_{\text{kin}} = \frac{r_0 k_p k_{\text{CT}}}{k_p + r_0 k_{\text{CT}}} \quad (\text{for } r_0 \geq 1, \text{ with } [x]_t = [C = C]_t) \quad (23)$$

$$k_{\text{kin}} = \frac{k_p k_{\text{CT}}}{k_p + r_0 k_{\text{CT}}} \quad (\text{for } r_0 \leq 1, \text{ with } [x]_t = [\text{RSH}]_t) \quad (24)$$

where $[x]_t$ denotes time–concentrations of the limiting reactant, n and m are empirical scaling exponents ($n + m = 1$) corresponding to the individual reaction orders with respect to each reactant concentration, k_{kin} can be understood as a lumped second-order rate parameter depending on the reaction system stoichiometry, r_0 , and

$$r_0 = \frac{[\text{RSH}]_0}{[C = C]_0} \quad (25)$$

Under continuous light irradiation, all rate equations are integrated from the onset of the reaction (time $t = 0$, $[x] = [x]_0$) to the gel point ($t = t_{\text{gel}}$, $[x] = [x]_{\text{gel}}$) to give the general analytical solution

$$X_t = 1 - \exp \left[\beta \left(\frac{1 - e^{-z_1 t}}{z_1} - t \right) \right], \quad \beta \text{ (s}^{-1}\text{)} = k_{\text{kin}} f[PB]_0 \quad (26)$$

where

$$X_t = 1 - \frac{[x]_t}{[x]_0} \quad (27)$$

is the fractional thiol (or vinyl) functional group conversion, depending on the particular case analyzed, while β can be viewed as a first-order operational parameter dependent on the catalytic cycle kinetic constants, reaction stoichiometry, and conditions of initiation. Equation 16 implies that the extent of the reaction, X_t , evolves in the form of a sigmoidal (S-shaped) curve.

Under dark reaction conditions following the cessation of irradiation from time $t = t_i$ preceded by an initial irradiation period $t = t_i$, the concentration of base remains virtually unchanged in time, i.e., $[B]_{t=t_i} = [B]_{\text{constant}} < f[\text{PB}]_0$, with the functional group conversion, $X_{t=t_i}$, now deviating from eq 26 according to a simple pseudo-first-order exponential decay function:

$$X_{t \geq t_i} = 1 - \frac{[x]_{t_i}}{[x]_0} e^{-\mu(t-t_i)}, \quad \mu \text{ (s}^{-1}\text{)} = k_{\text{kin}}[B]_{\text{constant}} \quad (28a)$$

where μ denotes a pseudo-first-order kinetic constant, $[x]_{t_i}$ is the concentration of limiting reactant at time t_i , and $[x]_0$ is its initial concentration. It ought to be noted that if $t_i = 0$, then $[x]_{t_i}/[x]_0 = 1$, and eq 28a is reduced to

$$X_t = 1 - \exp(-\mu t) \quad (28b)$$

which is also a limit case of eq 26 at sufficiently large values of z_i . Equivalently, eq 28b is also valid from time $t = 0$ for reaction systems involving strong base catalysts where photoinitiation is absent, while following the pseudo-steady-state approximation, i.e., $[B]_{\text{constant}} = [B]_0 = [\text{RS}^-]_t + [\text{RC}^-]_t$.

Empirical parameter(s), β and/or μ (as slopes), can be estimated at early stages of the reaction via a least-squares treatment of kinetic data plotted in accordance to linearized versions of eqs 26 and 28a, respectively.

Acid–Base Termination Kinetics: Induction Time

With bimolecular acid–base termination kinetics for the generated base, a lag period is theoretically predicted according to eq 29, during which no reaction is observed:

$$\tau = \frac{1}{z_i} \ln \left(\frac{f[\text{PB}]_0}{f[\text{PB}]_0 - [\text{HA}]_0} \right) \quad (29)$$

where τ is the induction time, and $[\text{HA}]_0$ ($< [\text{PB}]_0$) denotes the initial concentration of acidic impurities, usually unknown, which can be deduced by determining τ from experiment. Because of this inhibitory period, the reaction is expected to proceed at lower rates from times $t > \tau$, as described by eq 26, since β is now decreased to

$$\beta' = k_{\text{kin}} f([\text{PB}]_0 - [\text{HA}]_0) \quad (30)$$

The extent of inhibition, χ , associated with this induction period is given by

$$\chi = 1 - \frac{\beta'}{\beta} = f(1 - e^{-z_i \tau}) \quad (31)$$

and is related to the overall reaction rate (now expressed in s^{-1}) by

$$R_{\text{rxn}} = \frac{dX_t}{dt} = \beta(1 - \chi)(1 - e^{-z_i t}) \exp \left[\beta(1 - \chi) \left(\frac{1 - e^{-z_i t}}{z_i} - t \right) \right] \quad (32)$$

