# Nonclassical Dependence of Polymerization Rate on Initiation Rate Observed in Thiol−Ene Photopolymerizations

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Thiol−ene photopolymerizations have garnered significant attention as candidates for many applications including coatings,[1] adhesives,[2] dental materials,[3–5] and imprint lithography.[6] The great potential of these materials arises from their unique combination of attributes including resistance to oxygen inhibition,[1,7] generally rapid polymerization rates,[8] and their high gel-point conversions as compared to other radical-mediated polymerizations, a result of their step-growth polymerization mechanism.[1,9]

For free radical polymerizations, the termination mechanism typically dictates the dependence of polymerization rate on initiation rate ($R_i$) through the well-known "steady-state approximation".[10] The steady-state approximation asserts that the instantaneous rate of change in the active radical population is negligible relative to the rate of both radical production and termination, and thus the radical initiation rate is approximately equal to the radical termination rate.[10] For the ideal case where termination is exclusively bimolecular, through either recombination or disproportionation, the rate of chain-growth radical polymerization has been theoretically predicted and experimentally observed to scale with the square root of $R_i$. For cross-linking chain-growth polymerizations, deviations from the square-root dependence on $R_i$ are often attributed to unimolecular termination events which increase the scaling exponent above 0.5.[11] This termination mode results when the reactive center on the growing polymer chain becomes topologically trapped in the polymer matrix and unable to participate in either propagation or bimolecular termination events. The radical trapping hypothesis is consistent with ESR spectroscopic measurements, where the radical concentration continues to increase as long as irradiation is continued.[12,13] It should be noted that scaling exponents less than 0.5 have also been observed and explained by a variety of other termination mechanisms.[14,15] It has been previously reported that radical-mediated, step-growth thiol−ene polymerizations obey this classical square-root proportionality,[16–19] indicative of bimolecular termination.

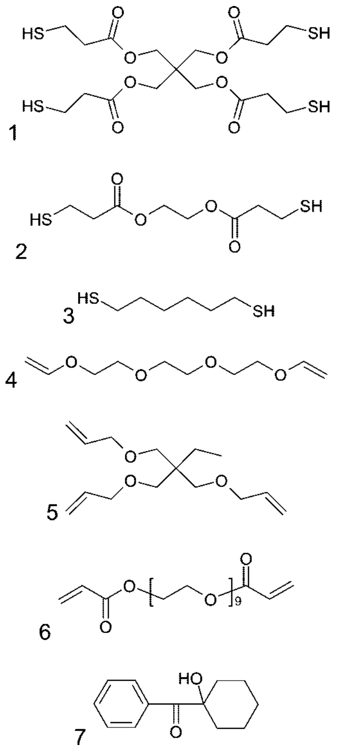

**Figure 1.** Materials used: (**1**) PETMP, (**2**) EGDMP, (**3**) HDT, (**4**) TEGDVE, (**5**) TMPTAE, (**6**) PEG(400)DA, and (**7**) Irgacure 184.

The monomers used in this study are shown in Figure 1 and cover a range of functionalities commonly used in thiol−ene systems, including 3-mercaptopropionates, alkyl thiols, vinyl ethers, and allyl ethers. The diacrylate monomer follows a classical chain-growth mechanism and is used as a control by which to compare. To eliminate effects due to monomer impurities, triethylene glycol divinyl ether (TEGDVE), trimethylolpropane triallyl ether (TMPTAE), ethylene glycol di(3-mercaptopropionate) (EGDMP), and hexanedithiol (HDT) were purified by distillation. Commercially available multifunctional allyl ethers are typically mixtures of multifunctional alcohols having various degrees of substitution. Pure TMPTAE was synthesized by reacting trimethylolpropane diallyl ether with allyl bromide in the presence of sodium hydride (see Supporting Information). Interestingly, neither TMPTAE nor pentaerythritol tetraallyl ether (synthesized from pentaerythritol triallyl ether) is miscible with pentaethritol tetra(3-mercaptopropionate) (PETMP); similarly, Carlsson et al.[20] found that TMPTAE was incompatible with trimethylolpropane tri(3-mercaptopropionate). Instead, EGDMP was used as comonomer in place of PETMP to provide a miscible monomer mixture containing the 3-mercaptopropionate functionality. All resins were formulated with Irgacure 184, a photoinitiator which, upon near-UV irradiation, cleaves to produce two carbon-centered radicals that subsequently initiate polymerization.

