

Chemical Recycling of Pop Bottles: The Synthesis of Dibenzyl Terephthalate from the Plastic Polyethylene Terephthalate

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Beyond a few well-established classic experiments¹ (1–6), attempting to expose the undergraduate student to synthetic polymer chemistry in the laboratory is a challenge because of safety concerns. Many polymerization reactions require harsh conditions—high temperature and pressure—and special reactors. Many procedures (even the classic experiments) employ toxic and dangerous chemicals (e.g., phosgene, isocyanates, benzoyl peroxide). In addition, an expensive catalyst, an inert atmosphere, and anhydrous conditions are often essential for success. The laboratory procedure described here circumvents many of these problems by having the students start with a common plastic and depolymerize it to produce a monomer building block using relatively mild conditions and nontoxic chemicals.

This laboratory procedure involves the chemical recycling of the condensation polymer polyethylene terephthalate (PET or PETE) from 2-liter pop² bottles. A similar PET depolymerization experiment recently appeared in this *Journal* (7). In that article, the authors describe the hydrolysis of PET by potassium *tert*-butoxide or potassium hydroxide in refluxing pentanol to yield terephthalic acid. We have developed a transesterification reaction that closely mimics the industrial process (7) developed by DuPont Chemical and others. The reaction employs an acid-catalyzed transesterification reaction of PET with methanol (methanolysis) at high temperature and pressure to yield dimethyl terephthalate and ethylene glycol (see Scheme I). At the present time, the physical recycling of PET is economically more viable than this chemical recycling process and consequently the chemical recycling of PET is not widely practiced.³

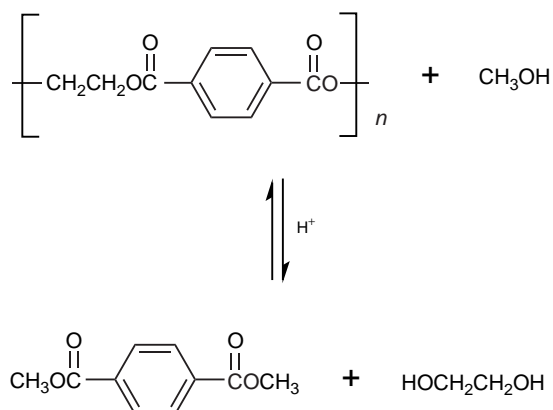
In our procedure, we have replaced the low-boiling methanol with its much higher boiling cousin benzyl alcohol (phenylmethanol, bp 205 °C). PET is converted to

dibenzyl terephthalate (DBT) in moderate yields by refluxing it with benzyl alcohol at atmospheric pressure in the presence of a zinc acetate catalyst (see Scheme II).

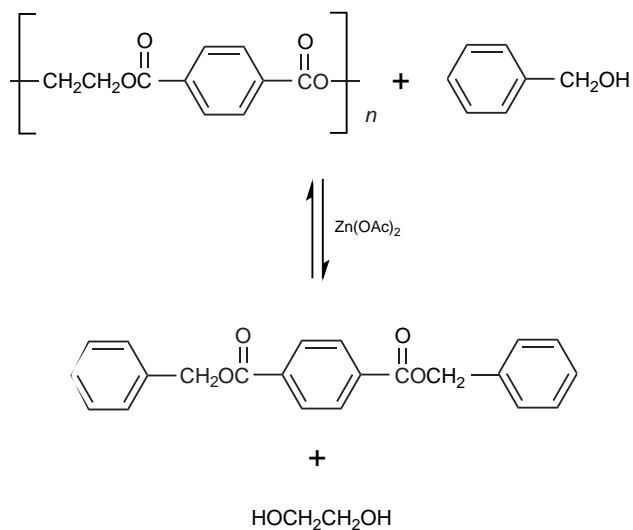
Target Audience

This experiment should be of interest to instructors who teach an introductory organic chemistry lab course or a polymer chemistry lab course. On our campus, this lab was developed to support a new general chemistry sequence targeted at engineering students. To make this two semester sequence more relevant to the audience, the overarching theme of “chemistry and the automobile” is folded into each topic covered in these courses (8).