Equation 29 also allows for determination of the light intensity that is necessary to deliver into the reaction system in order to neutralize a certain initial amount of protic species during a specified induction time, since z_i is directly proportional to the incident irradiation intensity, $z_i = \phi_1 I_{\text{inc}}$ (eq 2), where ϕ_1 (in $\text{cm}^2 \text{s}^{-1} \text{mW}^{-1}$) designates a coupled physicochemical photolysis–initiator constant. The preceding analysis is valid exclusively for strong photobases since they function as catalytic cycle amplifiers. With weak base catalysts, however, protic species such as water and Brønsted acids may also coreact with the intermediate carbanion of the catalytic cycle, preventing the reaction from proceeding.³⁶ We foresee that the same competitive inhibition process would occur in parallel to the presence of strong base catalysts due to generally much higher basicity of the intermediate carbanion relative to TMG.⁴³ However, this termination route is assumed to have significantly less contribution to the overall inhibition kinetics, since is a result of a secondary process. Details on the mathematical derivation of eq 29 can be found in section V of the Supporting Information. Equation 32 is obtained by performing a first derivative of eq 26 while having β affected by the complement of the extent of inhibition, $1 - \chi$.

Gelation Times

In multifunctional step-growth copolymerizations the critical (gel point) conversion, X_{crit} , is well-predicted by the classical Flory–Stockmayer equation

$$X_{\text{crit}} = \frac{1}{\sqrt{r_0(f_{\text{thiol}} - 1)(f_{\text{vinyl}} - 1)}} \quad (33)$$

where the number functionalities of thiol and vinyl monomers are represented by f_{thiol} and f_{vinyl} , respectively.^{44,45} Hence, monomers with a stoichiometric imbalance, r_0 , for which $X_{\text{crit}} < 1$ will form a cross-linked polymer when reacted via a step-growth mechanism. Gelation times, defined by

$$t_{\text{gel}} = t(X_{\text{crit}}) + \tau \quad (34)$$

corresponding to the incipient formation of an infinite network, can be predicted by introducing X_{crit} calculated via eq 33 directly into eq 26 and then solving the resulting expression with respect to time $t = t(X_{\text{crit}})$:

$$t(X_{\text{crit}}) = \frac{1}{\beta z_i} \left\{ \beta W \left[-\frac{(1 - X_{\text{crit}})^{z_i/\beta}}{e^1} \right] + \beta - z_i \ln(1 - X_{\text{crit}}) \right\} \quad (35)$$

This semianalytical equation makes use of the Lambert W function, also called the product log function (denoted W), which is the inverse of the xe^x function. Predicted gel times can be confirmed experimentally by comparison with those obtained from dynamic rheometry when applying the Winter–Chambon criterion and/or from conversion measurements via real-time infrared (FT-IR) spectroscopy using X_{crit} predicted by eq 33 and by subsequently checking their agreement with the theoretical value.^{46–48} It should be noted that the gel times are not solely dependent on the critical conversion achieved for a given comonomer number-average functionality and reaction system stoichiometry but are also related to the reaction kinetics, including conditions of initiation and intrinsic reactivity of thiol–vinyl groups.

An illustrative simulated tetrafunctional comonomer system composed of thiol A_4 and vinyl sulfone B_4 is simulated in Figure 6 to react at varied functional group mole ratios of $r_0 = 0.5$, 1, and 2 in the absence of acid–base termination.

RESULTS AND DISCUSSION

Rate Constants

The “flooding” technique, for which experimental results are depicted in Figure 1, was initially employed to determine the k_p/k_{CT} ratio derived from the corresponding kinetic constants measured experimentally using a non-cross-linking dithiol/monovinyl sulfone model compound system based on GDMP and ethyl vinyl sulfone (EVS) monomers. Experimental kinetic runs were conducted using an excess of thiol (plots a–c) while performing the same reaction under stoichiometric conditions (plot d) (see more details in section II of the Supporting Information). The observed kinetic behavior was clearly captured by the analytical model conceived for the base-catalyzed thiol–Michael addition reaction. These rate parameters were subsequently implemented to simulate numerically the mechanistic reaction system proposed via the software COPASI in order to inspect the analytical kinetic model developed. “Flooding” means essentially adjusting the experimental conditions of the reaction such that it becomes a pseudo-first-order kinetic process in one

single reactant's concentration by means of introducing a large relative excess of the other reactant, and vice versa. The concentration of the reactant in excess will remain essentially invariant during the reaction while the limiting reagent concentration and kinetics are isolated. Otherwise, a simple linearization of eqs 23 and/or 24 will allow determining the apparent values of the catalytic cycle rate parameters from a single discrete data plot by systematically varying r_0 in serial kinetic experiments (see section III of the Supporting Information for more details).

