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Laboratory Experiment

# Exploring Divergent Green Reaction Media for the Copolymerization of Biobased Monomers in the Teaching Laboratory

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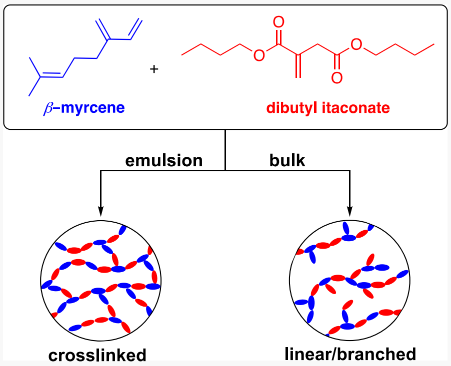

**ABSTRACT:** Polymerization reaction media can have a profound effect on the physical properties of the resultant polymer. This phenomenon is showcased in a new experiment for the organic chemistry and polymer science teaching laboratories wherein the radical copolymerization of biobased β-myrcene and dibutyl itaconate is performed using a nonhazardous aqueous emulsion solvent and compared to a bulk reaction. Both procedures demonstrate multiple green chemistry principles and application to sustainable polymer synthesis. The emulsion copolymerization produces a tacky, elastomeric cross-linked material, capable of swelling to many times its original volume in organic solvents, setting the stage for the exploration of the relationship between solvent polarity and swelling capacity. Conversely, the polymerization of β-myrcene and dibutyl itaconate in the bulk yields a viscous non-cross-linked polymer whose $^1$H NMR spectrum is suitable for student analysis and estimation of polymer number-average molar mass ($M_n$), monomer conversion, and copolymer composition. This inexpensive experiment models the use of renewable feedstocks, the effect of reaction medium on polymer architecture, the unique properties of cross-linked organogels, and the quantitative analysis of polymer structure using $^1$H NMR spectroscopy.

**KEYWORDS:** *Second-Year Undergraduate, Upper-Division Undergraduate, Organic Chemistry, Polymer Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Green Chemistry, Materials Science, NMR Spectroscopy, Polymerization*

## ■ INTRODUCTION

The impact of polymers on human life cannot be underestimated; polymers comprise many consumer goods used daily. However, a majority of synthetic polymers are derived from petroleum, a nonrenewable source, and are environmentally persistent or difficult to recycle. An estimated 8.3 billion metric tons of synthetic plastic have been manufactured since 1950, most of which has been relegated to landfills, incinerated, or leached into the environment.[1] As such, the scientific community is aggressively investigating the synthesis of sustainably sourced and degradable polymeric materials with properties and prices comparable to those of their petroleum-derived counterparts.[2]

The chemistry education enterprise is raising awareness of these research initiatives by introducing sustainable polymers into the undergraduate teaching laboratory.[3−8] Published laboratory experiments highlight classic industrially relevant polymers,[9,10] materials with advanced architectures and properties,[11−15] and modern polymerization[16−19] or characterization[20−22] techniques. These laboratory activities also help fulfill the macromolecular requirements put forth by the Committee on Professional Training of the American Chemical Society.[23,24]

This laboratory experiment features the radical copolymerization of sustainably sourced monomers, β-myrcene and dibutyl itaconate, and illustrates the effect of reaction medium and conditions on the structure of the resultant material (Scheme 1). An aqueous emulsion copolymerization of these two monomers produces a cross-linked copolymer network, suitable for gelation studies in various organic solvents to form organogels (Scheme 1a). Alternatively, polymerization in the bulk (solvent-less) yields a $CDCl_3$-soluble linear copolymer, most likely with branching (Scheme 1b), amenable for study by $^1$H NMR spectroscopy. Distinguishable proton resonances for both repeat units allow for calculation of monomer incorporation and copolymer ratio, and an initiator peak can

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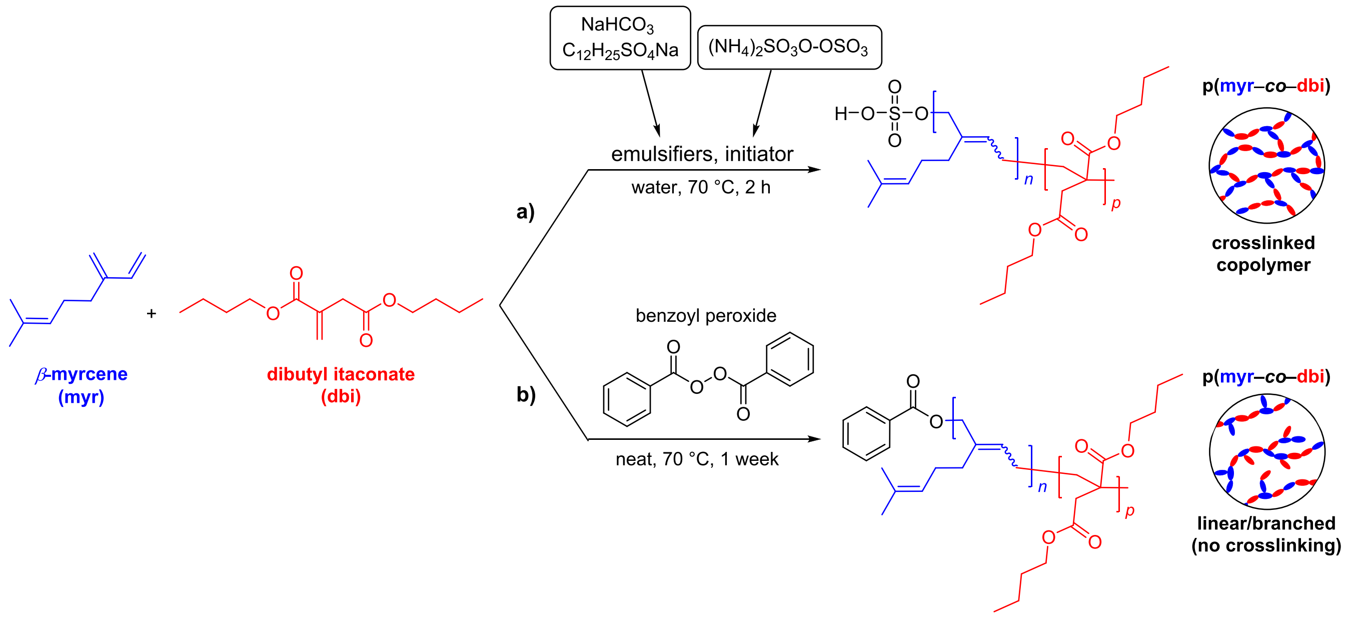
**Scheme 1. Divergent Reaction Media for the Radical Copolymerization of *β*-Myrcene and Dibutyl Itaconate: (a) Emulsion Polymerization Conditions and (b) Bulk Polymerization**



