

Investigating Radical Reactivity and Structure-Property Relationships through Photopolymerization

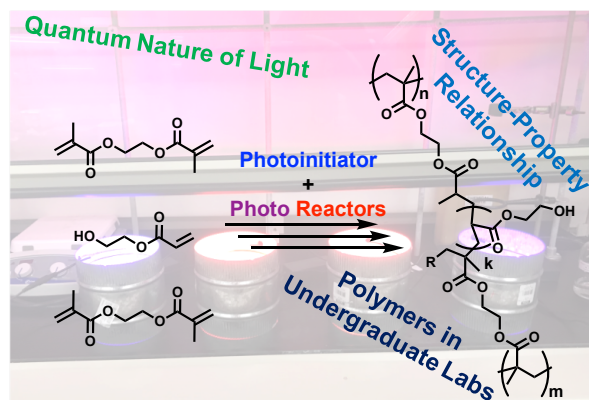
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ABSTRACT

The ACS Guidelines for bachelor's degrees in chemistry call for the curriculum to include polymer chemistry principles and the synthesis of different classes of macromolecules. Organic chemistry can provide an important introduction to polymer chemistry principles, and photochemically-induced radical polymerization is one method for generating polymers that is well suited to be explored in this course. The development and implementation of an experiment for undergraduate organic chemistry laboratory in which students explore both photochemistry and radical chemistry by synthesizing crosslinked polymers via photopolymerization is reported. An inquiry design is used to introduce polymerization reactions, and students learn about air-sensitive lab techniques. Students must pool their data to explain how molecular structure affects the physical properties of a macroscopic material.

GRAPHICAL ABSTRACT



KEYWORDS

Second-Year Undergraduate, Laboratory Instruction, Organic Chemistry, Polymer Chemistry, Inquiry-Based/Discovery Learning, Materials Science, Molecular Properties/Structure, Photochemistry, Polymerization

INTRODUCTION

Polymer synthesis is ubiquitous in modern chemical industry^{1,2}, and photochemistry constitutes a significant portion of these reactions.²⁻⁶ Most industrial chemists will work with polymers at some point in their careers,^{7,8} however, the breadth and depth of polymer chemistry are not fully represented in the undergraduate chemistry curriculum, and not all students have access to dedicated polymer chemistry courses at their institutions.⁷ Recent updates to the ACS Guidelines for bachelor's degree programs have called for increased instruction in polymer chemistry principles and the synthesis of different classes of macromolecules.^{9,10}

Several polymer chemistry experiments have been reported in the literature for upper-division undergraduate polymer chemistry and inorganic chemistry laboratory classes.¹¹⁻¹⁶ Polymer chemistry experiments in the organic laboratory have also been reported that investigate natural product isolation¹⁷ or involve radical polymerization using various alkene,¹⁸ ring-forming,¹⁸ and ring-opening¹⁸⁻¹⁹ polymerization techniques. None of these experiments involved photochemistry. Likewise, photochemistry experiments have been reported regarding the formation of dimers from aromatic and vinylic systems,^{20,21} heterogeneous catalysis,²² cycloadditions,²³ and photooxidation,^{20,24-25} but none have involved radical polymerization. Other reported photochemical experiments have been in the form of classroom demonstrations^{26,27} or intended for upper-level courses.²⁸ Photopolymerization provides an opportunity for students to learn about structure–property relationships because macroscopic changes in properties are readily apparent upon reaction with light. Photochemistry enables complex reactions to be performed under mild conditions, and using photochemistry in the teaching laboratory can reinforce the concept of the quantum nature of light.

Therefore, an organic laboratory experiment was developed in which students generate polymers *via* photopolymerization, while learning laboratory techniques for dealing with air-sensitive materials. The learning objectives for students are to

- synthesize crosslinked polymers
- investigate the effect of the wavelength of light on photopolymerization
- examine the effect of oxygen on radical reactions

