Chapter 1: https://doi.org/10.1039/D5SC04652A

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From the journal:
Chemical Science

Leveraging reactivity to gain precise control over macromolecular structures with photocatalysis in reversible-deactivation radical polymerizations

Jared G. Baker,[a] Joey Gloriod[a] and C. Adrian Figg *[a]

Abstract

Photocatalysis has gained a prominent role in reversible-deactivation radical polymerization (RDRP) techniques. Photocatalyzed polymerizations are appealing due to ease of implementation, oxygen tolerance, spatiotemporal and orthogonal control, and increased uniformity in polymer chain ends compared to exogenous initiation. Due to these attractive features, photocatalysis has been widely used and incorporated into atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization. Herein, recent examples of photocatalysis in RDRP techniques at the macroscopic, topological, and primary sequence levels of control are presented to highlight how photocatalysis has led to advances at all levels of polymer chemistry. For example, photocatalysis can be used for the selective photoactivation of distinct end-groups, enabling the synthesis of sequence-defined oligomers/polymers, or complex polymer topologies. However, there are still significant gaps in

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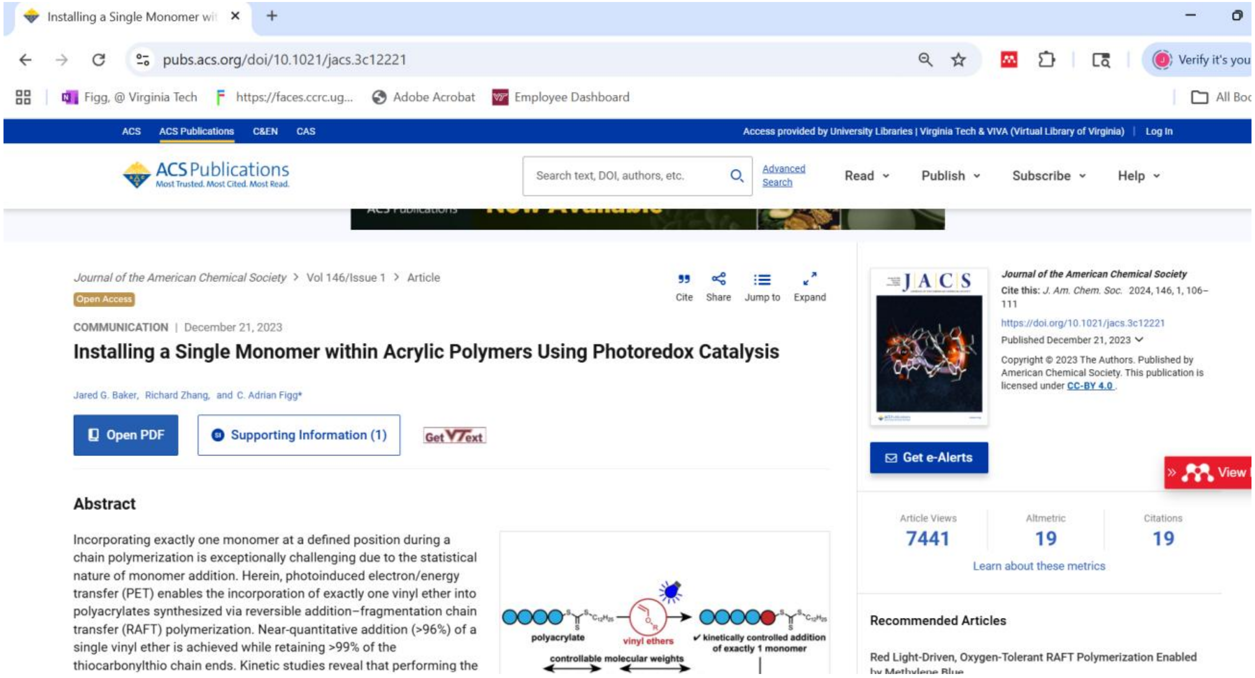

Journal of the American Chemical Society > Vol 146/Issue 1 > Article

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COMMUNICATION | December 21, 2023

Installing a Single Monomer within Acrylic Polymers Using Photoredox Catalysis

Jared G. Baker, Richard Zhang, and C. Adrian Figg*

Abstract

Incorporating exactly one monomer at a defined position during a chain polymerization is exceptionally challenging due to the statistical nature of monomer addition. Herein, photoinduced electron/energy transfer (PET) enables the incorporation of exactly one vinyl ether into polyacrylates synthesized via reversible addition−fragmentation chain transfer (RAFT) polymerization. Near-quantitative addition (>96%) of a single vinyl ether is achieved while retaining >99% of the thiocarbonylthio chain ends. Kinetic studies reveal that performing the

