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Science Education Title: Photochemical Initiation of Radical Polymerization Reactions

Overview:

In this video, we will carry out the photochemically initiated polymerization of styrene to generate polystyrene, which is an important commodity plastic. We will learn the fundamentals of photochemistry and use simple photochemistry to initiate radical polymerization reactions. Specifically, in this module we will examine the photochemistry of benzoyl peroxide and its role as a photoinitiator of styrene polymerization reactions. In the described experiments, we will understand the role of wavelength, photon absorption, and excited state structure on the efficiency (measured as quantum yield) of photochemical reactions.

Principles:

Organic polymers are ubiquitous chemicals in everyday life. Polyolefins, which are generated by polymerization of alkene monomers, comprise common plastics and rubbers found in drinking cups, soda bottles, car tires, and even some fabrics. Polystyrene, for example, is a polymer based on styrene monomers, and finds important applications in protective packaging (*i.e.* packing peanuts), water bottles, and disposable forks and knives. Polystyrene is generated on several million tons per year.

Polymer synthesis is a field of chemistry devoted to developing methods to initiate and control polymer growth in order to generate polymers with specific targeted applications. For example, the exact properties of polyolefin materials depend intimately on the polymer chain structure, and structural factors such as extent of chain branching can completely change the properties of polymeric materials built from the same monomer units.

Simple olefins do not spontaneously participate in polymerization chemistry, despite the fact that these reactions are thermodynamically downhill. To get efficient polymerization to proceed, either initiators or catalysts, which lower the kinetic barrier to polymerization, are required. Benzoyl peroxide is an example of an effective radical initiator for polymer growth. Photochemically promoted homolytic cleavage of the O–O bond results initially in the generation of carboxylate radicals and, following decarboxylation, in phenyl radicals and CO_2 (**Figure 1**). These phenyl radicals react with styrene to generate a new C–C bond and a benzylic radical. This initially formed benzylic radical can react with additional styrene in a radical chain reaction to eventually afford long-chains of polystyrene.

The basis of photochemistry is that photon absorption generates a molecular excited state, which participates in chemical reaction. In order to access the required molecular excited state, the molecule of interest (in this case benzoyl peroxide) needs to have absorbed light at the energy delivered. Benzoyl peroxide absorbs only in the UV portion of the spectrum; O–O homolysis can be initiated by irradiation with ~250 nm light. This wavelength is too short for the human eye to see. To illustrate the importance of photon absorption of

photochemistry, we will first examine the polymerization of styrene initiated by benzoyl peroxide directly under visible light irradiation. The absorption spectrum of benzoyl peroxide does not have significant absorption in the visible region (benzoyl peroxide is colorless) and photoinduced polymerization with visible light is not facile.

In order to overcome the poor absorptivity of many organic molecules towards visible light, photosensitizers are utilized. Photosensitizers are molecules that participate in photon absorption and then transfer energy to a different molecule to promote photochemical reactions. Benzophenone is a common photosensitizer; the photochemistry of this molecule is described in **Figure 2**. Photon absorption in the ground state generates a singlet excited state. Intersystem crossing affords the triplet ground state, which compared to the singlet excited state, is long lived. Energy transfer from the triplet excited state to benzoyl peroxide can lead to O–O bond cleavage and radical-chain initiation. The photosenstitizer is useful because unlike benzoyl peroxide, it has substantial absorption in the visible spectrum.

In competition with energy transfer to substrate, the triplet excited state can undergo relaxation to regenerate the singlet ground state; if this process is fast relative to energy transfer, then sensitization is not efficient. The efficiency of sensitization is measured by the quantum yield, which is a measure of the fraction of absorbed photons that are utilized productively in the targeted chemical reaction. In order for photosensitizers to work effectively, the excited state of the sensitizer must encounter the other reactant; in our case, the triplet excited state of benzophenone must encounter benzoylperoxide in order to accomplish energy transfer. The quantum yield of polymerization using bimolecular initiators is low if relatively few of the photogenerated benzophenone excited states result in generation of benzoyl radicals by O–O cleavage.

Quantum Yield = photoreactions accomplished / photons absorbed

Through the experiments that are outlined in this video, we will confront the topics of photochemistry, triplet sensitizers, and polymerization chemistry.

Procedure:

1. Measure the absorption spectrum of benzoyl peroxide.

    1.1. Benzoyl peroxide is commercially available. Prepare a solution of benzoyl peroxide in toluene. Using a 10 mL volumetric flask, add 10 mg of benzoyl peroxide. Fill the volumetric flask with toluene.

    1.2. Add 0.5 mL of the prepared solution to a UV-vis cuvette using a volumetric pipette. Add 3.5 mL of toluene.

    1.3. Prepare a second cuvette, filled only with pure toluene.

1.3.1.4.   Measure the absorption spectrum (300–800 nm wavelength range) of the toluene-filled cuvette. This spectrum should be used to subtract the solvent background from the spectrum of benzoyl peroxide - collected below.