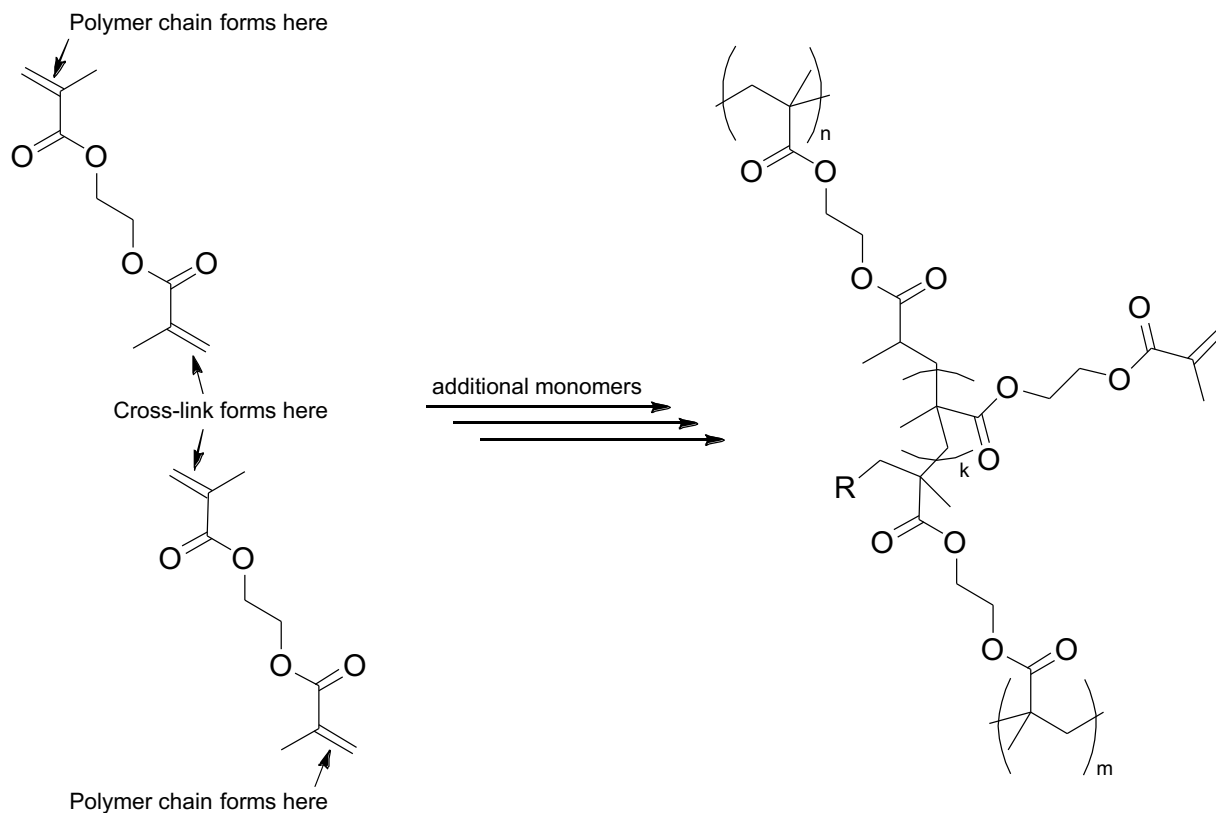
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- determine the effect of polymer structure on macroscopic properties
 - discuss the kinetics, thermodynamics, and mechanism of radical polymerizations

This experiment was designed as a guided-inquiry²⁹⁻³² experience, asking students to make predictions about what the outcomes will be, and then test those predictions. The entire procedure is not provided a priori for students. Rather, they must interpret their experimental results from the first part of the experiment to determine how to proceed in the second part of the experiment. Students must collaborate both within and between groups as they make predictions, share results, and build explanations. This process mimics real scientific practice where outcomes are discovered rather than confirmed, helping students to build their skills in critical thinking, communicating and collaborating with others.

Background

In this experiment, students synthesize crosslinked polymers from the monomers ethylene glycol dimethacrylate (EGDMA) and 2-hydroxyethyl acrylate (HEA) *via* photoinduced radical polymerization using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator.³³⁻³⁵ DMPA strongly absorbs ultraviolet light, but its absorbance diminishes at longer wavelengths. Therefore, the wavelength of light used to irradiate the samples affects whether DMPA produces the radicals which are necessary for successful polymerization.³³ The presence of oxygen also affects radical polymerization, because oxygen can react with propagating radical chains due to its diradical character, leaving relatively unreactive R-O-O* species and hindering the formation of a polymer.^{5,33} The first part of the experiment tasks students with investigating the effects of the wavelength of light used to initiate the reaction and the presence/absence of oxygen.