Reaction Rates and Kinetic Modeling

Modeling results shown in Figures 2 and 3 provide a qualitative kinetic description of the overall reaction behavior and dynamics of the photoinitiated thiol–Michael mechanism subjected to different conditions. For practical purposes, an efficiency $f = 1$ is assumed since decarboxylation of the complex photolysis intermediate is an entropy-driven process.^{17,49} Changes in the reaction stoichiometry, r_0 , by varying the initial concentration of reactants enable the rate-limiting step with first-order reactants concentration dependence to be determined from experiment. For example, doubling the initial vinyl concentration relative to a constant thiol concentration increases the reaction rate whereas doubling the initial thiol concentration while holding the vinyl concentration constant has no meaningful effect on the reaction rate, indicating that propagation is the rate-controlling step for this particular thiol–vinyl sulfone coreactant pair (Figure 2a–c). Hence, the following functional group scaling relationship $R_{\text{rxn}} \propto [\text{C}=\text{C}]^n [\text{RSH}]^m$ should be verified experimentally in stoichiometric systems, as in the thiol–ene case, for individual values of n and m between zero and unity. For this particular thiol–Michael system we found that $n = k_{\text{kin}}/k_p \approx 0.87$ and $m = k_{\text{kin}}/k_{\text{CT}} \approx 0.13$ (i.e., $m/n = k_p/k_{\text{CT}}$) when $r_0 = 1$, indicating that the reaction rate is more heavily dependent on the vinyl concentration than that of the thiol. Such predicted behavior is characteristic of reaction mechanisms exhibiting two alternating kinetically coupled elementary steps in the catalytic cycle, essentially controlled by the relative concentration of intermediate species, i.e., $[\text{RC}^-]_t/[\text{RS}^-]_t$ (eq 20). Even in the absence of known values for k_p and k_{CT} , the scaling exponents, n and m , are estimated using the reaction rates ratio, R_t of individual rates taken at different stoichiometries and under equimolar conditions, i.e., $R_t = R_{\text{rxn}}(r_0 = 1)/R_{\text{rxn}}(r_0 = 1)$, (see section IV of the Supporting Information). Increasing the light intensity and/or initial concentration of photobase results in an increase of the reaction kinetics as predicted from eq 21, fully consistent with previous experimental findings (Figure 3),³⁰ while varying k_p and k_{CT} together by the same factor affects the reaction rates proportionally (Figure 2d). Furthermore, one observes that the reaction kinetics are much more sensitive toward light intensity changes at low intensity as compared to differences in intensity at high intensities. Minor variations in the initial photobase concentration has a significant impact on the reaction kinetics under any circumstance studied here (Figure 3a,b). Plots c and d of Figure 3 compare the predicted effect of changes in light intensity and initial amount of photocatalyst on the evolution of photobase and how these are related to the respective thiol–Michael kinetic profiles. All the theoretical observations presented assert the need for an optimal control of the initial conditions upon quantifying the kinetic parameters from experiment in photoinduced base-catalyzed thiol–vinyl Michael addition reactions.

