ACS Macro Letters

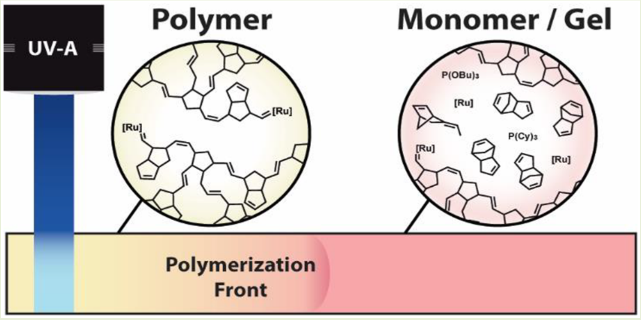
pubs.acs.org/macroletters Letter

Photoexcitation of Grubbs' Second-Generation Catalyst Initiates Frontal Ring-Opening Metathesis Polymerization

Katherine J. Stawiasz, Justine E. Paul, Kevin J. Schwarz, Nancy R. Sottos, and Jeffrey S. Moore*

Cite This: *ACS Macro Lett.* 2020, 9, 1563−1568 Read Online

ABSTRACT: In this work, a simple method is reported for control over initiation in frontal ring-opening metathesis polymerization (FROMP). This noncontact approach uses 375 nm light to excite Grubbs' second-generation catalyst in the presence of a phosphite inhibitor. Photoinitiated FROMP of dicylcopentadiene (DCPD) displays a similar cure profile to that of its thermally initiated counterpart, yielding a robust polymer with high glass transition temperature. Furthermore, this system is applied to enhance reaction rates in conventional ring-closing metathesis reactions.



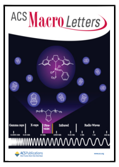
Bulk polymerizations convert neat or highly concentrated monomeric mixtures to polymers in an exothermic fashion while providing minimal contamination of products.[1] As a consequence, the polymeric materials thus obtained typically display both high optical clarity and molecular weights, without requiring significant postpolymerization purification or processing. Controlled bulk polymerizations, therefore, have reduced economic and environmental impacts on both the company and consumer. As a result, bulk polymerization is a ubiquitous technique employed in a variety of industrial settings.[2] Several key drawbacks exist, however, that directly stem from the associated reaction exothermicity and activation energy.[3] Uncontrolled heat dissipation, for example, results in localized hot spots, which may degrade the material or initiate autoacceleration phenomena (i.e., gel effects).[4] Elaborate reaction vessels equipped with mixing apparatuses may circumvent these effects, although with a sizable capital investment cost.[5]

Frontal polymerizations (FPs) are a useful subset of bulk polymerizations which harness the exothermic and autoaccelerating events in a controlled fashion to enable productive and rapid monomer consumption.[6] Highly localized and short-lived external stimuli activate a latent initiator or catalyst to induce a reaction zone (i.e., front). The resultant heat of polymerization promotes further reactions to rapidly polymerize the available monomer. While thermal initiation is easily implemented with a soldering iron, poor spatial and temporal control limits this process by requiring close contact to the heat source. In contrast, light-based stimuli enable spatiotemporal control over initiation. Several examples of ultraviolet light-triggered FP exist for systems involving acrylates, thiolenes, and epoxides.[7] Herein, we report a UV-A-initiated strategy for FP of strained olefin monomers.

Of all reported frontal polymerization systems, frontal ring-opening metathesis polymerization (FROMP) of highly strained olefin monomers is well suited for the rapid manufacturing of engineering materials.[8] Polymer thermosets are easily synthesized in minutes using a thermal stimulus such as a resistive wire in a system with Grubbs' second-generation catalyst (**GC2**, Scheme 1c), phosphite inhibitor, and dicyclopentadiene (DCPD) as the monomer (Figure 1a). In the case of frontally polymerized DCPD, poly(DCPD) is synthesized with nearly identical physical (e.g., T_g, optical clarity) and mechanical (e.g., stiffness, toughness, and impact resistance) properties to traditionally cured analogues.[9] Key to the development of FROMP was the realization of phosphite inhibitors which, when used as an additive, retard background reactivity of **GC2** and the monomer. This resulted in an increased pot life from mere minutes to of ca. 30 h, without significant loss in front speeds.[10] Prolonged pot life eases the processability requirements as more time exists to mix, store, form, and initiate polymerization. Indeed, a host of applications previously untenable such as composite manufacturing and 3D printing are realized with FROMP.[11]