The conventional mechanism for a thiol−ene photopolymerization is shown in Scheme 1. After initiation, the thiol−ene polymerization mechanism proceeds via sequential propagation and chain transfer steps. Termination, as shown in Scheme 1, is assumed to occur by bimolecular recombination of radical species, suggesting that thiol−ene photopolymerizations should obey classical bimolecular termination rate kinetics.

Photopolymerizations are particularly amenable to the determination of the effect of $R_i$ on the polymerization rate through simple variation of the incident irradiation intensity as, in most cases, $R_i$ is directly proportional to the irradiation intensity.[10] Vinyl ether conversions during irradiation of stoichiometric PETMP/TEGDVE resins at various irradiation intensities are presented in Figure 2. While the data are ill-fit by the classical scaling exponent of 0.5, an exponent of 0.94 ± 0.02 fits the data well throughout the polymerization and suggests an almost exclusively unimolecular termination mechanism, contradicting

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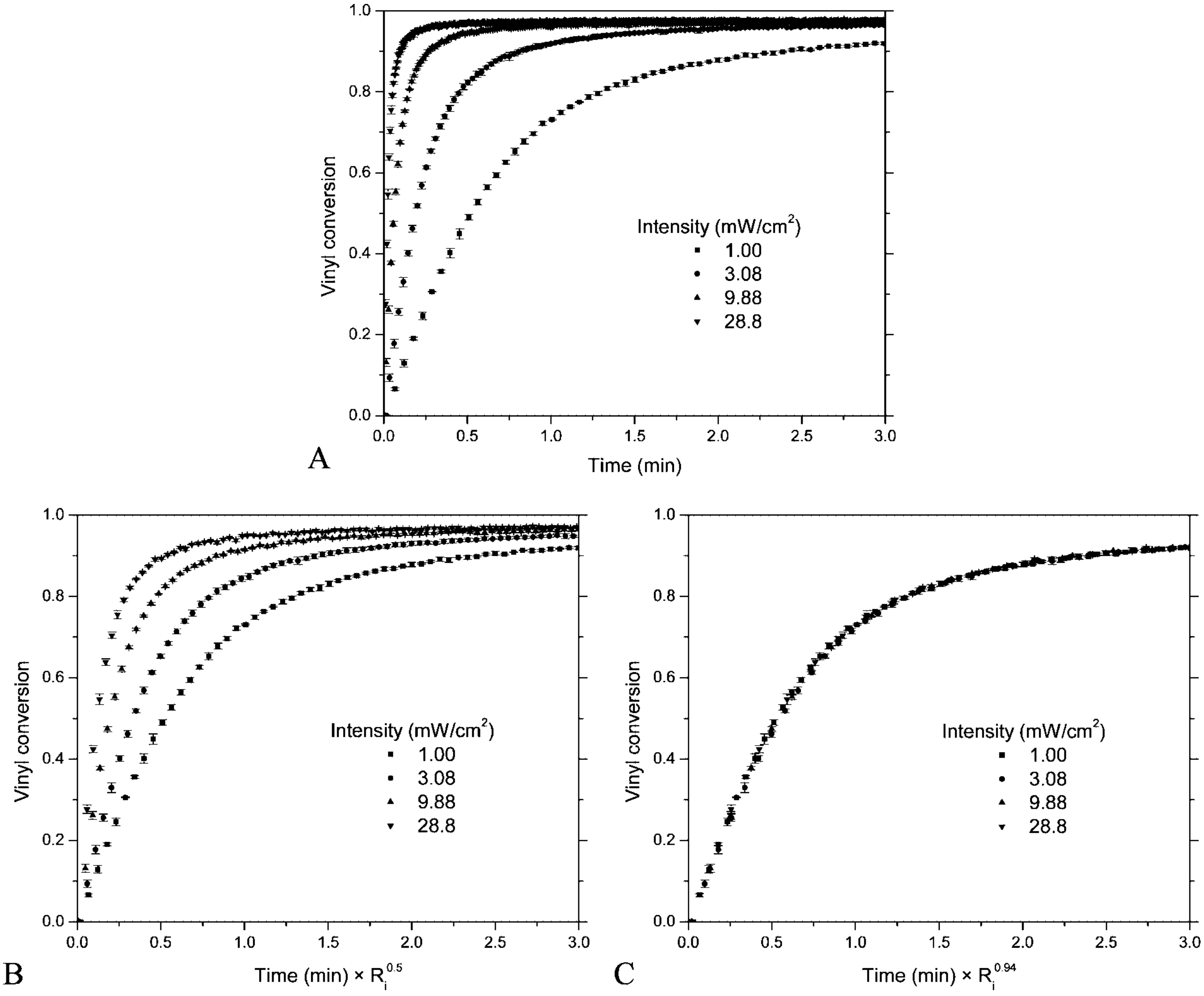