be used for estimation of the number-average molar mass ($M_n$). Incorporation of these divergent reaction conditions into a teaching laboratory experiment provides students with the opportunity to synthesize two tangibly different materials from the same monomers, one cross-linked and the other linear/branched, and to engage in discussions related to green polymer chemistry.

## ■ BACKGROUND

*β*-Myrcene (myr) is a naturally occurring terpene obtained from the pyrolysis of *β*-pinene, commonly derived from turpentine,[25] whose 1,4-butadiene subunit has a structural similarity to isoprene. Such diene substructures are highly amenable to free-radical polymerization, and the resulting rubbery materials abound in the commercial marketplace. The US Department of Energy has listed itaconic acid, the parent chemical of dibutyl itaconate (dbi), as a "Top Value-Added Chemical from Biomass".[26] This platform chemical is industrially relevant as a drop-in replacement for monomers such as acrylic acid, and more than 40,000 tons are produced annually by fungal fermentation of glucose.[27] The dibutyl ester of itaconic acid is inexpensive and has long been known to polymerize well in emulsion systems.[28] Recently, the emulsion copolymerization of myr and dbi was reported.[29] The authors synthesized a range of linear copolymer compositions of number-average molar mass ($M_n$) up to 65 kg/mol with glass transition temperatures ($T_g$) between −60 and −33 °C. The authors utilized slow addition of the two monomers to the aqueous emulsion (formed with sodium dodecyl sulfate (SDS) and sodium bicarbonate) to encourage formation of the linear polymer with a low gel fraction (minimized cross-linking).

### Emulsion Polymerization

In a continuation of our efforts to design laboratory experiments that teach polymer science, use green synthetic methodologies, and illustrate modern approaches to sustainable polymers,[5,8,30,31] this reported emulsion polymerization appeared to be an attractive lead to pursue. In the course of investigating the translation of the published experimental procedure to one amenable to the nonstringent conditions and time constraints of a teaching laboratory, it was discovered that the formation of cross-linked gels could be enhanced by replacing the carefully controlled reagent additions and stirring with aggressive shaking of the monomers with the emulsifiers before initiation of the polymerization.

The phases of emulsion polymerization were first articulated by Harkins[32] and elegantly summarized by Lovell and Schork in a recent review.[33] During 0−5% conversion (interval I), particles are nucleated within the aqueous phase and begin to form oligomeric radicals. At 5−40% monomer conversion (interval II), polymerization occurs at a constant rate in the presence of monomer-rich micelles. At 40−100% conversion (interval III), the polymerization is characterized by a decrease in propagation rate as monomer concentration within micelles decreases. Cross-linking due to chain-transfer events during interval III is likely as dibutyl itaconate is incorporated due to its easily abstractable H atom $\alpha$ to the ester carbonyl, generating a midchain stabilized radical. A high concentration of polymers within the micelle bearing a midchain radical leads to cross-linking. A student handout regarding polymer chain-transfer and termination mechanism is available in the Supporting Information (SI).

In contrast to the originally reported 20 h of heating, the new reaction conditions gave a good yield of cross-linked materials in 2 h, a suitable time frame for a teaching lab experiment. Precipitation and drying yielded tacky, stretchy copolymer gels that could not be melt-pressed even under 8000 lbs of force at 150 °C (well above the highest possible $T_g$) and recovered back to their original shape. This provided evidence toward extensive cross-linking. Furthermore, during preparation of a $^1$H NMR sample in deuterated chloroform, the copolymer quickly swelled to a gel in the NMR tube. This observation was a catalyst for development of an organogel experiment showcasing differential swelling capacity of the network in a range of organic solvents.