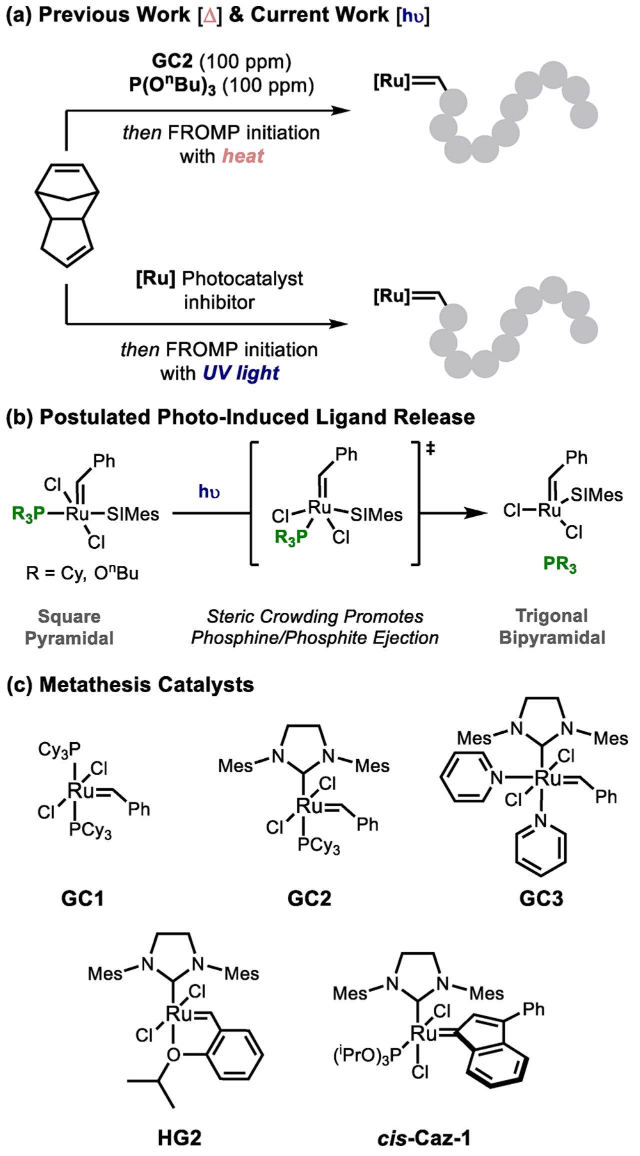
Due to the use of a latent catalyst, there exists a significant opportunity to design systems with new polymerization characteristics and even use alternative stimuli to improve FROMP. While many catalyst activation strategies exist in

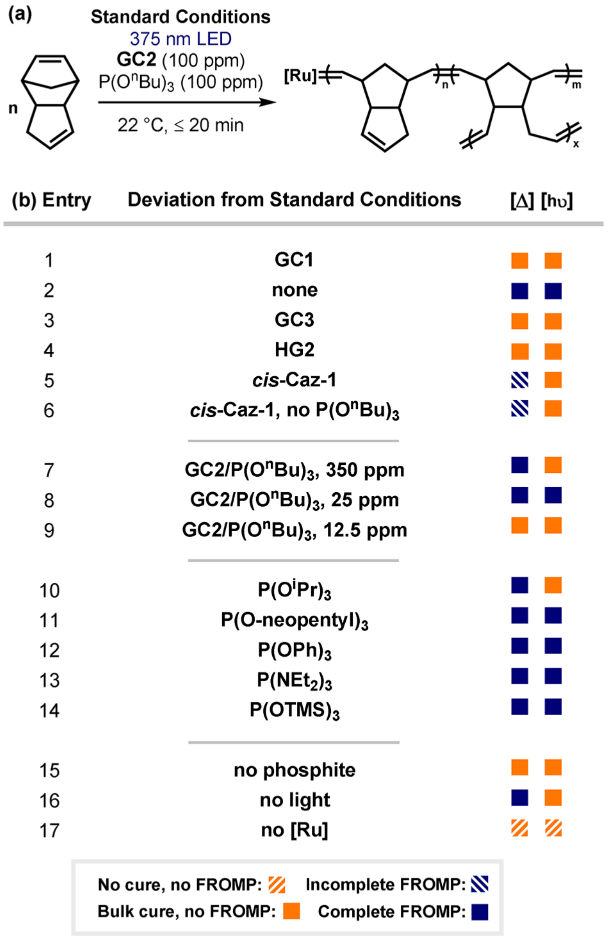
Received: July 1, 2020
Accepted: August 12, 2020
Published: October 20, 2020



https://dx.doi.org/10.1021/acsmacrolett.0c00486
ACS Macro Lett. 2020, 9, 1563−1568

Scheme 1. (a) Frontal Ring-Opening Metathesis Polymerization Initiated by a Heat or Light Source, (b) Potential Mechanism for Light-Promoted Phosphine Dissociation for the GC2/Phosphite System,[18] and (c) Ruthenium-Based Metathesis Catalysts Investigated in This Study (Cy = Cyclohexane, Mes = Mesitylene, Ph = Phenyl)