1.5. Measure the absorption spectrum (300–800 nm wavelength range) of the benzoyl peroxide-containing cuvette. To obtain the absorption spectrum of benzoyl peroxide, subtract the spectrum of toluene obtained in step 1.4. Many UV-vis software packages perform background subtraction automatically. If not, background subtraction can be accomplished using standard database software, such as Excel.

2.   Reaction of benzoyl peroxide and styrene in the absence of a photosensitizer.

2.1. Measure the tare weight of a 25-mL round-bottom flask.

2.1.2.2.   Prepare a solution of benzoyl peroxide and styrene in toluene by combining 1 mL of the solution prepared above to 10 mL toluene and 3 mL styrene-. Transfer the reaction solution to a 25-mL round-bottom flask, fit the flask with a rubber septum, and degas the reaction solution using the freeze-pump-thaw technique described in (see the "Schlenk Lines Transfer of Solvents" video in the *Essentials of Organic Chemistry* series). It is not important to exclude water from the reaction solution, only to remove dissolved O_2.

2.2.2.3.   IrradiateIn a ventilated fume hood, turn on the Hg-arc lamp and wait 10 minutes for the light bulb to warm up. Clamp the reaction flask to a stir plate and insert an N_2 needle into the septum. With magnetic stirring, irradiate the solution with a Hg-arc lamp using a 350-nm long-pass filter for 10 minutes.

2.3.2.4.   Concentrate the photoreaction on a rotovap. Weigh the If non-volatile residue and remains, obtain a mass of the flask. The weight of the non-volatile residue can be determined using the tare weight measured in step 2.1 Obtain a ^1H NMR spectrum of the residue in CDCl$_3$.

3. Measure the absorption spectrum of benzophenone.

3.1. Benzophenone is commercially available. Prepare a solution of benzophenone in toluene. Using a 10 mL volumetric flask, add 10 mg of benzophenone. Fill the volumetric flask with toluene.

3.2. Add 0.5 mL of the prepared solution to a UV-vis cuvette using a volumetric pipette. Add 3.5 mL of toluene.

3.3. Measure the absorption spectrum (300–800 nm wavelength range) of benzophenone.

3.4. Using the spectrum of toluene obtained in Step 1.4, perform a background subtraction to obtain the absorption spectrum of pure benzophenone.

4. Reaction of benzoyl peroxide and styrene in the presence of the photosensitizer benzophenone.

4.4.1. Measure the tare weight of a 25-mL round-bottom flask.

4.1.4.2.   Prepare a solution of benzoyl peroxide, benzophenone, and styrene in toluene by combining 1.0 mL of the benzoyl peroxide solution prepared in step 1.1, with 1.0 mL of the benzophenone solution prepared in step 3.1 with 10 mL toluene and 3 mL styrene. Transfer the reaction solution to a 25-mL round-bottom flask, fit the flask with a rubber septum, and degas the reaction solution using the freeze-pump-thaw technique (see the "Schlenk Lines Transfer of Solvents" video in the *Essentials of Organic Chemistry* series). It is not important to exclude water from the reaction solution, only to remove dissolved O_2.

4.2.4.3.   IrradiateIn a ventilated fume hood, turn on the Hg-arc lamp and wait 10 minutes for the light bulb to warm up. Clamp the reaction flask to a stir plate and insert an N_2 needle into the septum. With magnetic stirring, irradiate the solution with a Hg-arc lamp using a 350-nm long-pass filter for 10 minutes.

4.3.4.4.   Concentrate the photoreaction on a rotovap. Weigh theIf non-volatile residue andremains, obtain a mass of the flask. The weight of the non-volatile residue can be determined using the tare weight measured in step 4.1 Obtain a ^{1}H NMR spectrum of the residue in $CDCl_3$.

5. Control reaction of styrene in the presence of the photosensitizer benzophenone.

5.1. Measure the tare weight of a 25-mL round-bottom flask.

5.1.5.2.   Prepare a solution of benzophenone and styrene in toluene by combining 1.0 mL of the benzophenone solution prepared in step 3.1 with 10 mL toluene and 3 mL styrene. Transfer the reaction solution to a 25-mL round-bottom flask, fit the flask with a rubber septum, and degas the reaction solution using the freeze-pump-thaw technique (see the "Schlenk Lines Transfer of Solvents" video in the *Essentials of Organic Chemistry* series). It is not important to exclude water from the reaction solution, only to remove dissolved O_2.

5.2.5.3.   IrradiateIn a ventilated fume hood, turn on the Hg-arc lamp and wait 10 minutes for the light bulb to warm up. Clamp the reaction flask to a stir plate and insert an N_2 needle into the septum. With magnetic stirring, irradiate the solution with a Hg-arc lamp using a 350-nm long-pass filter for 10 minutes.