**Figure 2.** Vinyl ether fractional conversion vs time for PETMP/TEGDVE, formulated with 0.1 wt % Irgacure 184. (A) The raw conversion as a function of time data is presented as well as the raw data scaled assuming both (B) $R_p \sim R_i^{0.5}$ and (C) $R_p \sim R_i^{0.94}$ (for clarity, not all data points are plotted). The small error bars demonstrate the ability of our approach to reproducibly measure conversion; the precision of these data is representative of all results presented within this investigation.

the notion that all thiol−ene photopolymerizations obey the classical square-root proportionality.[16–19]

Beyond unimolecular termination, several physical effects might be invoked to explain this observed deviation from classical square-root dependence. For example, if the sample being polymerized were not optically thin, a conversion gradient would be introduced throughout the thickness of the sample during photopolymerization. Additionally, if there were inadequate photoinitiator, the initiation rate would drop below its initial value and would limit the validity of any scaling based on initiation rates. Finally, as polymerizations are typically exothermic, rapid reaction rates in thick samples frequently lead to nonisothermal conditions during polymerization. Although any one of these phenomena could result in misleading values for the scaling exponent, rigorous examination of the experimental conditions used here discounts each as a possibility (see Supporting Information).

The effect of varying the initiation rate on the poly(ethylene glycol 400) diacrylate (PEG400DA) polymerization closely matches that predicted by classical termination rate kinetic theory (0.59 ± 0.01 rather than 0.5; see Table 1) with the small deviation likely resulting from the aforementioned possibility of unimolecular termination in chain-growth systems due to topological restrictions. This behavior is consistent with the low gel point conversion observed in cross-linking chain-growth systems, potentially less than 5%.[21] As a large proportion of propagating radicals are attached to the high molecular weight polymer, there is a large probability that a propagating radical will be trapped in the polymer matrix, unable to undergo further propagation or bimolecular termination.

The initiation rate scaling exponents for several monomer formulations are presented in Table 1. The chemistry of both the thiol and vinyl functionalities appears to affect the scaling exponent, where the proportionality is lower for an alkyl thiol than for a 3-mercaptopropionate and is lower for an allyl ether than for a vinyl ether. Within the margin of error, purging with nitrogen does not result in a significant effect on the scaling exponent. Reddy et al.[18] reported agreement with an exponent of 0.5 for a 3-mercaptopropionate/allyl ether system, which is significantly different from the exponent 0.66 ± 0.02 for EGDMP/TMPTAE found here for the analogous system used in the current work; however, the scaling of their data would likely be improved by a larger exponent. Lee et al.[19] reported an exponent of 0.53 for an alkyl thiol/allyl system, close to the value of 0.56 ± 0.03 for HDT/TMPTAE, a similar system used in the current work. The deviation from classical bimolecular termination for a step-growth system, such as a thiol−ene polymerization, is unexpected as the molecular weight grows geometrically before gelation, making topological trapping of propagating radicals unlikely early in the polymerization.