(b) Entry	Deviation from Standard Conditions	[Δ]	[hυ]
1	GC1	🟧	🟧
2	none	🟦	🟦
3	GC3	🟧	🟧
4	HG2	🟧	🟧
5	*cis*-Caz-1	▨	🟧
6	*cis*-Caz-1, no P(O^{n}Bu)$_3$	▨	🟧
7	GC2/P(O^{n}Bu)$_3$, 350 ppm	🟦	🟧
8	GC2/P(O^{n}Bu)$_3$, 25 ppm	🟦	🟦
9	GC2/P(O^{n}Bu)$_3$, 12.5 ppm	🟧	🟧
10	P(O^{i}Pr)$_3$	🟦	🟧
11	P(O-neopentyl)$_3$	🟦	🟦
12	P(OPh)$_3$	🟦	🟦
13	P(NEt$_2$)$_3$	🟦	🟦
14	P(OTMS)$_3$	🟦	🟦
15	no phosphite	🟧	🟧
16	no light	🟦	🟧
17	no [Ru]	▧	▧

No cure, no FROMP: ▧ Incomplete FROMP: ▨
Bulk cure, no FROMP: 🟧 Complete FROMP: 🟦

Figure 1. (a) Scheme for light-promoted FROMP reaction. (b) Optimization and control reaction experiments leading to light-promoted FROMP reaction. Standard conditions: 10 mL monomer solution (95 wt % DCPD, 5 wt % 5-ethylidene-2-norbornene (ENB)) and 100 ppm GC2/P(O^{n}Bu)$_3$. A soldering iron was used for thermally initiated cases, while a 375 nm LED was used for photo-FROMP. In all entries, phosphite and catalyst loadings are equal.

other metathesis reactions (e.g., redox switches, acid, light, and ultrasound), current FROMP systems have only exploited thermal initiation.[12]

Light is an attractive stimulus to achieve spatial and temporal control over reaction events in a noncontact manner.[13] Many strategies have been developed to harness light to control olefin metathesis reactions.[14] These strategies include the use of a photoswitchable N-heterocyclic carbene (NHC) ruthenium catalyst, the merger of a photoredox catalyst with a latent bis-NHC ruthenium catalyst, and the use of latent ruthenium catalysts that isomerize through a geometric switch from *cis*-dichloro to *trans*-dichloro (***cis*-Caz-1**, Scheme 1c).[15] A common mechanistic theme throughout these strategies is the increased lability of an apical ligand (phosphine or NHC) to promote catalyst activation.[16] With these considerations in mind, we undertook a study to investigate photo-FROMP (Scheme 1a).

Due to the requirements necessary to initiate and maintain FROMP, the ideal approach to photo-FROMP is to identify a light source/sensitizer capable of activating the previously developed, thermally propagated system (**GC2**, P(O^{n}Bu$_3$)).[17] Previous reports demonstrated that exposure of Grubbs' first-generation catalyst (**GC1**) to UV light causes a photochemical release of the phosphine ligand.[18] The release of the ligand in the presence of a suitable monomer results in an increase of catalyst activity. Many in-depth studies on the mechanism of **GC2** indicate that the dissociation of a phosphine ligand is a critical step in both the activity of the catalyst and its lifetime.[19] We hypothesized that catalyst activation by photoinduced phosphine or phosphite release promotes controlled initiation of FROMP (Scheme 1b).

To test our hypothesis, we first evaluated Grubbs' ruthenium catalysts with P(O^{n}Bu)$_3$ using a 375 nm, 318 mW/cm^2 LED (Figure 1b, entries 1−4). Not only was **GC2** responsive to light but also it initiated frontal polymerization in 6 min at 100 ppm catalyst loading (Figure 2a and SI Figure S2). In contrast, rapid gelation followed the addition of **GC1** to DCPD/P(O^{n}Bu)$_3$, and a detectable front was not observed. Moreover,