Thiol–Michael vs Thiol–Ene Photopolymerizations

One of the fundamental mechanistic differences between radical-induced thiol–ene photopolymerizations and photoinitiated base-catalyzed thiol–Michael additions is the assumption of the pseudo-stationary-state condition (as a theoretical approximation) for the intermediate catalytic species, i.e., $[RS^*]_t + [RC^*]_t \approx \text{constant}$, which is notably absent in the photoinduced thiol–Michael case. In particular, this difference arises from the lack of a relevant termination reaction in the thiol–Michael case in contrast to the radical–radical termination reactions that are prominent in thiol–ene reactions. This key difference is reflected in thiol–ene systems by the steady-state polymerization rate being proportional to the rate of initiation raised to a power α , as an empirical scaling exponent, i.e., $R_{\text{rxn}} \propto R_i^\alpha \propto (I_{\text{inc}}[PI]_0)^\alpha$,⁵⁰ indicative of the presence of a termination mechanism for the catalytic intermediates; unimolecular if $\alpha = 1.0$ ($[RS^*]_t + [RC^*]_t = R_i/k_t$) most likely caused by physical entrapment of propagating radicals within the polymer matrix, and bimolecular if $\alpha = 0.5$ ($[RS^*]_t + [RC^*]_t = (R_i/2k_t)^{1/2}$) due to radical–radical (re)combinations. Hence, the inherently distinct kinetic features manifested by the two general rate equations (cf. eq 21 vs eq 8 of ref 51). According to eq 21, the thiol–Michael reaction rate not only follows a first-order dependence in one of the reactants concentration (or half-order dependence on both concentrations, i.e., first order overall) as in thiol–enes but is also proportional to the amount of base generated during photoinitiation, which rules out the possibility for a constant scaling exponent (α). Figure 4 captures well the dynamics of this mechanistic discrepancy for the two step-growth reactions sharing equal reactivity between functional groups and the same initiation rates. Although in practice this comparison may be somewhat unrealistic given the dissimilar chemical natures of vinyl functional groups (and concomitant reactivities with thiols), the catalytic cycle intermediates, and the initiation conditions involved in the two chemistries, it provides a conceptual framework to explain the different mechanistic implications on the overall reaction kinetics resulting from the two systems. To maintain simplicity, it is assumed in the radical-mediated pathway that photolysis produces only one active radical center instead of two and that the bimolecular termination rate constants, accounting for homo- and heterocoupling radical–radical (re)combination reactions, share the same value. As anticipated, we observe that termination of the radical intermediates has an enormous impact on the thiol–ene output kinetics due to lessening of the radical concentration available for propagation/chain transfer. From a qualitative analysis viewpoint, not only are the reaction rates lower in comparison to the thiol–Michael mechanism but also the conversions attained are inferior for a given time interval when termination becomes kinetically dominant, even though both reaction mechanisms allow for a late gel-point conversion and yield the same final addition product. Contrarily to thiol–ene photopolymers, however, the thiol–Michael network development, in the absence of vitrification, is expected to proceed kinetically until near-quantitative conversions of functional groups, even under dark reaction conditions once photoinitiation has commenced. For example, at simulated times $t_i = 71$ s (~21% conversion) and 114 s (~40% conversion) the UV light is turned off and the thiol–Michael reaction instantly switches from a complex pseudo-first-order kinetics to a simple pseudo-first-order rate law, proceeding now at slightly lower rates than those achieved under continuous irradiation. This difference is not surprising since the concentration of anionic intermediates increases linearly with the amount of base produced during continuous irradiation (eqs 14a and 14b) but remains

constant from those points in time onward once illumination has ceased. The lack of a termination mechanism for the anionic intermediates in thiol–Michael additions enables the polymerization to continue in living mode without requiring a constant input of light for propagation, thus rendering unique potential for extended dark-cure reactions. Such kinetic behavior contrasts with that of the radical-mediated pathway where thiol–ene reactions are almost immediately interrupted due to the effective exhaustion of the reactive radical intermediates.

Inhibition Kinetics

Several multifunctional thiols currently employed in network-forming systems are synthetically derived from commercially available alcohol and vinyl monomers.^{13,52} Yet, they are known to contain trace amounts of acidic species, as impurities, that temporally suppress the thiol–Michael reaction in its initial stages and reduce the conversion rates if not properly eliminated prior to the reaction.⁵³ This inhibitory effect is characterized by the development of an induction time, τ , given by eq 29, derived from an acid–base neutralization equilibrium established as bimolecular termination mechanism for the photogenerated base. Figure 5a describes the effect of the induction time on the reaction kinetics obtained from numerical computations of the mechanistic scheme detailed in Table 1. As predicted by the combination of eqs 26 and 29–32, the longer the duration of the induction period (i.e., the greater the extent of inhibition) the lower the ultimate reaction rates attained will be. These become increasingly smaller for protic concentrations progressively closer to the initial amount of photobase and will even inhibit the reaction completely under extreme conditions, i.e., when $[HA]_0 = [PB]_0$ ($\beta'/\beta = 0$) (Figures 5a,b). Therefore, for a fixed amount of inhibitory species, the reaction rates can be adjusted by manipulating the initial amount of photobase, $[PB]_0$, together with light intensity delivered, I_{inc} (Figures 5b,c), although an increase in the values of the two variables, separately or combined, will not eliminate the induction time entirely. This kinetic prediction appears to differ from that of the nucleophile-catalyzed thiol–Michael addition reaction using TPP/MsOH initiator system as time-lapse mechanism, where the reaction rate was found to remain largely unchanged regardless of the length of the induction period tested.²⁶ Nevertheless, similar inhibition kinetics would be expected to develop for nucleophile-driven thiol–Michael additions despite the distinct initiation mechanisms promoted by the two catalysts. The initial amount of acidic impurities can be estimated by plotting experimental data according to Figure 5d while applying the expression

$$[HA]_0 = \chi [PB]_0 = f [PB]_0 (1 - e^{-\text{slope} \cdot \varphi_i}) \quad (36)$$