5.3.5.4.   Concentrate the photoreaction on a rotovap. ~~Weigh the~~If non-volatile residue ~~and~~remains, obtain a mass of the flask. The weight of the non-volatile residue can be determined using the tare weight measured in step 5.1 Obtain a ^{1}H NMR spectrum of the residue in $CDCl_3$.

Representative Results:

The results will include absorption spectra that will be recorded on the day of the experiment as well as NMR data from the reactions.

Discussion of Results

Based on the UV-vis absorption spectra that we collected, we can see that benzoyl peroxide does not ~~absorb a~~display substantial ~~amount of~~absorption in the visible ~~light~~spectrum. The lack of visible-light-absorption is consistent with the lack of polymerization chemistry that is observed when a sample of styrene is photolyzed in the presence of benzoyl peroxide. ~~Benzophenone~~The residue left behind following evaporation of the photoreaction described in step 2 contains only benzoyl peroxide; no styrene-derived products have been generated.

In contrast to benzoyl peroxide, benzophenone does absorb a substantial amount of visible light ~~(out to~~ (>300 nm). Photolysis of a mixture of benzophenone, benzoyl peroxide, and styrene ~~is observed to generate~~results in the formation of some polystyrene. ~~We~~The polymerization results in the formation of an oily, non-volatile residue that remains after evaporation of the photoreaction. In addition, ^{1}H NMR analysis of the residue indicates the presence of polystyrene.

Finally, we have also ~~saw~~seen that benzophenone alone is not a competent photoinitiator. Only when the sensitizer, initiator, and substrate are all present does polymerization proceed.

Summary:

In this video, we have seen the impact of the structure on the reactivity of radical initiators for olefin polymerization chemistry. We have examined photochemical conditions 1) that did not contain appropriate absorbers, 2) that contained appropriate absorbers but not appropriate initiators, and 3) that contained both initiator and absorber molecules. These systems highlight the role of photon absorption and the importance of quantum efficiency on photochemical reactions.

Applications:

Radical initiators are important tools for the production of polymer materials. ~~In addition to the~~ Photo-initiated polymerization reactions ~~that we have seen above, photo-initiated polymerizations~~find application in a variety of areas. For example, photochemically initiated polymerization chemistry can be used to make designer materials in which the

monomer that is incorporated in changed on demand, which allows precise control over the molecular structure of the material that results~~. In addition, we have seen the importance of absorption on the generation of radical intermediates. These observations highlight the importance of molecular design in identifying highly efficient polymerization initiators.~~. A second application is in using photochemically initiated polymerization to pattern polymerization reactions to generate specific shapes or distributions of polymerized material.

In this experiment, we saw the critical impact of photosensitizers on the efficiency of photochemical reactions. The concepts explored here underpin ~~a whole field of science~~an important area of polymerization chemistry, which endeavours to identify highly efficient sensitizers and initiators. One example which we can understand based on our experiments is the use of unimolecular initiator-sensitizer hybrids (example is illustrated in **Figure 3**).[1] By combining the sensitizer, which has strong absorption in the visible spectrum, and the radical initiation benzoyl peroxide in the same molecule, we effectively increase the quantum yield of sensitization and thus more efficiently initiate polymerization. These observations highlight the importance of molecular design in identifying highly efficient polymerization initiators.

Commented [HK8]: Could you please provide one more example for this application. The first paragraph is more generic and the second paragraph gives one example discussing the unimolecular initiator-sensitizer, but preferably we would like to have 2 concrete application examples. Thanks!

References

1. Greene, F. D.; Kazan, J. Preparation of Diacyl Peroxides with N,N'-Dicyclohexylcarbodiimide *J. Org. Chem.* **1963**, *28*, 2168-2171.
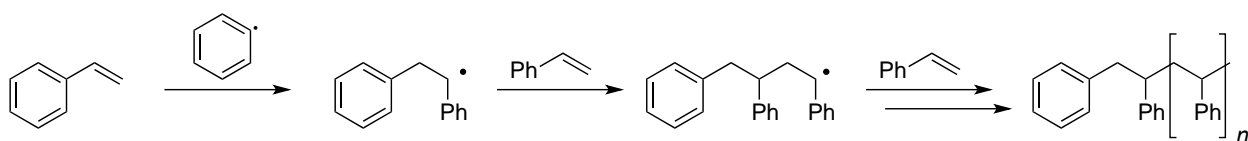
Legend

Figure 1. a. O–O bond cleavage eventually leads to the formation of phenyl radicals, which can initiate polymerization. b. Illustration of the radical-chain polymerization initiated by phenyl radicals.

Figure 2. Diagram of photosensitization. Photon absorption by benzophenone initially generates the first singlet excited state (S_1). Intersystem crossing provides access to the first triplet excited state (T_1). Energy transfer from the triplet excited state to benzoyl peroxide leads to productive photochemistry.

Figure 3. Illustrated is a unimolecular sensitizer-initiator hybrid. The molecule achieves high quantum efficiency for polymerization by combining a benzophenon-like moiety with a benzoyl peroxide unit.

Figure 1.

Figure 2.

Figure 3.