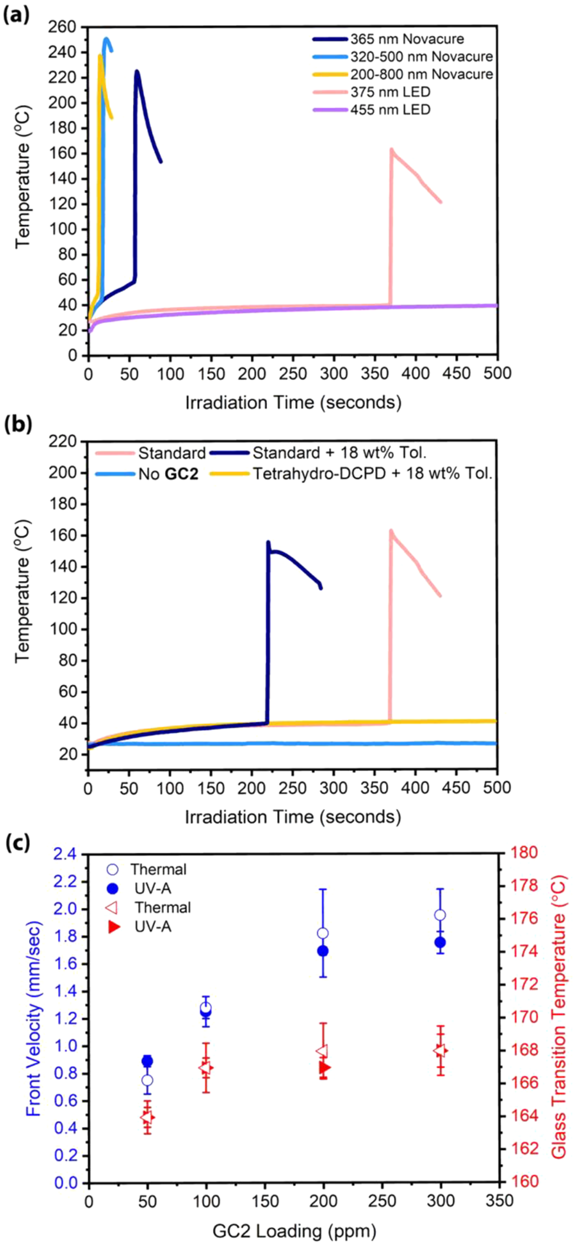


Figure 2. (a) Initiation times for photo-FROMP reactions based on wavelength and power. Temperature was measured using a thermocouple. Conditions: 10 mL of monomer solution and 100 ppm of **GC2**/P(O^{n}Bu)$_3$. (b) Solution temperature over time, measured by a thermocouple. Standard (pink): 10 mL of monomer solution and 100 ppm of **GC2**/P(O^{n}Bu)$_3$. No **GC2** (light blue): same as standard, without catalyst. Standard in toluene (purple): 10 mL of solution of 82:18 DCPD:toluene by volume and 100 ppm of **GC2**/P(O^{n}Bu)$_3$. Tetrahydro-DCPD conditions (yellow): 10 g of tetrahydro-DCPD monomer (no ENB) and 100 ppm of **GC2**/P(O^{n}Bu)$_3$. (c) Comparison of front speeds and T_g between light and thermal initiation. See also SI Table S1 and Table S4.

subsequent attempts to initiate FROMP with thermal and photo stimuli failed with this formulation. For the dipyridine derivative of Grubbs' third-generation catalyst (**GC3**) and Hoveyda–Grubbs II (**HG2**), instantaneous, exothermic polymerization was observed upon addition of the catalyst to DCPD/P(O^{n}Bu)$_3$.

We next evaluated a latent ruthenium catalyst previously developed for applications in photomediated ring-closing metathesis (RCM), cross metathesis (CM), and ring-opening metathesis polymerization (ROMP) that might provide for improved initiation rates (Figure 1b, entries 5 and 6). Despite reports that ***cis*-Caz-1** can facilitate light-promoted ROMP, our setup only promoted slow curing of DCPD. While ***cis*-Caz-1** enabled heat-initiated FROMP, the polymerization front was highly unstable, and the polymerization was extinguished prematurely.

Varying **GC2** and phosphite inhibitor loadings from 350 to 12.5 ppm resulted in large differences in the ability to initiate frontal polymerization (Figure 1b, entries 2 and 7–9, and SI Figure S2). At 350 ppm of **GC2**/P(O^{n}Bu)$_3$, thermal initiation occurred to provide a stable front; at these concentrations, however, photoignition did not occur. At lower loadings (ca. 25 ppm **GC2**/P(O^{n}Bu)$_3$), both thermal and photoinitiation afforded detectable polymer fronts. Loadings lower than 12.5 ppm resulted in slow, nonfrontal curing over several hours regardless of the initial stimulus.

The choice of phosphorus-centered inhibitor had little influence on frontal polymerization initiation via heat or light (Figure 1b, entries 10–14). Initiation times did vary slightly between P(NEt$_2$)$_3$, which displayed the fastest initiation, and P(O^{i}Pr)$_3$, which showed the slowest initiation time. Light initiation was not observed using P(O^{i}Pr)$_3$ as the inhibitor, even after 2 h of exposure, but instead led to significant bulk curing. The absence of added phosphorus inhibitor altogether resulted in immediate reaction and gelation before all components were homogeneously mixed. Finally, the removal of a light stimulus or ruthenium catalyst resulted in a slow bulk cure or no reaction at all, respectively (Figure 1b, entries 16 and 17).

The energy of the incident photostimulus affected the efficacy of FROMP. Changes to the wavelength and power density caused a significant variation in the initiation time. A 375 nm LED at 318 mW/cm^2 initiated FROMP within ca. 6 min (Figure 2a). Shorter wavelength light (365 nm) with an order of magnitude increase in power density (4750 mW/cm^2) reduced the initiation time to ca. 55 s. Increasing the power density further to 17 000 mW/cm^2 and broadening the spectrum of light to 320–500 nm resulted in initiation times as low as 15 s. Notably, if the wavelength of light used (455 nm) was outside of the major absorbance band for **GC2** (λ_{max} = 342 nm), frontal polymerization was not observed even after 20 min (Figure 2a).