The theoretical analysis presented here clearly foretells the emergent need for a tight control of the reacting monomers purity and photoinitiation conditions in thiol–Michael addition reactions so that the “click” character associated with this chemistry is not altered when applied to photopolymerization systems that require rapid curing kinetics. However, it may be advantageous for chemical systems that need to remain kinetically quiescent until triggered, although at the ultimate expense of lower reaction rates.

Gelation Kinetics

The reaction kinetics and comonomer functionality both have an effect on the gel times as theoretically predicted by eqs 33 and 35 combined. Figure 6 maps the influence of the rate constant ratio k_p/k_{CT} on the gelation time t_{gel} as defined by eq 34 at three distinct feed ratios of thiol-to-vinyl groups and is exemplified with a representative multifunctional $A_4 + B_4$ comonomer system under specified initial conditions. The relative concentration of thiocarbanions in the polymerizing system, $[RC^-]/[RS^-]_0$, is equal to this catalytic ratio under equimolar amounts of functional groups but will be also dependent on the concentration of thiol and vinyl groups at different molar ratios (eq 20). For a given polymerizing system, the graph clearly shows that the gel times are bound between two delimiters: one open (asymptotic) lower limit for extreme values of k_p/k_{CT} and one closed (fixed) upper limit at $k_p/k_{CT} = 1$. The sensitivity of the gelation time to values of the k_p/k_{CT} ratio can be essentially ascribed to the analytical forms taken by the k_{kin} parameter expression (eqs 22–24). Both open limits correspond to critical gelation times, which occur when the t_{gel} becomes nearly independent of k_p/k_{CT} , fully consistent with the theoretical predictions put forward by Okay and Bowman⁵⁴ as described for radical thiol–ene systems. If $k_p/k_{CT} \gg r_0$, then the mole fraction of carbanions within the total amount of anionic species, m , approaches unity. Such a condition arises from predominant addition of the thiolate anion across the vinyl due to strong nucleophilicity of the thiolate anion combined with high electron withdrawing capacity of the vinyl moiety. The result is the rapid production of a less reactive/basic carbanion, thus making the chain-transfer reaction the rate-determining step. For values of $k_p/k_{CT} \ll r_0$ the reverse situation happens; the mole fraction of thiolate anions within the total amount of anionic species, n , approaches unity instead. This outcome implies very low reactivity between the thiolate anion and the vinyl group leading to extremely low amounts of a highly basic thiolate carbanion, which makes propagation the rate-controlling step. For this particular composition such critical conditions are achieved at $k_p/k_{CT} \approx 10^2$ and $k_p/k_{CT} \approx 10^{-2}$, regardless of the feed ratio evaluated. Beyond these critical values the gel times become essentially insensitive to changes in k_p/k_{CT} .

Finally, when $k_p = k_{CT}$ at any given value of r_0 , the gelation times converge to the corresponding closed upper limits, thus showing that $k_p/k_{CT} = 1$ is the least favorable kinetic condition if one intends to attain a short time to gelation for a given feed ratio. Increasing the rate of initiation by raising the initial concentration of photobase or by increasing the light intensity delivered (separately or combined) will also shorten the gelation times as predicted by eq 35. A similar kinetic dependence of the gel times on the k_p/k_{CT} ratio was found for other representative multifunctional systems (results not shown).