**Scheme 1. Conventional Thiol−Ene Photopolymerization Mechanism**

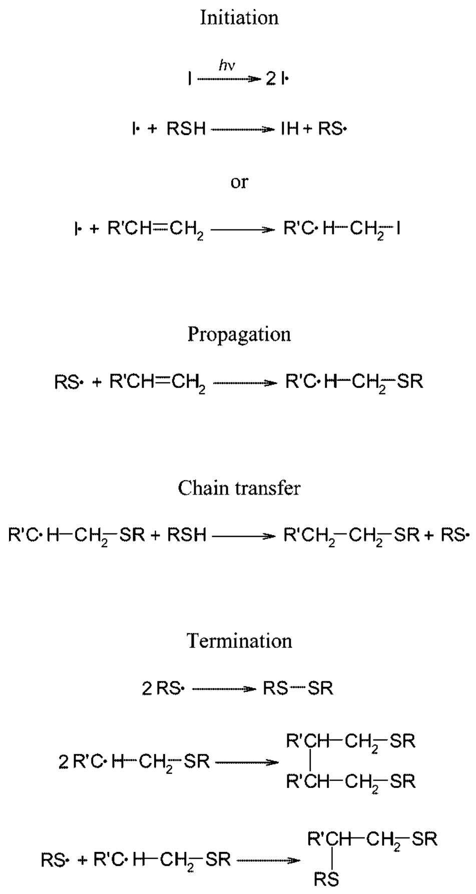

**Table 1. Initiation Rate Scaling Exponents for Several Thiol−Enes and a Single Acrylate Formulation**

| formulation | scaling |
|---|---|
| PETMP/TEGDVE | 0.94 ± 0.02 |
| EGDMP/TEGDVE | 0.88 ± 0.01 |
| EGDMP/TMPTAE | 0.66 ± 0.02 |
| EGDMP/TMPTAE, $N_2$ purged | 0.66 ± 0.02 |
| HDT/TMPTAE | 0.56 ± 0.03 |
| PEG400DA | 0.59 ± 0.01 |

Additionally, all of the systems examined formed rubbery polymers at full conversion, thus avoiding the potential additional complexity of radical trapping associated with vitrification. Moreover, ESR experiments have failed to demonstrate appreciable buildup in the radical concentration during thiol−ene photopolymerizations, discounting the possibility of trapped radicals leading to unimolecular termination. Thus, any deviation from a $R_i$ exponent of 0.5 for a thiol−ene polymerization would suggest that an as yet unidentified termination mechanism is occurring.

One major implication of the scaling exponent differences is that the relative polymerization rates for various monomer combinations are intensity dependent. For example, it is widely believed that thiol/vinyl ether formulations react more rapidly than equivalent thiol/allyl ether formulations;[1,22] however, while we find this to be the case at high irradiation intensities, there should exist a crossover to larger polymerization rates for the EGDMP/TMPTAE formulation than for the EGDMP/TEGDVE formulation at reduced irradiation intensities (see Supporting Information). Indeed, crossovers in the polymerization rates of the HDT/TMPTAE formulation, the EGDMP/TMPTAE formulation, and each of the TEGDVE formulations should be observed at even lower irradiation intensities.

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**Supporting Information Available:** Descriptions of all materials and experimental methods, a detailed examination of photoinitiator loss and the thin film approximation, a heat rise approximation and initiation rate scaling determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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