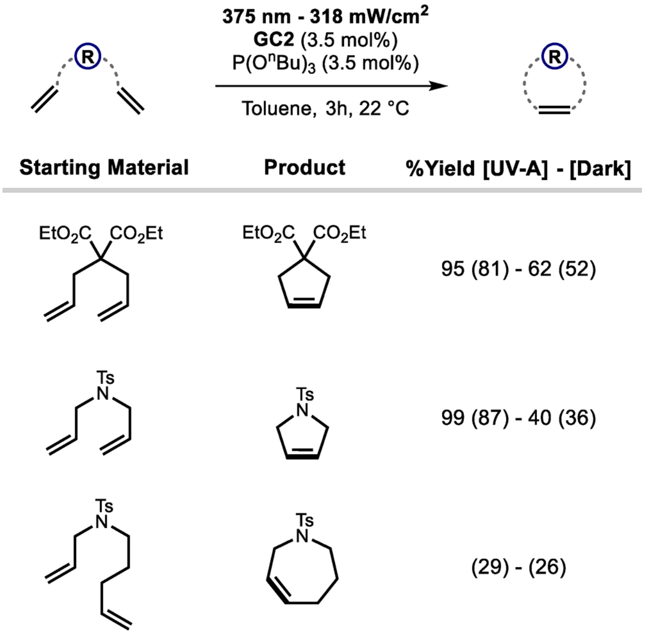
A series of control experiments were carried out to delineate the cause of initiation as a photo, photothermal, or thermal effect (Figure 2b). Using standard conditions (Figure 1b, entry 2) in a test tube with a T-type thermocouple (SI, Figure S1), the solution warmed from 22 to 39 °C before initiation is observed. When **GC2** was removed, no initiation and no increase in temperature were observed, showing that **GC2** is necessary to generate heat. Notably, when tetrahydro-DCPD (SI, Figure S6) dissolved in a minimal amount of toluene was used in place of DCPD, the temperature profile matched that of the standard run. This implicated photon absorption and nonradioactive decay from **GC2** as the thermal source as opposed to background polymerization. Lastly, to determine if the heat generated during light-promoted FROMP is sufficient to initiate FROMP on its own, differential scanning calorimetry (DSC) was used by running isothermal holds at a range of temperatures for 20 min. The minimum temperature for thermal FP initiation is 50 °C (DSC), while the temperature observed for initiation using a 375 nm LED at

318 mW/cm^2 was 39 °C (thermocouple) (see SI, Figure S3 and Table S2 for isothermal DSC study). The irradiated sample never reaches 50 °C before frontal polymerization occurs, and initiation promoted by photoexcitation of **GC2** is highly likely. This finding is consistent with light-promoted phosphine or phosphite dissociation.

Nearly all polymerization characteristics and polymer thermomechanical properties matched that of pDCPD produced by thermally initiated FROMP (Figure 2c and SI Table S3). Front speeds increased from 0.8 mm/s to 1.75 mm/s with increasing catalyst and inhibitor concentration, consistent with what we observed in the thermal case. The glass transition temperatures (T_g) of the various **GC2** loadings were comparable for both initiation methods and were higher than previous reports (T_g ca. 140 °C) since a solvent-free system was used in this study.[20] Regardless of the stimulus used for initiation of frontal polymerization, the final polymer product properties were not affected.

With an optimized system in hand, we next explored the ability of **GC2** to accelerate other types of metathesis reactions, such as ring-closing metathesis, using light (Scheme 2). For each substrate, two different conditions were tested: no light (dark) with phosphite, and light with phosphite. Across all cases of RCM (Scheme 2), the use of 375 nm light significantly improved yields over reactions run in the absence of light. Reactions run with ambient light and no UV-A light stimulus showed identical results to those run in the absence of light.

Scheme 2. Application of UV-A Light to Accelerate Ring-Closing Metathesis[a]



[a]Reactions were run on a 0.1 mmol scale using 5 mm thin-wall precision quartz NMR tubes. Isolated yields are reported in parentheses. NMR yields, where possible, are reported without parentheses.

Our work details a noncontact strategy for spatiotemporal control over initiation in frontal ring-opening metathesis polymerization of DCPD at room temperature using 375 nm light as a stimulus and **GC2** as a catalyst. The resulting polymer has properties equal to its thermally initiated counterparts. A series of differential scanning calorimetry tests provide the evidence that FROMP occurs by photoinitiation as opposed to thermal initiation, though the exact mechanism is unknown. While the front is thermally propagated, this photoinitiated process opens the door to further exploration of **GC2** as a photocatalyst.