SUMMARY AND CONCLUSIONS

A general kinetic model has been developed that predicts the base-catalyzed thiol–Michael photopolymerization behavior comprising a photocaged superbases generator. The model incorporates catalytic cycle kinetics coupled with monomolecular photodissociation of the photobase initiator. Analytical equations derived from a proposed reaction mechanism reveal step-growth polymerization rates proportional to the amount of base produced during

photoinitiation and that scale in the first power with respect to thiol or vinyl functional group concentrations individually or first-order overall in both reactants concentrations. Such complex pseudo-first-order kinetics, expressed as $R_{\text{rxn}} = -d[x]/dt = k_{\text{kin}}[B][x]$ with $k_{\text{kin}} = g(k_p, k_{\text{CT}}, r_0)$, are controlled by the ratio of propagation to chain-transfer kinetic parameters (k_p/k_{CT}), dependent on functional group chemistry, which also determines the rate-limiting step and time to reach the gel-point conversion. For thiol–vinyl combinations where $k_p/k_{\text{CT}} \gg 1$ the chain-transfer reaction is rate-limiting, and the reaction rate is pseudo-first-order in the thiol concentration (i.e., $R_{\text{rxn}} \propto [B][\text{RSH}]^1[\text{C}=\text{C}]^0$); when $k_p/k_{\text{CT}} \ll 1$, propagation is the rate-controlling step and the reaction rate becomes pseudo-first-order only with respect to the vinyl concentration (i.e., $R_{\text{rxn}} \propto [B][\text{C}=\text{C}]^1[\text{RSH}]^0$). Finally, when the two reaction steps occur at a comparable rate, i.e., $k_p/k_{\text{CT}} \approx 1$, the reaction rate is expected to be pseudo-half-order in each reactant's concentration (i.e., $R_{\text{rxn}} \propto [B][\text{C}=\text{C}]^{1/2}[\text{RSH}]^{1/2}$). In the thiol–vinyl sulfone system studied here we found for stoichiometrically balanced mixtures that $R_{\text{rxn}} \propto [B][\text{C}=\text{C}]^{0.9}[\text{RSH}]^{0.1}$ (overall). Gelation develops earlier as k_p/k_{CT} reaches a critical point; thereafter, the gel time becomes practically unaffected by this ratio. Importantly, the model demonstrates the influence of inhibitory protic species on the output kinetics showing that higher extents of inhibition yield lower reaction rates. The living nature of this anionic polymerization mechanism allows for extended dark cure, which contrasts with the radical-mediated thiol–ene mechanism. Further knowledge of the absolute rate parameters in different binary thiol–vinyl Michael systems with assessment of the apparent partial reaction orders, activation energies, relative reactivities, and selectivities is pivotal for the quantitative prediction and modeling of the reaction kinetics when applied to more complex macromolecular network systems involving multiple photopolymerization chemistries with distinct mechanistic aspects.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Temporal evolution of vinyl sulfone conversion from measured data (symbols) and model predictions (lines) at different UV-light intensities and molar ratios of thiol–vinyl sulfone groups. (a–c) Relative excess of thiol groups ($r_0 \sim 22$) at varying light intensities. (d) Equimolar amounts of functional groups ($r_0 = 1$). Estimated kinetic parameters for all fits are identical: $k_p = 0.14 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{CT} = 0.96 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$, by recursively fitting the theoretical model/mechanism to all experimental data simultaneously. In (d) fitting was performed at early stages of the reaction as above 300 s deviation occurred most likely caused by an increase in viscosity of the formed product which takes place at progressively higher conversions. Standard deviations from five repeat measurements are shown. All modeled lines (eq 26) fall within the corresponding error bars for the ranges considered demonstrating the unique ability of our theoretical approach in accurately describing the measured kinetic data. The sigmoidal characteristic of the conversion–time curve was conserved with different initial conditions. Experimental procedure is detailed in section II of the Supporting Information.

Figure 2.

Kinetic modeling results showing the effect of several reaction variables on the output kinetics using $k_p/k_{CT} = 0.15$.^b (a–c) Changes in the thiol–vinyl stoichiometric ratio r_0 , with $z_1 = 1.25 \times 10^{-2} \text{ s}^{-1}$ ($I_{inc} = 30 \text{ mW/cm}^2$) and $[PB]_0 = 76.3 \text{ mM}$ (2.0 wt %). (d) Influence of relative changes in the k_{kin} parameter in the conversion rate using a proportionality factor = 5 with $r_0 = 1$, $z_1 = 1.25 \times 10^{-2} \text{ s}^{-1}$, and 2.0 wt % PB. Normalized reaction rates are determined from R_{rxn}/R_{max} , where R_{max} denotes the maximum rate in the thiol–Michael system where $r_0 = 1$. Initiation efficiency is assumed to be $f = 1$.

^bValues of $k_p = 0.14 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{CT} = 0.96 \text{ M}^{-1} \text{ s}^{-1}$ used in the mechanistic kinetic modeling were measured for a model compound system based on ester 3-mercaptopropionate and vinyl sulfone functionalities using the “flooding” technique with respect to the thiol and by carrying out the same reaction under equimolar conditions (see section II of the Supporting Information). Further work on the relative reactivities with respect to various thiol and electron-deficient vinyl groups is now in progress, and these values must be considered as tentative at present.