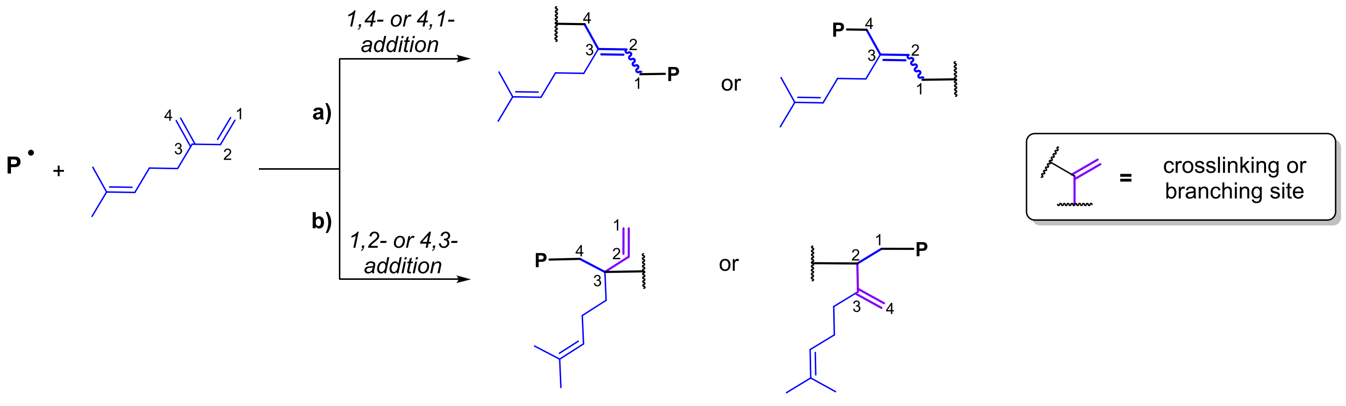


**Figure 1.** Addition of the propagating chain (P•) to myr: (a) major pathway through 1,4- or 4,1-addition to diene and (b) minor 1,2- or 4,3-addition resulting in dangling alkenes available for branching or cross-linking.

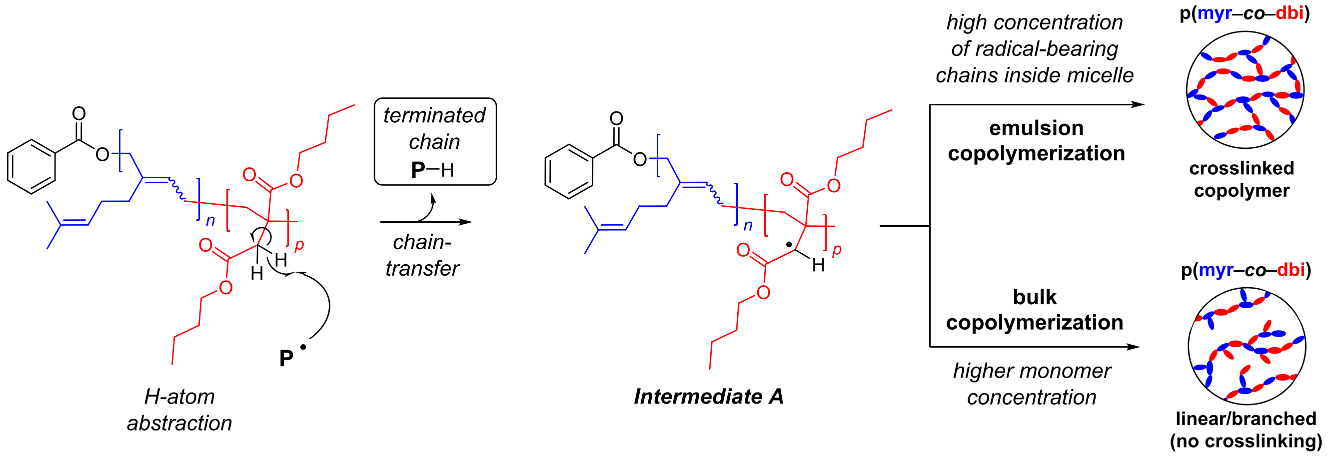


**Figure 2.** Formation of a midchain radical intermediate present in emulsion and bulk polymerization systems.

## Swelling of Network Polymers

According to eq 1, the degree to which a network swells is controlled by the free energy of the swelled network ($\Delta G$), proposed by Flory and Rehner.[34] This term is composed of the free energy of mixing of the polymer and solvent ($\Delta G_m$) and the free energy of elasticity (mechanical distortion of the network, $\Delta G_{el}$).

$$\Delta G = \Delta G_m + \Delta G_{el} \tag{1}$$

This experiment demonstrates the tremendous effect the identity of the solvent has on the contribution of the $\Delta G_m$ term as related through the Gibbs free energy equation. Favorable solvent−repeat unit interactions increase swelling capacity ("like-dissolves-like") by enhancing the enthalpy of mixing ($\Delta H_m$), a component of the free energy of mixing. Students can also visualize how networks swell to at least a minimal degree in any solvent due to entropy ($\Delta S_{el}$, the primary contributor to the $\Delta G_{el}$ term) as chains gain degrees of freedom to access more conformations. Cross-linked networks swell much more extensively when immersed in a good solvent, that is, one with a relatively favorable enthalpic mixing parameter with the repeat units.[35] Phrased another way, the polymer segments between cross-links are solvated by molecules of similar polarity.

## Cross-Linking and Branching Mechanistic Considerations

Suitable for student instruction with this experiment is study of the radical mechanism and discussion of potential sites for alkene cross-linking or branching. Regardless of reaction medium (emulsion or bulk), the majority of myr monomers add in a 1,4- or 4,1-fashion, producing *cis*- or *trans*-trisubstituted alkene subunits in the polymer backbone, as depicted in Figure 1a. Cross-linking and branching can arise from a minority fraction of 1,2- or 4,3-additions of myrcene onto a propagating chain, affording a dangling vinyl or geminal disubstituted alkene (Figure 1b). This phenomenon is commonplace in free-radical polymerization reactions.[36]

Similar to the emulsion polymerization, albeit with different outcomes, several termination and chain-transfer events characterize free-radical bulk polymerization, the most common being disproportionation (through $\alpha$-H atom abstraction) and chain−chain coupling (Figure 2). Bulk polymerization gives predominantly branched polymer through chain-transfer events and does not lead to extensive cross-linking because of decreased proximity of midchain radicals due to high monomer concentration.