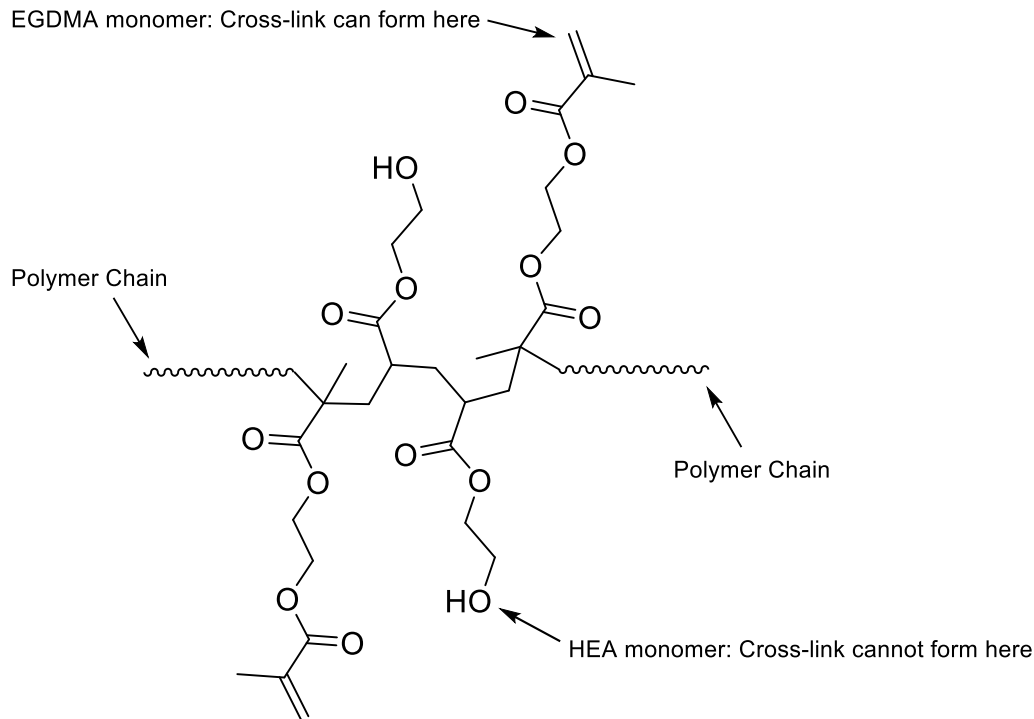
During polymerization, difunctional monomers such as EGDMA form crosslinks that connect separate polymer chains (Scheme 1), and the amount of crosslinking in a polymer affects its macroscopic physical properties. In a heavily crosslinked polymer, its individual chains have less range of motion and cannot slide past one another as easily, causing the polymer to be hard, rigid, and brittle. A less highly crosslinked polymer has more range of motion among its individual chains, and, therefore, is softer and more elastic.



80 **Scheme 1.** Formation of a crosslinked polymer from EGDMA. The R group represents the initiator and the polymer is shown to have terminated by hydrogen abstraction for simplicity. Each chain k, m, and n is composed of EGDMA monomers.

The amount of crosslinking in a polymer can be controlled by the nature of the monomers from which it is formed and their mole-to-mole ratios. In this experiment, adding a monofunctional

85 monomer such as HEA reduces the amount of crosslinking in the generated polymer because crosslinks cannot be formed from HEA as the molecule has only one double bond which reacts when forming the initial polymer chain (Scheme 2).



Scheme 2. Polymer chain composed of HEA and EGDMA monomers. Crosslinks can be formed from EGDMA monomers due to the presence of a second vinyl group. Incorporation of HEA reduces crosslinking due to HEA lacking a second vinyl group.

This experiment provides students an opportunity to investigate radical reactivity, a topic typically taught in second-year organic chemistry at the end of the first semester or the beginning of the second semester. The data reported herein were collected during the final week of an organic laboratory course for chemistry majors, but this experiment could also be implemented in a nonmajors course after the students have studied radical reactivity. The post-lab questions assess concepts related to radical reactions, polymerizations, and photochemistry, including resonance stabilization, steric effects, free energy, UV-Vis spectral analysis, and photoinitiation arrow-pushing mechanisms (Supporting Information, Student Lab Manual, p. S8-S11).