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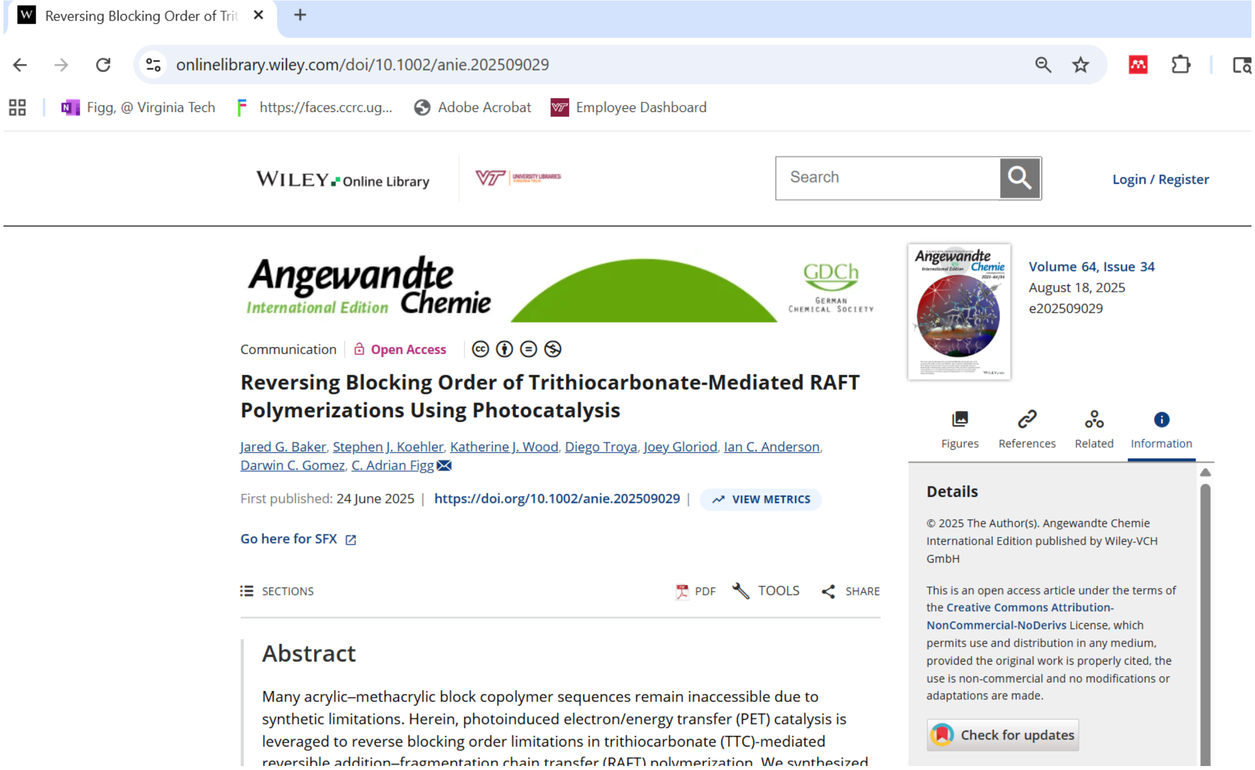

Communication | Open Access

Reversing Blocking Order of Trithiocarbonate-Mediated RAFT Polymerizations Using Photocatalysis

Jared G. Baker, Stephen J. Koehler, Katherine J. Wood, Diego Troya, Joey Gloriod, Ian C. Anderson, Darwin C. Gomez, C. Adrian Figg

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Abstract

Many acrylic–methacrylic block copolymer sequences remain inaccessible due to synthetic limitations. Herein, photoinduced electron/energy transfer (PET) catalysis is leveraged to reverse blocking order limitations in trithiocarbonate (TTC)-mediated reversible addition–fragmentation chain transfer (RAFT) polymerization. We synthesized

Chapter 6: https://pubs.rsc.org/en/content/articlelanding/2024/py/d4py00874j

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From the journal:
Polymer Chemistry

Customizing STEM organogels using PET-RAFT polymerization†

Check for updates

Zaya Bowman, ‡[a] Jared G. Baker, ‡[ab] Madeleine J. Hughes, [a] Jessica D. Nguyen, [a] Mathew Garcia, [a] Nahome Tamrat, [a] Joshua C. Worch [ab] and C. Adrian Figg *[ab]

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Abstract

Photoinduced electron/energy transfer (PET) reversible addition–fragmentation chain transfer (RAFT) polymerization results in more uniform polymer networks compared to networks synthesized by thermally initiated RAFT polymerizations. However, how PET-RAFT polymerizations affect molecular weight control and physical properties during parent-to-daughter block copolymer network synthesis is unclear. Herein, we synthesized a structurally tailored and engineered macromolecular (STEM) organogel composed of poly(methyl acrylate) and a degradable crosslinker. Chain extensions on the STEM organogel were performed using PET-RAFT polymerization of either methyl acrylate (MA) or *N*,*N*-dimethylacrylamide (DMA) with or without additional crosslinker. We found that physical properties were dependent on monomer composition and crosslinking. The swelling ratios of the diblock networks were similar in DMAc. Conversely, swelling ratios in water increased by 430% for networks extended with MA and 5200% for networks extended with DMA compared to the parent organogels. Rheological analysis showed a tunable modulus from 1000–4000 Pa. However, size exclusion chromatography analysis of the degraded gels revealed that the PET-RAFT polymerization chain extension yielded disperse block copolymers with poor control over the molecular weight. These results indicate that PET-RAFT polymerizations can be used to expand organogel networks to block

Supplementary files

Supplementary information
PDF (6053K)

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