The $^1$H NMR spectrum of the linear/branched polymer obtained from radical bulk polymerization has distinguishable proton resonances suitable for analysis by students in both introductory and advanced laboratory courses. As an initial introduction to the NMR calculations, student are instructed to assume that each polymer chain formed in the bulk medium contains only one initiator. With this assumption, the spectrum allows determination of copolymer: (i) overall $M_n$ relative to the benzoyl initiator; (ii) percent conversion of each monomer; and (iii) the relative ratio of myr and dbi repeat units in the backbone. In reality, chain−chain coupling events, both along the backbone and at branch points, complicate an accurate $^1$H NMR end-group analysis (EGA) calculation of $M_n$ for the polymer. Student assignments explore the mechanistic events that could lead to chains bearing more than one initiator in the upper division polymer laboratory course.

## ■ EXPERIMENTAL SECTION

### Materials and Instrumentation

The dibutyl itaconate (≥98%), benzoyl peroxide, and sodium dodecyl sulfate were purchased from Millipore Sigma and used without further purification. The *β*-myrcene (90% with 1000 ppm BHT inhibitor) was purchased from Millipore Sigma. The inhibitor, butylated hydroxytoluene, was removed from the *β*-myrcene by transferring it to a separatory funnel and washing it with an equal volume of 2 M NaOH, and the neat monomer was dried with a small amount of magnesium sulfate. Ammonium persulfate and sodium bicarbonate were purchased from Fisher Scientific and used without further purification. All solvents used in the swelling tests were those found in each of the teaching laboratory courses, purchased in bulk from various suppliers, and used without purification.

Polymers were synthesized in 20 mL scintillation vials stirred at 70 °C on a vial heating block resting on a hot plate. A vacuum oven (60 °C) was used to dry the emulsion polymerization polymer under reduced pressure after transfer to small aluminum pans (2−3 in.).

Student $^1$H NMR spectra were obtained on a Varian Inova 300 MHz spectrometer at University of Minnesota or a Bruker FourierHD 300 MHz at Augsburg University. Spectra of the monomers, available in the SI, were obtained on a Bruker Avance III HD 400 MHz spectrometer. $^1$H NMR chemical shifts in $CDCl_3$ were referenced to residual $CHCl_3$ (7.26 ppm). Concentrations of ca. 10 mg/0.5 mL $CDCl_3$ are suggested for good signal-to-noise in student polymer NMR spectra.

### Experiment Overview

Two laboratory periods are required for completing the experiment. The first day is the longer of the 2 days, for which instructors should allot 3−4 h. All courses used for trials were 3 h and 50 min in length and comfortably fit the described procedure. The emulsion polymerization is started first to allow the recommended 2 h of heating. Theoretically, the emulsion polymerization could be heated for 1.5 h to fit into a 2 h and 50 min lab period, but the yield will be reduced. After heating, the product is readily isolated in one step and transferred to an aluminum dish for vacuum oven drying for minimally 24 h.

During the heating of the emulsion polymerization, the reactants for the bulk polymerization are combined and heated on a vial heating block until the next laboratory period. For courses meeting once a week, the bulk polymerization was heated for 1 week out of convenience even though 48 h is sufficient time for completion.

The second day of the experiment, requiring about 1.5−2 h, is dedicated to exploring the swelling properties of the cross-linked copolymers and preparation of a $^1$H NMR sample of the copolymer from bulk polymerization.

### Emulsion Polymerization Procedure

The synthesis of the cross-linked myr and dibutyl itaconate copolymer network is conducted in a 20 mL scintillation vial with 20 mmol total monomer (myr + dbi) in an aqueous emulsion formed using sodium dodecyl sulfate (SDS) and sodium bicarbonate. The polymerization is initiated by an aqueous solution of ammonium persulfate (APS) (0.1 mol %) and then stirred vigorously at 70 °C for 2 h on a vial heating block. Proper stirring is critical for maintaining a proper emulsion; when significant phase separation is observed, the yield suffers substantially, and only linear polymer is formed, due to a low monomer concentration in the aqueous micelles.

After the 2 h heating period, the emulsion copolymerization mixture is poured into acidified ethanol (Figure 3a) to protonate the surfactant, thus breaking the emulsion. The resulting milk-white latex suspension is vigorously stirred with a spatula or glass stirring rod, and the polymer coagulates into a rubbery mass (Figure 3b). After rinsing the mass with deionized water, excess water and residual ethanol are kneaded out, and the material is dried under vacuum at 60 °C for a minimum of 24 h.

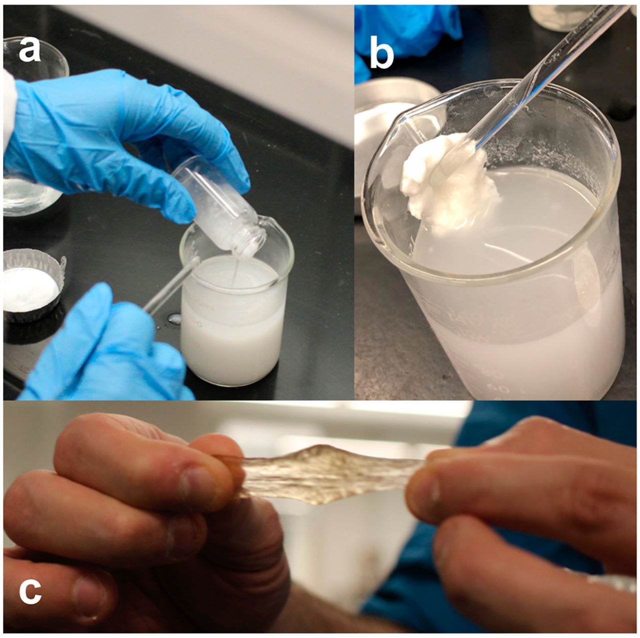


**Figure 3.** (a) Precipitation, (b) coagulation, and (c) final appearance of cross-linked poly(myr-*co*-dbi) from the emulsion polymerization reaction.