EXPERIMENTAL PROCEDURES

This experiment is conducted in two parts and can be carried out in one, three- or four-hour laboratory period, followed by a short session in a second lab period in which the masses of the samples are recorded. It is recommended that students work in groups of three. To begin the

experiment, students brainstorm optimal physical properties for a polymer that they could encounter in their everyday lives, such as a dental resin (Supporting Information, Student Lab Manual, Q1). They also predict the macroscopic properties of different polymers based on submicroscopic structural depictions (Supporting Information, Student Lab Manual, Q2). Students answer these questions while their samples for Part 1 react. In Part 1, each group prepares six samples of EGDMA and DMPA in *N,N*-dimethylformamide (DMF). (Alternatively, acetone can be used as the solvent.) Three samples are capped, while the other three are covered with septa and deoxygenated using a nitrogen balloon (Figure 1).

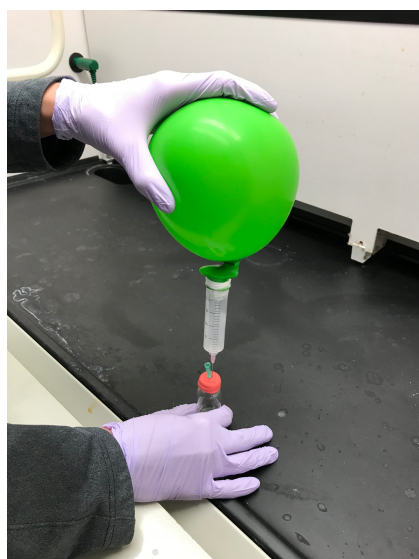


Figure 1. Deoxygenation of samples using a nitrogen balloon and syringe

Students place two samples, one under normal atmosphere and one under nitrogen, into each of three different photoreactors: red (620-650 nm), violet (395-405 nm), and ultraviolet (365 nm). After the samples react, students use their observations to determine which conditions (i.e., wavelength and presence/absence of oxygen) are most favorable to synthesize polymer, and to decide which photoreactor to use for Part 2. In Part 2 of the experiment, each group generates three more samples, each with a different mole-to-mole ratio of HEA to EGDMA. Students choose ratios within suggested guidelines of one sample with less than a 10:1 ratio of HEA to EGDMA, one between 10:1 and 25:1, and one between 25:1 and 50:1. These samples are reacted in molds (plastic ice cube trays) to ensure easy removal so that the students can both see and feel the variation in hardness and brittleness

amongst the polymers. Each polymer sample is weighed and placed in a beaker of deionized water. At the beginning of the next lab period, the samples are weighed again in order to calculate the swelling ratio, i.e., the amount of water absorbed by the polymer per mass of polymer.

HAZARDS

HEA and EGDMA are moderately toxic and should not be removed from a fume hood during lab. *N,N*-Dimethylformamide and acetone are flammable, irritating to the eyes, and can be absorbed through the skin. DMF is also potentially hazardous to fertility and unborn children, so extra caution should be taken if DMF is used. All sample preparation should be done in a fume hood. Photoreactors should be covered with aluminum foil while the samples react. The generated polymers should only be handled once fully crosslinked (no longer flowing) and while wearing gloves. Protective nitrile gloves and goggles should be worn at all times during the experiment, and students should be cautioned about the use of sharp needles.

RESULTS AND DISCUSSION

The experiment was performed in fall 2017 by 67 undergraduates in a first-semester, majors' organic chemistry laboratory course as the final experiment of the semester. Observations for 62 students in Part 1 aligned with expected results, namely, no polymerization with the red photoreactor for any sample regardless of atmosphere, full polymerization under nitrogen and only partial polymerization under ambient atmosphere in the violet photoreactor, and full polymerization regardless of atmosphere after 45 min in the UV photoreactor. The five remaining students submitted unreadable, missing, or incomplete observations for Part 1. In Part 2, all students chose to run their reactions in the UV photoreactor, and 60 students clearly noted differences in flexibility among the three copolymers they synthesized with varying HEA to EGDMA mole-to-mole ratios. Higher amounts of HEA translated to softer, more flexible polymers, and increased water-absorbency, with 50:1 HEA to EGDMA resulting in typically 77% increases in mass and pure EGDMA seeing 0-1% increases. This correct trend in water absorbency was reported by 53 students.