Figure 3.

Kinetic modeling results showing the effect of variations in the initiation conditions on the output kinetic profiles using $k_p/k_{CT} = 0.15$ and $r_0 = 1$.^b (a) Effect of incident light intensity, I_{inc} (in mW/cm²). (b) Influence of initial amount of photobase (in wt %). (c) Photobase conversion dependence on light intensity as a function of time. (d) Temporal variations in photobase concentration at different initial amounts (solid lines) and corresponding first-order conversion profile(s) (dashed line). $I_{inc} = 2, 5, 10, 20, 30, 40, 60, 80$, and 100 mW/cm². Efficiency in base formation f is assumed to be 1.

Figure 4.

Comparative plots between the kinetics of thiol–Michael addition (black solid line and full colored lines) and radical thiol–ene reactions (colored dashed lines). Changes from complex pseudo-first-order kinetics (continuous irradiation, eq 26) to simple pseudo-first-order decay kinetics (dark conditions, eq 28a) in the thiol–Michael profiles is indicated by the colored arrows at times $t_1 = 70.7$ s (red line) and 114.3 s (blue line). Model parameters: $z_1 = 1.25 \times 10^{-2} \text{ s}^{-1}$ ($I_{\text{inc}} = 30 \text{ mW/cm}^2$), $k_{\text{f}} = k_{\text{H}} = 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{r}} = 1.0 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{p}} = 0.14 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{CT}} = 0.96 \text{ M}^{-1} \text{ s}^{-1}$,^b $k_{\text{t}} = k_{\text{t1}} = k_{\text{t2}} = k_{\text{t3}}$; $[\text{PB}]_0 = [\text{PI}]_0 = 76.3 \text{ mM}$, and $r_0 = 1$ ($[\text{RSH}]_0 = [\text{C}=\text{C}]_0 = 4.95 \text{ M}$); $k_{\text{CT2}} = 0$, $k_{\text{e}} = 0$ and $k_{\text{t}}^- = 0$. Numerical values of bimolecular radical–radical termination rate constants are given in the inset. The radical-mediated thiol–ene mechanism used in the numerical simulations is given in section VI of the Supporting Information (PI = general radical photoinitiator).

Figure 5.

Simulation plots showing the influence of a bimolecular termination mechanism on the kinetics of the base-mediated thiol-Michael addition reaction. (a) Effect of variations in the amount of protic species ($[HA]_0 = 0.05-0.075$ M) on the vinyl conversion as a function of time. The unnoticeable differences between analytical (solid gray line) and simulated (dashed line) kinetic profiles where no termination is involved demonstrate the ability of our analytical approach (eq 26) to reproduce accurately the mechanism proposed. The induction time increases with incremental amounts of inhibitory species, which also affects the reaction rates. (b) Maximum reaction rates as a function of the extent of inhibition at three different UV-light intensities: I_{inc} (mW/cm²) = 10 (light gray curve), 30 (full solid curve), and 50 (dark gray curve). Open circles correspond to maximal rates at acidic concentrations $[HA]_0 = 0-0.075$ M. Tridimensional evolution of the reaction rate over time as a function of the extent of inhibition is given in section VII of the Supporting Information. (c) Effect of light intensity delivered on the duration of the induction period, with $[HA]_0 = 0.05$ M. (d) Reciprocal relationship between induction time and incident irradiation intensity (τ vs $1/I_{inc}$, slope $\times \phi_1 = z_1 \times \tau$). Kinetic simulation profiles were computed numerically in the application software COPASI: (a) $z_1 = 1.25 \times 10^{-2}$ s⁻¹ ($I_{inc} = 30$ mW/cm²), $[HA]_0$ (M) = (see inset); (b) z_1 (s⁻¹) = 4.15×10^{-3} ($I_{inc} = 10$ mW/cm²), 1.25×10^{-2} ($I_{inc} = 30$ mW/cm²), 2.1×10^{-1} ($I_{inc} = 50$ mW/cm²); (c) z_1 (s⁻¹) = 2.1×10^{-3} (5 mW/cm²), 4.2×10^{-3} (10 mW/cm²), 8.3×10^{-3} (20 mW/cm²), 1.25×10^{-2} (30 mW/cm²), 1.7×10^{-2} (40 mW/cm²),

2.1×10^{-2} (50 mW/cm²), and 2.5×10^{-2} (60 mW/cm²); $k_f = 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_r = 1.0 \text{ M}^{-1} \text{ s}^{-1}$, $k_p = 0.14 \text{ M}^{-1} \text{ s}^{-1}$, $k_{CT} = 0.96 \text{ M}^{-1} \text{ s}^{-1}$, $k_t = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $[\text{PB}]_0 = 76.3 \text{ mM}$, and $r_0 = 1$ ($[\text{RSH}]_0 = [\text{C}=\text{C}]_0 = 4.95 \text{ M}$); $k_{CT2} = 0$, $k_e = 0$, and $k_t^- = 0$.