During the second laboratory period, students examine the resulting elastic, lightly colored material (Figure 3c). Swelling experiments are performed using five or more solvents that range in polarity from nonpolar to polar by tearing five small pieces (20−30 mg each) of dried cross-linked polymer and placing each in a 2 dram vial. Approximately 1.5 mL of any of the five solvents ranging in polarity is added to each vial, and qualitative observations of the swelling behavior are made over the course of an hour.

### Bulk Polymerization Procedure

While the emulsion copolymerization mixture is stirring, the bulk polymerization is performed. Student pairs are assigned the synthesis of one of three possible copolymers, which vary in mole feed ratios from 1:1 to 3:1 myr to dbi, respectively, for a total of 5 mmol of the combined monomers. After thorough mixing of the monomers in a 20 mL scintillation vial, the polymerization is initiated by adding 4 mol % benzoyl peroxide. During the heating period, the bulk polymerization mixture will increase significantly in viscosity to the point that the mixture no longer stirs, producing a sticky, flowing copolymer (Figure 4). During the second lab period, students use a small aliquot of their bulk polymerization polymer for $^1$H NMR analysis.

**Figure 4.** Linear/branched poly(myr-*co*-dbi) from the bulk polymerization reaction.

## ■ HAZARDS

*β*-Myrcene is flammable, has a detectable odor, and should be handled in the hood with gloves. Dibutyl itaconate is not classified as a hazardous substance but may be a skin or eye irritant. The 190 proof ethanol (acidified with 3% v/v 37% aqueous solution of HCl) for precipitation of the polymer should be stored in a closed container until just prior to use to avoid loss of HCl gas over time. This solution is corrosive and should be neutralized before disposal. The precipitated polymer must also be rinsed with water, and gloves should be worn when kneading out excess liquid. Ethanol, methanol, tetrahydrofuran, hexanes, ethyl acetate, *t*-butyl methyl ether, isopropyl alcohol, and acetone are all flammable solvents and potential irritants. Dimethyl sulfoxide can be an irritant upon ingestion or exposure to skin. Chloroform, chloroform-*d*, and methylene chloride are inhalation hazards and suspected carcinogens. Heating of the sealed vials in a reaction block should be performed in a hood with the sash closed to serve as a safety shield.

## ■ RESULTS AND DISCUSSION

### Classroom Implementation

This experiment was successfully implemented in three different laboratory courses with students working in pairs: two second-year undergraduate organic chemistry courses [small university (Augsburg University, spring 2019) and large university (University of Minnesota (U of MN) summer 2019)] and an advanced polymer elective laboratory (spring 2019, spring 2020). The second-year undergraduate laboratory classes were composed of students from a variety of majors and skill sets, only a small percentage of whom were chemistry or chemical engineering majors. The polymer laboratory course consisted of exclusively upper division chemistry, chemical engineering, and materials science majors. As such, laboratory materials and assignments were tailored to these different levels of sophistication.

For the upper division polymer science course (version A), two 50 min lectures introduced subclasses of polymer networks, such as elastomers and thermosets, polymer network architecture, the theory of sol fraction and gel fraction, thermodynamics of polymer solvation, and types of intermolecular interactions (e.g., fluid−fiber matrix). Selected applications of organogels to oil spill cleanup[37] and drug delivery[38] were also discussed. The second-year organic laboratory experiment version (B) focused on an introduction to polymer structure, terminology, and synthesis. Both versions of lecture content included discussions of the ubiquitous presence of plastics in society, their accumulation in the environment, and strategies for designing more sustainable polymers.

The two polymer syntheses offer an opportunity to explore contrasting green reaction media and their associated learning outcomes (Table 1). The emulsion polymerization illustrates how the application of micelles enables use of water as the solvent through its hydrophilic exterior with the majority of the organic monomers reacting in the hydrophobic, nonpolar interior. Alternatively, no solvent, or reaction in the bulk, yields a different copolymerization product. Both reactions model Green Chemistry Principle 5 in avoiding auxiliaries if possible and/or use of safer solvents, and Green Chemistry Principle 7, which is the use of renewable feedstocks.[39]

**Table 1. Comparison of Learning Objectives for Emulsion vs Bulk Copolymerization of *β*-Myrcene and Dibutyl Itaconate**

| Emulsion Copolymerization | Bulk Copolymerization |
|---|---|
| Aqueous emulsion reaction medium | Solvent-less reaction |
| Cross-linked polymers | Linear/branched polymers |
| Polymer isolation by pH change | $^1$H NMR composition analysis |
| Gel formation by swelling | Monomer ratio incorporation study |
| Opaque, stretchy, elastomeric, tacky material | Clear, viscous, sticky material |

### Emulsion Polymerization Typical Student Results

Typical student yields for the cross-linked network range from 40% to 65%, which, when applied to a 20 mmol reaction, results in approximately 1.5 g of material. Shortening the heating period to only one hour caused the yield to suffer considerably (below 20%, 0.5 g). The isolated and dried cross-linked networks readily swell in relatively nonpolar organic solvents, to a lesser degree in moderately polar solvents, and unnoticeably in water. The dielectric constant ($\varepsilon$) is a measure of a solvent's ability to insulate charges from one another and is a useful metric for predicting polymer−solvent interactions. Students used this concept to explain the nature of a particular solvent's interaction with the polymer network and compare the predictions to swelling test experiments.