Learning Outcomes

Students discuss in-lab questions and perform mass calculations for Part 2 while their samples in Part 1 reacted, and then continue to answer the in-lab questions and post-lab questions as their samples in Part 2 reacted. The student report for this experiment included three pre-lab questions, four in-lab questions, nine post-lab questions, and required observations for Part 1 and Part 2 (see Supporting Information, Student Lab Manual). In addition to examining content knowledge regarding radical stability and reactivity, photon energy, and polymerization reaction thermodynamics, the students were also asked to draw inferences and make predictions regarding the connection between polymer structure and macroscopic properties. In general, students successfully predicted these properties based on submicroscopic depictions of polymers with varying amounts of crosslinking. For example, the second in-lab question asked students to predict how a polymer's properties would change as the amount of crosslinking increases. Forty-eight students correctly predicted that more highly crosslinked structures would translate to harder, more rigid polymers due to the compound being more tightly packed, having "more bonds," or having less range of motion at the atomic level. Consider an example student response:

"As the amount of cross linking increases, the hardness of the polymer increases and the flexibility decreases. This is true because higher amounts of cross-linking causes the polymer to be tightly packed so the hardness increases and the flexibility decrease[s]. Low amount of cross-linking means loosely-packed polymers thus more flexibility, and more liquid-like."

Other students provided similar predictions concerning the properties of a highly crosslinked polymer, but were unable to clearly articulate why they thought the polymer would have these properties. It is important to note that for many students, this lab may have been among their first formal experiences with synthetic macromolecules, networks and polymer crosslinking.

In Question 10, students revisited their initial ideas about the structure and properties of dental resins from Question 1. Students were asked to discuss which polymer sample they had synthesized would best match the desired properties of a dental resin polymer and why the other polymer samples did not align with those properties. Thirty-four students correctly correlated the differences in

hardness and flexibility with differences in the amount of crosslinking present in the polymer.

Consider an example response:

185 *“Out of all the polymers generated, the deoxy in ultraviolet light aligned best with our desired properties. The other ones didn’t align because they didn’t form quick enough, weren’t hard enough or they crumbled under touch. The greater the cross linkage the harder the material.”*

Other students described the properties of the polymers they had made, but did not connect their observations to the submicroscopic structures of the polymers.

In Question 5, students were asked to consider that molecular oxygen has diradical character and
190 to use this information to explain why the presence of oxygen could interfere with polymerization. Fifty-five students reasoned that the diradical nature of oxygen can cause undesired termination events and as a result, inhibit polymerization. Consider an example student response:

195 *“The diradical character of O₂ provides sites for the radical initiator or propagating polymer chain to terminate. The radical on a propagating polymer chain would react with one of the radicals on molecular oxygen. This would remove a radical species from the reaction, thereby inhibiting propagation and terminating the chain. So, when O₂ is present in a radical polymerization, less polymerization will occur, as seen in the only-partially-reacted sample reacted with O₂ present in violet light, while the same sample under the same conditions, but deoxygenated instead, polymerized quickly and entirely.”*

200 An analysis of students’ lab reports revealed that some students were confused about two concepts in this experiment. Question 6b presented the UV-Vis spectrum for DMPA and asked students to explain the difference in polymer reactivity between the red and ultraviolet photoreactors, using this spectrum as evidence. Most students gave superficial responses in which they either described what the graph presented while not explaining its connection to polymerization, or they simply stated that if
205 there is high absorbance, the reaction will “work.” A representative student response was:

210 *“Based on the spectrum, the difference in reactivity between the red & UV photoreactor is supported. The UV photoreactor was extremely reactive, whereas the red was very inactive. This is because the absorbance spectrum for DMPA only absorbs light of shorter wavelength, such as UV. For light of higher wavelength, such as red, DMPA is inactive, so it is unable to absorb any light at such a wavelength.”*

It is possible that these students did not understand what would constitute an *explanation* of reactivity, rather than a *description* of the spectrum itself, because they were unable to connect the

information encoded in the spectrum to the properties and submicroscopic structure of the polymer samples. Previous research indicates that students do not offer submicroscopic explanations unless they are specifically prompted to do so,³⁶ and that may have been the case with this question, despite a submicroscopic description being necessary to connect their experimental observations to the UV-vis spectrum and complete a sufficient explanation. Only 19 students related the absorbance of light to the generation of radicals that are necessary for the polymerization reaction, as typified in this example response:

220 *“DMPA only absorbs light between the wavelengths of ~320-390nm. Red has a much larger wavelength so it most likely isn’t being absorbed by the DMPA. If the light isn’t being absorbed then radicals won’t be formed, and polymerization can’t occur.”*

The second concept with which students struggled was the enthalpy change in the reaction and its connection to the bonds of the structures reacting. In Question 9a, students were given the bond energies for C–O and C–C single bonds and for C=O and C=C double bonds. They were asked to use these bond energies to explain why styrene can polymerize in the presence of an initiator, but benzaldehyde does not. Only four students realized that it was necessary to calculate the enthalpy change using the provided bond energies to explain the difference in reactivity. Forty-seven students simply discussed the relative strengths of C=O and C=C double bond energies, while six students calculated pi bond energies, but compared them between molecules without considering the sigma bonds formed *via* polymerization. The response below is representative of the most typical answer:

235 *“Styrene will readily polymerize whereas benzaldehyde will not because C–C double bonds have less energy than C–O double bonds. A C–C double bond has 602 kJ/mol whereas benzaldehyde has 799 kJ/mol. Since it has less bond energy, C–C double bonds are easier to break than C–O double bonds.”*

Students’ difficulties with this question could be attributed to challenges with calculating enthalpy changes since general chemistry.³⁷ Nonetheless, this question provides a useful opportunity to help students think about the bonding involved in the structures which ultimately is responsible for reactivity (or lack thereof) and the macroscopic properties.

240 After the students were provided feedback on their lab reports, they answered four multiple choice questions pertaining to this experiment on the course final exam. (All four exam questions and student

response statistics can be found in the Supporting Information, Instructor's Manual, p. S11-S13.)

These questions assessed students on their experimental observations from Part 1, the radical reactivity of vinyl groups, and how radical stability affects polymerization reactions. Overall, the students performed well on these exam questions, with each question answered correctly by a majority of the students. One of these four final exam questions directly pertained to Question 9a discussed above, and the students' performance on the final exam question showed marked improvement over their lab report responses (See Box 1).

Box 1. Final Exam Question Concerning Vinyl Group Reactivity

Why are compounds containing vinyl ($-\text{CH}=\text{CH}_2$) groups good monomers for polymerization?

- A. The process is entropically favorable.
- B. The pi bond of the $\text{C}=\text{C}$ double bond is weaker than the sigma bond formed on polymerization.
- C. The $\text{C}=\text{C}$ double bond is weaker than a $\text{C}\equiv\text{C}$ triple bond, so polymerization is favored over dehydrogenation.
- D. The $\text{C}=\text{C}$ double bond is weaker than the double bonds found in most other functional groups ($\text{C}=\text{O}$, $\text{C}=\text{N}$, etc.).
- E. The vinyl group can easily form a diradical when irradiated.

Correct Answer: B

Student Response Counts (66 students. One student in the course did not take the final exam.)

- A. 4
- B. 35
- C. 4
- D. 9
- E. 14

ASSOCIATED CONTENT

Supporting Information

The Student Lab Manual, Instructor's Manual, and Final Exam Data are available on the ACS

Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX.

Student Lab Manual (DOCX)

Instructor's Manual and final exam data (DOCX)

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Notes

260 The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank C. Scott Hartley, Bryan McLean, and the students who consented to participate in this study. We also thank the members of the Bretz, Yezierski, and Konkolewicz Research Groups for their
265 assistance in developing and pilot testing this experiment. This work was supported in part by Grant No. 1432466 from the National Science Foundation. Any opinions, findings, and conclusions expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