Much research has gone into the development of ruthenium-based metathesis photocatalysts; however, the use of Grubbs' second-generation catalyst has been underexplored as a photocatalyst. Here we showed the feasibility of using a bench-stable, commercially available catalyst to remove the synthetic and economic burden of catalyst synthesis typically required for ruthenium-based metathesis photocatalysts.[21] We anticipate that this research will facilitate the use of **GC2** for applications that range from light-induced patterning to photolithography. Ongoing research efforts aim to elucidate the operative mechanism for the observed behavior as this will aid in the development of new methods which use **GC2** in photochemical applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00486.

> Instrumentation, materials for FROMP, general procedure 1 for thermally activated FROMP, general procedure 2 for UV-activated FROMP, determination of UV-A initiation time, DSC experiments, penetration depth, UV-Vis spectra, general procedure 3 for RCM, synthetic procedures, NMR characterization (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jeffrey S. Moore − *Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States;* orcid.org/0000-0001-5841-6269; Email: jsmoore@illinois.edu

Authors

Katherine J. Stawiasz − *Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States;* orcid.org/0000-0003-2518-0557

Justine E. Paul − *Department of Materials Science and Engineering and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States*

Kevin J. Schwarz − *Department of Chemistry, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States*

Nancy R. Sottos − *Department of Materials Science and Engineering and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States;* orcid.org/0000-0002-5818-520X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmacrolett.0c00486

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the Air Force Office of Scientific Research with Award FA9550-16-1-0017 and the National Science Foundation with Award CMMI 19-33932 for financial support. We are also grateful to the NMR and mass spectrometry facilities at the University of Illinois.

■ REFERENCES

(1) (a) Ebewele, R. O. *Polymer Science and Technology*; CRC Press LLC: New York, 2000; Chapter 10. (b) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons, Inc.: Staten Island, NY, 2004.

(2) Nesvadba, P. Radical Polymerization in Industry. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; American Cancer Society, 2012. DOI: 10.1002/9781119953678.rad080.

(3) (a) Norrish, R. G. W.; Smith, R. R. CATALYSED POLYMERIZATION OF METHYL METHACRYLATE IN THE LIQUID PHASE. *Nature* **1942**, *150* (3803), 336−337. (b) Schulz, V. G. V.; Harborth, G. Über den mechanismus des explosiven polymerisationsverlaufes des methacrylsäuremethylesters. *Makromol. Chem.* **1947**, *1* (1), 106−139. (c) Trommsdorff, V. E.; Köhle, H.; Lagally, P. Zur polymerisation des methacrylsäuremethylesters1. *Makromol. Chem.* **1948**, *1* (3), 169−198.

(4) (a) Wang, W.; Fang, J.; Pan, X.; Hua, M.; Jiang, J.; Ni, L.; Jiang, J. Thermal Research on the Uncontrolled Behavior of Styrene Bulk Polymerization. *J. Loss Prev. Process Ind.* **2019**, *57*, 239−244. (b) Tulig, T. J.; Tirrell, M. On the Onset of the Trommsdorff Effect. *Macromolecules* **1982**, *15* (2), 459−463. (c) Tulig, T. J.; Tirrell, M. Molecular Theory of the Trommsdorff Effect. *Macromolecules* **1981**, *14* (5), 1501−1511.

(5) (a) Ebewele, R. O. *Polymer Science and Technology*; CRC Press LLC: New York, 2000; Chapter 10. (b) Abliz, D.; Duan, Y.; Steuernagel, L.; Xie, L.; Li, D.; Ziegmann, G. Curing Methods for Advanced Polymer Composites - A Review. *Polym. Polym. Compos.* **2013**, *21*, 341.

(6) (a) Pojman, J. A. In *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K., Möller, M., Eds.; Elsevier: Amsterdam, 2012; Vol. *4*, pp 957−980. (b) Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. Free-Radical Frontal Polymerization: Self-Propagating Thermal Reaction Waves. *J. Chem. Soc. J. Chem. Soc., Faraday Trans.* **1996**, *92* (16), 2825−2837.