In one class implementation, the solvent polarity gradient was modeled by using chloroform, tetrahydrofuran, acetone, dimethyl sulfoxide, and water. In a second course, ethyl acetate, methyl *tert*-butyl ether, acetone, methanol, and water were the solvents explored. In yet another iteration, students were required to design a gradient solvent study from a list of 11 solvents. In Figure 5, solvents are shown in ascending dielectric constants from left to right with each containing a piece of cross-linked polymer after 60 min. Substantial swelling occurs in nonpolar solvents, such as hexane ($\varepsilon$ = 1.89) and chloroform ($\varepsilon$ = 4.81); minimal swelling occurs in moderately polar solvents like acetone ($\varepsilon$ = 20.7), and no observable swelling is detected in water ($\varepsilon$ = 80.1).[40] The swelled polymer network was less dense than chlorinated solvents like

**Figure 5.** Swelling tests of 20−30 mg of cross-linked poly(myr-*co*-dbi) after ~60 min in a variety of solvents lined up from left to right with ascending dielectric constants.

chloroform and dichloromethane, causing it to float. Time interval photos from 5 to 60 min of Figure 5 are provided in the SI.

### Bulk Polymerization Typical Student Results

The copolymer synthesized by bulk polymerization was analyzed by $^1H$ NMR spectroscopy in $CDCl_3$. Students used end-group analysis (EGA) to calculate an approximate $M_n$ value relative to the furthest downfield aromatic initiator resonance (d, 8.1 ppm) and the integrations of the alkene resonances of poly(myr) (4.9−5.2 ppm) and the ester triplets of poly(dbi) (3.8−4.1 ppm) as illustrated in Figure 6.

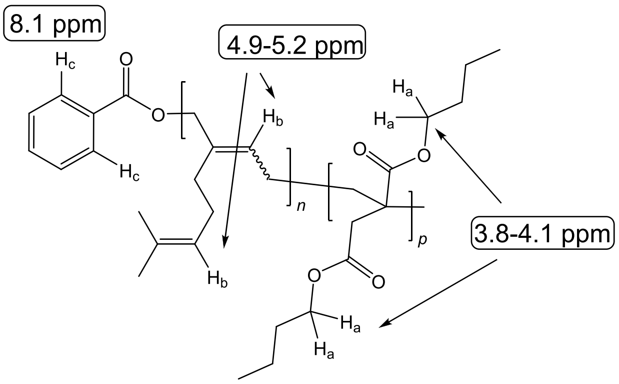


**Figure 6.** Key $^1H$ NMR resonances of poly(myr-*co*-dbi) used for end-group analysis.

Representative spectra of the starting materials and a student product are available in the SI. Groups of students synthesized copolymers with varying ratios of myr and dbi, and their $^1H$ NMR interpretations and data were polled for group discussion, adding a discovery-based and cooperative learning dimension to the experiment.

Not surprisingly, students' calculated $M_n$ values varied from ca. 10 to 30 kg/mol (theoretical $M_n$ values 16−20 kg/mol) due to automated sample submissions, student inexperience in performing these calculations, and the previously mentioned inaccuracies from radical couplings containing phenyl moieties. It was noted that the use of PTFE-capped vials afforded more consistent $M_n$ values, most likely by minimizing the loss of the volatile myr monomer over the course of the reaction.

### Student Survey Results for Spring 2020 Polymer Course

Student experimental data and feedback were collected via a Google Form survey and determined to be exempt of IRB review (U of MN, IRB ID: STUDY00011272). Tables 2 and 3 are results from a student survey of the U of MN polymer laboratory course during the spring of 2020. Students performed day 1 of the two syntheses; however, school closure from the COVID-19 pandemic made it necessary to provide photos of the swelling experiment on this second trial. $^1H$ NMR spectral data was collected for each student sample and provided for student workup and analysis. The experimental results, interpretations, and conclusions were submitted as a full laboratory report.

**Table 2. U of MN Polymer Laboratory Course ($N = 45$), Spring 2020, Likert Question Results**

| Statement | Average[a] | Standard Deviation |
|---|---|---|
| The introduction gave a clear overview of the experiment and learning outcomes | 5.04 | 0.74 |
| Emulsion Polymerization: The experimental procedure was clearly written and easy to follow | 5.27 | 0.91 |
| Bulk Polymerization: The experimental procedure was clearly written and easy to follow | 5.44 | 0.66 |
| Radical Polymerization Assignment: My understanding of radical polymerization mechanisms was enhanced by this assignment | 4.96 | 0.83 |
| The $^1H$ NMR assignment instructions for the bulk polymer were helpful in my interpretation of the NMR spectrum | 4.96 | 1.07 |
| My NMR interpretation skills were enhanced through this experiment | 4.67 | 0.98 |
| My understanding of cross-linked organogels and the relationship between their swelling behavior in terms of enthalpy and entropy was improved with this lab | 4.73 | 1.19 |
| Lab 4 is a valuable addition to the 4223W curriculum | 5.24 | 0.74 |

[a] Based on the Likert scale: 1 = strongly disagree; 2 = disagree; 3 = slightly disagree; 4 = slightly agree; 5 = agree; 6 = strongly agree.

Two assignment sheets, one focused on $^1H$ NMR interpretation and one focused on the radical mechanism and swelling behavior of the copolymers, guided students through the major learning outcomes and interpretations required for their reports. As depicted in Table 2, students felt their understanding of radical polymerization, $^1H$ NMR

**Table 3. U of MN Polymer Laboratory Course ($N = 45$), Spring 2020, Experimental Results**

| Question | Expected Result | % Reporting This Observation |
|---|---|---|
| Emulsion Polymerization Product: Was a trend observed for swelling behavior of the organogel product with solvent dielectric constant/polarity? Describe. | "The trend observed was that less polar solvents, that is solvents with smaller dielectric constant, exhibited greater swelling" | 100% |
| Bulk Polymer $^{1}$H NMR: Compare the feed ratio of monomers used to that determined by $^{1}$H NMR. | myr:dbi 1:1 → feed ratio similar[a] to that calculated from $^{1}$H NMR spectrum | 100% |
| | myr:dbi 2:1→ feed ratio similar[a] to that calculated from $^{1}$H NMR spectrum | 63% |
| | myr:dbi 3:1→ feed ratio similar[a] to that calculated from $^{1}$H NMR spectrum | 57% |

[a] Approximated to the nearest whole number

interpretative skills, and understanding of the thermodynamics of organogel behavior was enhanced through these exercises. Gratifyingly, 87% of the students agreed or strongly agreed that the experiment was a "valuable addition" to the polymer laboratory course.