REFERENCES

- 270 1. Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M. Catalysis as an Enabling Science for Sustainable Polymers. *Chem. Rev.*, **2018**, *118* (2), 839-885.
2. Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Müllhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.*, **2017**, *117* (15), 10212-10290.
3. Chen, M.; Zhong, M.; Johnson, J. A. Light-Controlled Radical Polymerization: Mechanisms,
275 Methods, and Applications. *Chem. Rev.*, **2016**, *116* (17), 10167-10211.
4. Dadashi-Silab, S.; Doran, S.; Yagci, Y. Photoinduced Electron Transfer Reactions for Macromolecular Syntheses. *Chem. Rev.*, **2016**, *116* (21), 10212-10275.
5. Ligon, S. C.; Husár, B.; Wutzel, H.; Holman, R.; Liska, R. Strategies to Reduce Oxygen Inhibition in Photoinduced Polymerization. *Chem. Rev.*, **2014**, *114* (1), 557-589.
- 280 6. Vitale, A.; Bongiovanni, R.; Ameduri, B. Fluorinated Oligomers and Polymers in Photopolymerization. *Chem. Rev.*, **2015**, *115* (16), 8835-8866.
7. Finkenstaedt-Quinn, S. A.; Halim, A. S.; Chambers, T. G.; Moon, A.; Goldman, R. S.; Gere, A. R.; Shultz, G. V. Investigation of the Influence of a Writing-to-Learn Assignment on Student Understanding of Polymer Properties. *J. Chem. Educ.*, **2017**, *94* (11), 1610-1617.
- 285 8. Howell, B. A. Incorporating Polymer Science Lecture Topics into the Beginning Organic Chemistry Course To Engage Students' Interest in Current and Future Applications. *J. Chem. Educ.*, **2017**, *94* (11), 1655-1661.
9. Wenzel, T. J.; McCoy, A. B.; Landis, C. R. An Overview of the Changes in the 2015 ACS Guidelines for Bachelor's Degree Programs. *J. Chem. Educ.*, **2015**, *92* (6), 965-968.

- 290 10. Ford, W. T. Introducing the *Journal of Chemical Education's* "Special Issue: Polymer Concepts across the Curriculum." *J. Chem. Educ.*, **2017**, 94 (11), 1595-1598.
11. Beers, K. L.; Woodworth, B.; Matyjaszewski, K. Controlled/Living Radical Polymerization in the Undergraduate Laboratories. 1. Using ATRP to Prepare Block and Statistical Copolymers of n-Butyl Acrylate and Styrene. *J. Chem. Educ.*, **2001**, 78 (4), 544-547.
- 295 12. Matyjaszewski, K.; Beers, K. L.; Woodworth, B.; Metzner, Z. Controlled/Living Radical Polymerization in the Undergraduate Laboratories. 2. Using ATRP in Limited Amounts of Air to Prepare Block and Statistical Copolymers of n-Butyl Acrylate and Styrene. *J. Chem. Educ.*, **2001**, 78 (4), 547-550.
13. Nguyen, T. L. U.; Bennet, F.; Stenzel, M. H.; Barner-Kowollik, C. Reversible Addition
300 Fragmentation Chain Transfer (RAFT) Polymerization in Undergraduate Polymer Science Lab. *J. Chem. Educ.*, **2008**, 85 (1), 97-99.
14. Rushton, G. T.; Furmanski, B.; Shimizu, K. D. Plastic Antibodies: Molecular Recognition with Imprinted Polymers. An Introductory Polymer Chemistry Laboratory Investigation. *J. Chem. Educ.*, **2005**, 82 (9), 1374-1377.
- 305 15. Tsarevsky, N. V.; Woodruff, S. R.; Wisian-Neilson, P. J. An Undergraduate Chemistry Laboratory: Synthesis of Well-Defined Polymers by Low-Catalyst-Concentration ATRP and Postpolymerization Modification to Fluorescent Materials. *J. Chem. Educ.*, **2016**, 93 (8), 1452-1459.
16. Tillman, E. S.; Roof, A. C.; Palmer, S. M.; Zarko, B. A.; Goodman, C. C.; Roland, A. M. Synthesis of Chromophore-Labeled Polymers and Their Molecular Weight Determination Using UV-Vis
310 Spectroscopy. *J. Chem. Educ.*, **2006**, 83 (8), 1215-1217.
17. Volaric, L.; Hagen, J. The Isolation of Rubber from Milkweed Leaves. An Introductory Organic Chemistry Lab. *J. Chem. Educ.*, **2002**, 79 (1), 91-93.
18. Viswanathan, T.; Watson, F.; Yang, D. T. C. Undergraduate Organic and Polymer Lab Experiments that Exemplify Structure Determination by NMR. *J. Chem. Educ.*, **1991**, 68 (8), 685-
315 688.
19. Schneiderman, D. K.; Gilmer, C.; Wentzel, M. T.; Martello, M. T.; Kubo, T.; Wissinger, J. E. Sustainable Polymers in the Organic Chemistry Laboratory: Synthesis and Characterization of a Renewable Polymer from δ -decalactone and L-lactide. *J. Chem. Educ.*, **2014**, 91 (1), 131-135.
20. Aung, T.; Liberko, C. A. Bringing Photochemistry to the Masses: A Simple, Effective, and
320 Inexpensive Photoreactor, Right Out of the Box. *J. Chem. Educ.*, **2014**, 91 (6), 939-942.
21. Penn, J.; Orr, R. A Microscale Immersion Well for Photochemical Reactions. *J. Chem. Educ.*, **1989**, 66 (1), 86-88.
22. Chen, X.; Halasz, S. M.; Giles, E. C.; Mankus, J. V.; Johnson, J. C.; Burda, C. A Simple Parallel Photochemical Reactor for Photodecomposition Studies. *J. Chem. Educ.*, **2006**, 83 (2), 265-267.