Figure 6.

Effect of the k_p/k_{CT} ratio on the gelation time (eq 34) for a representative tetrafunctional ($A_4 + B_4$) thiol–Michael reaction system at three different initial mole ratios, r_0 , of thiol and vinyl functionalities, with $\tau = 0$ (no inhibition). $r_0 = 0.5$ (long dashed lines), 1 (solid line), and 2 (short dashed lines). $z_1 = 1.25 \times 10^{-2} \text{ s}^{-1}$ ($I_{\text{inc}} = 30 \text{ mW/cm}^2$), $f = 1$, and $[\text{PB}]_0 = 76.3 \text{ mM}$. Vertical lines emanate from top of the graph correspond to asymptotes of the gelation time. Gel times are sensitive to changes in the k_p/k_{CT} ratio and k_{kin} for a given set of initial conditions.

Scheme 1. Mechanistic Scheme Proposed for the Photoinitiated Base-Catalyzed Thiol–Michael Addition of Thiols to Electron-Deficient Vinyls and Observed (Net) Resulting Reaction^a

Table 1

Mechanistic Rate Equations and Kinetic Constant Assignments for the Photoinitiated Thiol–Michael Addition Reaction with Acid–Base Neutralization Included as Termination Mechanism

$$\frac{d[\text{PB}]_t}{dt} = -z_i[\text{PB}]_t \quad (\text{rate of photolysis}) \quad (3)$$

$$\frac{d[\text{B}]_t}{dt} = \xi_i[\text{PB}]_t - [\text{B}]_t(k_f[\text{RSH}]_t + k_t^-[\text{HA}]_t) + [\text{HB}^+]_t(k_r[\text{RS}^-]_t + k_{\text{CT}2}[\text{RC}^-]_t + k_t^+[\text{A}^-]_t) \quad (4)$$

$$\frac{d[\text{RSH}]_t}{dt} = k_r[\text{HB}^+]_t[\text{RS}^-]_t - [\text{RSH}]_t(k_f[\text{B}]_t + k_{\text{CT}1}[\text{RC}^-]_t) \quad (5)$$

$$R_p = \frac{d[\text{C}=\text{C}]_t}{dt} = -k_a[\text{RS}^-]_t[\text{C}=\text{C}]_t + k_e[\text{RC}^-]_t \quad (\text{rate of propagation}) \quad (6)$$

$$\frac{d[\text{P}]_t}{dt} = [\text{RC}^-]_t(k_{\text{CT}1}[\text{RSH}]_t + k_{\text{CT}2}[\text{HB}^+]_t) \quad (7)$$

$$\frac{d[\text{RS}^-]_t}{dt} = [\text{RSH}]_t(k_f[\text{B}]_t + k_{\text{CT}1}[\text{RC}^-]_t) + [\text{RS}^-]_t(k_t[\text{HB}^+]_t + k_a[\text{C}=\text{C}]_t) \quad (8)$$

$$\frac{d[\text{RC}^-]_t}{dt} = k_a[\text{RS}^-]_t[\text{C}=\text{C}]_t - [\text{RC}^-]_t(k_{\text{CT}1}[\text{RSH}]_t + k_{\text{CT}2}[\text{HB}^+]_t) \quad (9)$$

$$\frac{d[\text{HB}^+]_t}{dt} = [\text{B}]_t(k_f[\text{RSH}]_t + k_t^-[\text{HA}]_t) - [\text{HB}^+]_t(k_r[\text{RS}^-]_t + k_{\text{CT}2}[\text{RC}^-]_t + k_t^+[\text{A}^-]_t) \quad (10)$$

$$\frac{d[\text{HA}]_t}{dt} = -\frac{d[\text{A}^-]_t}{dt} = k_t^+[\text{HB}^+]_t[\text{A}^-]_t - k_t^-[\text{B}]_t[\text{HA}]_t \quad (\text{rate of termination}) \quad (11)$$