With respect to the experimental results, students uniformly observed the expected trend in swelling behavior with polarity/dielectric constant (Table 3). Additionally, data from the $^{1}$H NMR spectral analysis indicated that the majority of students observed monomer ratios, to the whole number approximation, to the feed ratios. The 1:1 ratio of monomers was the most consistent. Student data suggested that feed ratios of 2:1 or 3:1 myr:dbi tended to incorporate more myrcene than expected. See the SI for further discussion on this topic.

Finally, when students were queried about what *three* aspects of the experiment they appreciated the most from a list of eight possible statements (see SI for full survey questions), the most frequent responses were the following:

- "learning about organogels" (56%),
- "performing the emulsion polymerization as a new green medium for reaction" (51%), and
- "synthesizing a polymer from potentially renewable feedstocks" (51%).

## CONCLUSION

This green chemistry laboratory experiment illustrates the role of the reaction medium in the radical copolymerization of biobased starting materials. An emulsion polymerization of two sustainably derived monomers uses water as the solvent and facile precipitation of the cross-linked product by acidification of the medium. The resulting organogel material demonstrates the swelling behavior in nonpolar organic solvents. In contrast, a bulk polymerization with varying ratios of the same two monomers results in a linear/branched copolymer with distinguishable sets of protons in the $^{1}$H NMR spectrum for end-group and composition analysis.

These learning outcomes uniquely complemented other experiments in the authors' course curricula. However, one could envision expanding the scope of this chemistry to additional explorations in advanced courses to include reactivity ratios, kinetics, and/or quantification of gelation capacity. All reactants are readily available with an estimated low cost of ∼\$2.00 per student. According to student feedback, implementations in introductory organic chemistry laboratory courses and an upper division undergraduate polymer laboratory class were well-received and described as valuable additions to the curriculum.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00688.

Instructor information, version A for polymer laboratory course, spectra, 7 day kinetics study, version B for organic chemistry laboratory course, and Google Form survey questions (PDF, DOCX)

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Science Advances* **2017**, *3* (7), No. e1700782.

(2) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature* **2016**, *540* (7633), 354−362.

(3) Donahue, C. J.; Exline, J. A.; Warner, C. Chemical Recycling of Pop Bottles: The Synthesis of Dibenzyl Terephthalate from the Plastic Polyethylene Terephthalate. *J. Chem. Educ.* **2003**, *80* (1), 79−82.

(4) Robert, J. L.; Aubrecht, K. B. Ring-Opening Polymerization of Lactide To Form a Biodegradable Polymer. *J. Chem. Educ.* **2008**, *85* (2), 258−260.

(5) 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 $\delta$-Decalactone and l-Lactide. *J. Chem. Educ.* **2014**, *91* (1), 131−135.

(6) Tamburini, F.; Kelly, T.; Weerapana, E.; Byers, J. A. Paper to Plastics: An Interdisciplinary Summer Outreach Project in Sustainability. *J. Chem. Educ.* **2014**, *91* (10), 1574−1579.

(7) Chan, J. M. W.; Zhang, X.; Brennan, M. K.; Sardon, H.; Engler, A. C.; Fox, C. H.; Frank, C. W.; Waymouth, R. M.; Hedrick, J. L. Organocatalytic Ring-Opening Polymerization of Trimethylene Carbonate To Yield a Biodegradable Polycarbonate. *J. Chem. Educ.* **2015**, *92* (4), 708−713.

(8) Fahnhorst, G. W.; Swingen, Z. J.; Schneiderman, D. K.; Blaquiere, C. S.; Wentzel, M. T.; Wissinger, J. E. Synthesis and Study of Sustainable Polymers in the Organic Chemistry Laboratory: An Inquiry-Based Experiment Exploring the Effects of Size and Composition on the Properties of Renewable Block Polymers. In *Green Chemistry Experiments in Undergraduate Laboratories*; ACS Symposium Series; American Chemical Society, 2016; Vol. *1233*, pp 123−147.

(9) Cammidge, A. N. An Undergraduate Experiment in Polyester (PET) Synthesis. *J. Chem. Educ.* **1999**, *76* (2), 236−237.

(10) Duval-Terrié, C.; Lebrun, L. Polymerization and Characterization of PMMA. Polymer Chemistry Laboratory Experiments for Undergraduate Students. *J. Chem. Educ.* **2006**, *83* (3), 443−446.

(11) Poon, T.; Eller, C. F.; Eller, L. R.; Jones, K. M.; Massello, W.; Norris, C. M.; Oelrich, J. A.; Pluim, T. A.; McIntyre, J. P.; Dorigo, A. E.; et al. The Preparation of a UV-Light-Absorbing Polymer: A Project-Oriented Laboratory Experiment for the Introductory Organic Chemistry Curriculum. *J. Chem. Educ.* **1999**, *76* (11), 1523−1524.

(12) Royappa, A. T. Synthesis and Characterization of a Hyperbranched Copolymer. *J. Chem. Educ.* **2002**, *79* (1), 81−84.

(13) 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 Spectroscopy. *J. Chem. Educ.* **2006**, *83* (8), 1215−1217.