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- 325 23. Thompson, M. P.; Agger, J.; Wong, L. S. Paternò-Büchi Reaction as a Demonstration of Chemical Kinetics and Synthetic Photochemistry Using a Light Emitting Diode Apparatus. *J. Chem. Educ.*, **2015**, 92 (10), 1716-1720.
24. Rosenfeld, S. M. A Simple Photochemical Experiment for the Advanced Laboratory. *J. Chem. Educ.*, **1986**, 63 (2), 184-185.
- 330 25. VanDeMark, M. R.; Kumler, P. L. A Combined Photochemistry, Organic Qualitative Analysis Experiment. *J. Chem. Educ.*, **1973**, 50 (7), 512-514.
26. Rodriguez, F.; Mathias, L. J.; Kroschwitz, J.; Carraher, Jr., C. E. Classroom Demonstrations of Polymer Principles. Part I. Molecular Structure and Molecular Mass. *J. Chem. Educ.*, **1987**, 64 (1), 72-76.
- 335 27. Rodriguez, F.; Mathias, L. J.; Kroschwitz, J.; Carraher, Jr., C. E. Classroom Demonstrations of Polymer Principles. Part II. Polymer Formation. *J. Chem. Educ.*, **1987**, 64 (10), 886.
28. Vaughan, P. P.; Cochran, M.; Haubrich, N. Quinone Photoreactivity: An Undergraduate Experiment in Photochemistry. *J. Chem. Educ.*, **2010**, 87 (12), 1389-1391.
29. Gaddis, B. A.; Schoffstall, A. M. Incorporating Guided-Inquiry Learning into the Organic
340 Chemistry Laboratory. *J. Chem. Educ.*, **2007**, 84 (5), 848-851.
30. Domin, D. S. A Review of Laboratory Instruction Styles. *J. Chem. Educ.*, **1999**, 76 (4), 543-547.
31. Fay, M. E.; Grove, N. P.; Towns, M. H.; Bretz, S. L. A Rubric to Characterize Inquiry in the Undergraduate Chemistry Laboratory. *Chem. Educ. Res. Pract.*, **2007**, 8 (2), 212-219.
32. Bruck, L. B.; Bretz, S. L.; Towns, M. H. Characterizing the Level of Inquiry in the Undergraduate
345 Laboratory. *J. Coll. Sci. Teach.*, **2008**, 38 (1), 52-58.
33. Mucci, V.; Vallo, C. Efficiency of 2,2-Dimethoxy-2-phenylacetophenone for the Photopolymerization of Methacrylate Monomers in Thick Sections. *J. Appl. Polym. Sci.*, **2012**, 123, 418-425.
34. Monleòn Pradas, M.; Gòmez Ribelles, J. L.; Serrano Aroca, A.; Gallego Ferrer, G.; Suay Antòn, J.;
350 Pissis, P. Interaction Between Water and Polymer Chains in Poly(hydroxyethyl acrylate) Hydrogels. *Colloid Polym. Sci.*, **2001**, 279, 323-330.
35. Natale, L. C.; Rodrigues, M. C.; Alania, Y.; Braga, R. R. Resin Materials Containing Calcium Phosphate Nanoparticles Functionalized with EGDMA Derivatives. *Dent. Mater.*, **2017**, 33 (1), e14-e15.
- 355 36. Williamson, V.; Huffman, J.; Peck, L. Testing Students' Use of the Particulate Theory. *J. Chem. Educ.*, **2004**, 81 (6), 891-896.
37. Bunce, D. M.; VandenPlas, J. R.; Soulis, C. Decay of Student Knowledge in Chemistry. *J. Chem. Educ.*, **2011**, 88 (9), 1231-1237.