(7) (a) Mariani, A.; Bidali, S.; Fiori, S.; Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A. UV-Ignited Frontal Polymerization of an Epoxy Resin. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (9), 2066−2072. (b) Nason, C.; Roper, T.; Hoyle, C.; Pojman, J. A. UV-Induced Frontal Polymerization of Multifunctional (Meth)Acrylates. *Macromolecules* **2005**, *38* (13), 5506−5512. (c) Nason, C.; Pojman, J. A.; Hoyle, C. The Effect of a Trithiol and Inorganic Fillers on the Photo-Induced Thermal Frontal Polymerization of a Triacrylate. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (24), 8091−8096. (d) Sangermano, M.; D'Anna, A.; Marro, C.; Klikovits, N.; Liska, R. UV-Activated Frontal Polymerization of Glass Fibre Reinforced Epoxy Composites. *Composites, Part B* **2018**, *143*, 168−171. (e) Cabral, J. T.; Hudson, S. D.; Harrison, C.; Douglas, J. F. Frontal Photopolymerization for Microfluidic Applications. *Langmuir* **2004**, *20* (23), 10020−10029. (f) Bomze, D.; Knaack, P.; Liska, R. Successful Radical Induced Cationic Frontal Polymerization of Epoxy-Based Monomers by C−C Labile Compounds. *Polym. Chem.* **2015**, *6* (47), 8161−8167. (g) Crivello, J. V. Investigation of the Photoactivated Frontal Polymerization of Oxetanes Using Optical Pyrometry. *Polymer* **2005**, *46* (26), 12109−12117. (h) Fan, S.; Liu, S.; Wang, X.-Q.; Wang, C.-F.; Chen, S. Laser-Ignited Frontal Polymerization of Shape-Controllable Poly(VI-Co-AM) Hydrogels Based on 3D Templates toward Adsorption of Heavy Metal Ions. *Appl. Phys. A: Mater. Sci. Process.* **2016**, *122* (6), 599. (i) Potzmann, P. M.; Lopez Villanueva, F. J.; Liska, R. UV-Initiated Bubble-Free Frontal Polymerization in Aqueous Conditions. *Macromolecules* **2015**, *48* (24), 8738−8745. (j) Zhou, J.; Jia, S.; Fu, W.; Liu, Z.; Tan, Z. Fast Curing of Thick Components of Epoxy via Modified UV-Triggered Frontal Polymerization Propagating Horizontally. *Mater. Lett.* **2016**, *176*, 228−231. (k) Zhou, Z.-F.; Yu, C.; Wang, X.-Q.; Tang, W.-Q.; Wang, C.-F.; Chen, S. Facile Access to Poly(NMA-Co-VCL) Hydrogels via Long Range Laser Ignited Frontal Polymerization. *J. Mater. Chem. A* **2013**, *1* (25), 7326−7331.

(8) Robertson, I. D.; Yourdkhani, M.; Centellas, P. J.; Aw, J. E.; Ivanoff, D. G.; Goli, E.; Lloyd, E. M.; Dean, L. M.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; White, S. R. Rapid Energy-Efficient Manufacturing of Polymers and Composites via Frontal Polymerization. *Nature* **2018**, *557* (7704), 223−227.

(9) (a) Delaude, L.; Noels, A. F. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Seidel, A., Ed.; John Wiley & Sons, Inc.: Malden, 2007; Vol. *26*, pp 920−958. (b) Woodson, C. S., Jr.; Grubbs, R. H. Polymeric composites including dicyclopentadiene and related monomers. US patent 6,310,121 B1 (2001). (c) Vallons, K. A. M.; Drozdzak, R.; Charret, M.; Lomov, S. V.; Verpoest, I. Assessment of the Mechanical Behaviour of Glass Fibre Composites with a Tough Polydicyclopentadiene (PDCPD) Matrix. *Composites, Part A* **2015**, *78*, 191−200.

(10) Robertson, I. D.; Dean, L. M.; Rudebusch, G. E.; Sottos, N. R.; White, S. R.; Moore, J. S. Alkyl Phosphite Inhibitors for Frontal Ring-Opening Metathesis Polymerization Greatly Increase Pot Life. *ACS Macro Lett.* **2017**, *6* (6), 609−612.

(11) Robertson, I. D.; Yourdkhani, M.; Centellas, P. J.; Aw, J. E.; Ivanoff, D. G.; Goli, E.; Lloyd, E. M.; Dean, L. M.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; White, S. R. Rapid Energy-Efficient Manufacturing of Polymers and Composites via Frontal Polymerization. *Nature* **2018**, *557* (7704), 223−227.

(12) (a) Teator, A. J.; Bielawski, C. W. Remote Control Grubbs Catalysts That Modulate Ring-Opening Metathesis Polymerizations. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55* (18), 2949−2960. (b) Monsaert, S.; Lozano Vila, A.; Drozdzak, R.; Van Der Voort, P.; Verpoort, F. Latent Olefin Metathesis Catalysts. *Chem. Soc. Rev.* **2009**, *38* (12), 3360−3372.

(13) (a) Göstl, R.; Senf, A.; Hecht, S. Remote-Controlling Chemical Reactions by Light: Towards Chemistry with High Spatio-Temporal Resolution. *Chem. Soc. Rev.* **2014**, *43* (6), 1982−1996. (b) Teator, A. J.; Lastovickova, D. N.; Bielawski, C. W. Switchable Polymerization Catalysts. *Chem. Rev.* **2016**, *116* (4), 1969−1992. (c) Leibfarth, F. A.; Mattson, K. M.; Fors, B. P.; Collins, H. A.; Hawker, C. J. External Regulation of Controlled Polymerizations. *Angew. Chem., Int. Ed.* **2013**, *52* (1), 199−210.

(14) Vidavsky, Y.; Lemcoff, N. G. Light-Induced Olefin Metathesis. *Beilstein J. Org. Chem.* **2010**, *6* (1), 1106−1119.