(14) Moorhead, E. J.; Wenzel, A. G. Two Undergraduate Experiments in Organic Polymers: The Preparation of Polyacetylene and Telechelic Polyacetylene via Ring-Opening Metathesis Polymerization. *J. Chem. Educ.* **2009**, *86* (8), 973−975.

(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) Beers, K. L.; Matyjaszewski, K.; Woodworth, B. 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.

(17) Nguyen, T. L. U.; Bennet, F.; Stenzel, M. H.; Barner-Kowollik, C. Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization in Undergraduate Polymer Science Lab. *J. Chem. Educ.* **2008**, *85* (1), 97−99.

(18) Tillman, E. S.; Contrella, N. D.; Leasure, J. G. Monitoring the Nitroxide-Mediated Polymerization of Styrene Using Gel Permeation Chromatography and Proton NMR. *J. Chem. Educ.* **2009**, *86* (12), 1424−1426.

(19) Koshut, W. J.; Arnold, A. M.; Smith, Z. C.; Wright, Z. M.; Sydlik, S. A. Teaching Polymer Theory through the Living Polymerization and Characterization of Poly(Methyl Methacrylate) and Poly(Butyl Methacrylate) Homo- and Copolymers. *J. Chem. Educ.* **2019**, *96* (5), 895−904.

(20) Horta, A.; Pastoriza, M. A. The Molecular Weight Distribution of Polymer Samples. *J. Chem. Educ.* **2007**, *84* (7), 1217−1221.

(21) Izunobi, J. U.; Higginbotham, C. L. Polymer Molecular Weight Analysis by $^1$H NMR Spectroscopy. *J. Chem. Educ.* **2011**, *88* (8), 1098−1104.

(22) Wackerly, J., Wm.; Dunne, J. F. Synthesis of Polystyrene and Molecular Weight Determination by $^1$H NMR End-Group Analysis. *J. Chem. Educ.* **2017**, *94* (11), 1790−1793.

(23) Kosbar, L. L.; Wenzel, T. J. Inclusion of Synthetic Polymers within the Curriculum of the ACS Certified Undergraduate Degree. *J. Chem. Educ.* **2017**, *94* (11), 1599−1602.

(24) American Chemical Society, Committee on Professional Training. *Undergraduate Professional Education in Chemistry: ACS Guidelines and Evaluation Procedures for Bachelor's Degree Programs*; American Chemical Society: Washington, DC, 2015.

(25) Behr, A.; Johnen, L. Myrcene as a Natural Base Chemical in Sustainable Chemistry: A Critical Review. *ChemSusChem* **2009**, *2* (12), 1072−1095.

(26) Bozell, J. J.; Petersen, G. R. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the US Department of Energy's "Top 10" Revisited. *Green Chem.* **2010**, *12* (4), 539−554.

(27) El-Imam, A. A.; Du, C. Fermentative Itaconic Acid Production. *Journal of Biodiversity, Bioprospecting and Development* **2014**, *1* (2), 1−8.

(28) Cowie, J. M. G.; Henshall, S. A. E.; McEwen, I. J.; Veličković, J. Poly(Alkyl Itaconates): 4. Glass and Sub-Glass Transitions in the Di-Alkyl Ester Series, Methyl to Hexyl. *Polymer* **1977**, *18* (6), 612−616.

(29) Sarkar, P.; Bhowmick, A. K. Green Approach toward Sustainable Polymer: Synthesis and Characterization of Poly(Myrcene-Co-Dibutyl Itaconate). *ACS Sustainable Chem. Eng.* **2016**, *4* (4), 2129−2141.

(30) Knutson, C. M.; Schneiderman, D. K.; Yu, M.; Javner, C. H.; Distefano, M. D.; Wissinger, J. E. Polymeric Medical Sutures: An Exploration of Polymers and Green Chemistry. *J. Chem. Educ.* **2017**, *94* (11), 1761−1765.

(31) Knutson, C. M.; Hilker, A. P.; Tolstyka, Z. P.; Anderson, C. B.; Wilbon, P. A.; Mathers, R. T.; Wentzel, M. T.; Perkins, A. L.; Wissinger, J. E. Dyeing to Degrade: A Bioplastics Experiment for the College and High School Classroom. *J. Chem. Educ.* **2019**, *96* (11), 2565−2573.

(32) Harkins, W. D. A General Theory of the Mechanism of Emulsion Polymerization. *J. Am. Chem. Soc.* **1947**, *69*, 1428−1444.

(33) Lovell, P. A.; Schork, F. J. Fundamentals of Emulsion Polymerization. *Biomacromolecules* **2020**, *21*, 4396.

(34) Flory, R.; Rehner, J. Statistical mechanics of cross-linked polymer networks. I. Rubber like Elasticity. *J. Chem. Phys.* **1943**, *11* (11), 512−520.

(35) Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*; CRC Press, 2007; pp 247−284, 381−415.

(36) Cawse, J. L.; Stanford, J. L.; Still, R. H. Polymers from renewable sources. III. Hydroxy-terminated myrcene polymers. *J. Appl. Polym. Sci.* **1986**, *31* (7), 1963−1975.

(37) Nam, C.; Li, H.; Zhang, G.; Lutz, L. R.; Nazari, B.; Colby, R. H.; Chung, T. C. M. Practical Oil Spill Recovery by a Combination of Polyolefin Absorbent and Mechanical Skimmer. *ACS Sustainable Chem. Eng.* **2018**, *6*, 12036−12045.

(38) Vintiloiu, A.; Leroux, J. C. Organogels and Their Use in Drug Delivery — A Review. *J. Controlled Release* **2008**, *125*, 179−192.

(39) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford, 1998.

(40) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 87th ed.; Taylor & Francis, 2006; pp 6-153−6-175.