(15) (a) Teator, A. J.; Tian, Y.; Chen, M.; Lee, J. K.; Bielawski, C. W. An Isolable, Photoswitchable N-Heterocyclic Carbene: On-Demand Reversible Ammonia Activation. *Angew. Chem., Int. Ed.* **2015**, *54* (39), 11559−11563. (b) Theunissen, C.; Ashley, M. A.; Rovis, T. Visible-Light-Controlled Ruthenium-Catalyzed Olefin Metathesis. *J. Am. Chem. Soc.* **2019**, *141* (17), 6791−6796. (c) Eivgi, O.; Guidone, S.; Frenklah, A.; Kozuch, S.; Goldberg, I.; Lemcoff, N. G. Photoactivation of Ruthenium Phosphite Complexes for Olefin Metathesis. *ACS Catal.* **2018**, *8* (7), 6413−6418. (d) Diesendruck, C. E.; Tzur, E.; Ben-Asuly, A.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. Predicting the Cis−Trans Dichloro Configuration of Group 15−16 Chelated Ruthenium Olefin Metathesis Complexes: A DFT and Experimental Study. *Inorg. Chem.* **2009**, *48* (22), 10819−10825. (e) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky, Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. Photoactivation of Ruthenium Olefin Metathesis Initiators. *Organometallics* **2009**, *28* (16), 4652−4655. (f) Aharoni, A.; Vidavsky, Y.; Diesendruck, C. E.; Ben-Asuly, A.; Goldberg, I.; Lemcoff, N. G. Ligand Isomerization in Sulfur-Chelated Ruthenium Benzylidenes. *Organometallics* **2011**, *30* (6), 1607−1615.

(16) Eivgi, O.; Lemcoff, N. G. Turning the Light On: Recent Developments in Photoinduced Olefin Metathesis. *Synthesis* **2018**, *50* (01), 49−63.

(17) (a) Robertson, I. D.; Yourdkhani, M.; Centellas, P. J.; Aw, J. E.; Ivanoff, D. G.; Goli, E.; Lloyd, E. M.; Dean, L. M.; Sottos, N. R.;

Geubelle, P. H.; Moore, J. S.; White, S. R. Rapid Energy-Efficient Manufacturing of Polymers and Composites via Frontal Polymerization. *Nature* **2018**, *557* (7704), 223−227. (b) Robertson, I. D.; Dean, L. M.; Rudebusch, G. E.; Sottos, N. R.; White, S. R.; Moore, J. S. Alkyl Phosphite Inhibitors for Frontal Ring-Opening Metathesis Polymerization Greatly Increase Pot Life. *ACS Macro Lett.* **2017**, *6* (6), 609−612.

(18) Kunkely, H.; Vogler, A. Photoreactivity of Bis-(Tricyclohexylphosphine)Benzylidene Ruthenium Dichloride (Grubbs's Catalyst). *Inorg. Chim. Acta* **2001**, *325* (1), 179−181.

(19) (a) Sanford, M. S.; Love, J. A.; Grubbs, R. H. Mechanism and Activity of Ruthenium Olefin Metathesis Catalysts. *J. Am. Chem. Soc.* **2001**, *123* (27), 6543−6554. (b) Sanford, M. S.; Ulman, M.; Grubbs, R. H. New Insights into the Mechanism of Ruthenium-Catalyzed Olefin Metathesis Reactions. *J. Am. Chem. Soc.* **2001**, *123* (4), 749−750.

(20) Ivanoff, D. G., Sung, J., Butikofer, S. M., Moore, J. S., Sottos, N. R. Crosslinking Agents for Enhanced Performance of Thermosets Prepared via Frontal Ring-Opening Metathesis Polymerization. Submitted.

(21) (a) Teator, A. J.; Tian, Y.; Chen, M.; Lee, J. K.; Bielawski, C. W. An Isolable, Photoswitchable N-Heterocyclic Carbene: On-Demand Reversible Ammonia Activation. *Angew. Chem., Int. Ed.* **2015**, *54* (39), 11559−11563. (b) Theunissen, C.; Ashley, M. A.; Rovis, T. Visible-Light-Controlled Ruthenium-Catalyzed Olefin Metathesis. *J. Am. Chem. Soc.* **2019**, *141* (17), 6791−6796. (c) Eivgi, O.; Guidone, S.; Frenklah, A.; Kozuch, S.; Goldberg, I.; Lemcoff, N. G. Photoactivation of Ruthenium Phosphite Complexes for Olefin Metathesis. *ACS Catal.* **2018**, *8* (7), 6413−6418. (d) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky, Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. Photoactivation of Ruthenium Olefin Metathesis Initiators. *Organometallics* **2009**, *28* (16), 4652−4655. (e) Aharoni, A.; Vidavsky, Y.; Diesendruck, C. E.; Ben-Asuly, A.; Goldberg, I.; Lemcoff, N. G. Ligand Isomerization in Sulfur-Chelated Ruthenium Benzylidenes. *Organometallics* **2011**, *30* (6), 1607−1615.