This lab is performed by second semester general chemistry students (mostly mechanical engineering majors). Prior to completing this lab, these students have completed a three-week section on organic chemistry in lecture, followed by a three-week section on the synthesis and properties of synthetic polymers. This lab is preceded by several labs that expose the students to examples of organic synthesis, simple and fractional distillation, liquid–liquid extraction, and the characterization of products by IR spectroscopy and gas chromatography. The students have also completed several labs dealing with polymers. One polymer lab involves the identification of commodity plastics using density and IR spectroscopy. A second polymer lab involves some standard polymer syntheses.¹ Because of safety concerns, several of these procedures are performed as demonstrations by the lab instructor.



Scheme I. Transesterification reaction of PET with methanol.



Scheme II. Transesterification reaction of PET with benzyl alcohol in the presence of a zinc catalyst.

Plastics and the Automobile

Plastics are ubiquitous in the modern automobile (9). They have numerous exterior (e.g., bumper, body panels, trim, and lighting systems), interior (e.g., instrument panels, upholstery, air ducts, and carpeting), and under-the-hood (e.g., air-intake and fuel-intake systems) applications. Plastics are also essential to the fuel and electrical systems of the automobile and are finding increased use in power train and chassis applications. Plastic components offer many advantages over other materials—steel, nonferrous alloys, ceramics, and glass. Plastics are lightweight, which leads to lighter parts, a lighter car, and better gas mileage. They can be easily molded into complex shapes. This property permits the engineer to make optimal use of limited space. Plastics permit the engineer greater design freedom than other types of material. This often leads to several parts being combined into a single integrated piece thus lowering production costs. In the engine compartment plastics are attractive because they are more corrosion resistant than metals, can handle harsh chemicals (e.g., fuels and motor oils), and reduce noise and vibrations. A diverse set of needs can be met by the vast array of available plastics. Illustrations of specific polymers used in varied automotive applications include: HDPE in fuel tanks; polycarbonate and polymethyl methacrylate in automotive lighting systems; ABS (acrylonitrile butadiene styrene terpolymer) in radiator grills; polypropylene (and many other plastics) in instrument panels and air ducts; polyurethane foams in upholstery cushioning; microcellular polyurethane in spring aids; glass-filled nylon, styrenics, and polyester, among others, in component housing (e.g., in alternators and battery cases); fluoropolymers in seal rings; polyethersulphone in bearing cages; aramid fiber in brake pads; nylon and polyphenylene sulfide in water pumps; polyetherimide resins in transmission sensors; and styrene butadiene rubber in tires.

Polyesters, the focus of this article, can be subdivided into two broad classes: the thermoplastic polyesters and thermoset polyesters (10). The most common thermoplastic polyester is polyethylene terephthalate, which is used in three general product types: films (e.g., magnetic tapes and photographic films), fibers (e.g., DuPont's Dacron and Kodak's Kodel), and molding resins (e.g., soda and water bottles). In the automobile, polyester fibers are woven to provide seating textile and seat belts, and also find use as reinforcements in tires and hoses. Polybutylene terephthalate (PBT), a second thermoplastic polyester, along with PET are excellent insulators and find extensive use in automobile electrical connector applications (9, 10).

PET and PBT are part of a middle tier of plastics, whose hydrocarbon backbone is part aliphatic and part aromatic. The thermoplastic olefins (e.g., polyethylene and polypropylene) and nylon 6,6 make up the bottom tier. The hydrocarbon backbone of these polymers is aliphatic. The hydrocarbon portion of the backbone of the top tier of polymers is entirely aromatic and includes such polymers as polyether sulfone, polyphenylene sulfide, and polyetherether ketone. The cost per pound increases on moving from the bottom tier to the top tier. However, structural integrity also improves on moving from the bottom to the top tier. Resistance to heat, fire, and chemicals generally improves on

switching to a higher tier. Thus selecting PET or PBT often represents a balance between cost and performance (9).

Thermoset polyesters, the second broad class of polyesters, are also called unsaturated polyesters because they contain carbon-carbon double bonds that are the sites where crosslinking occurs. In order to lower the price and improve the performance of thermoset polyesters, they are typically modified with reinforcements and fillers. Sheet molding compound (SMC) employs a thermoset polyester. The Corvette body panel is one well-known example of the use of SMC in the automobile (9, 10).

One unique example of the use of PET in the automobile is Daimler-Chrysler's composite concept vehicle, which they hope to market in third world countries in the near future (11). Because the body of the vehicle is made from just four plastic panels mounted on a steel frame, it weighs only 1,200 pounds, gets 50 miles to the gallon, and will be priced at \$6,000 or less. A 160-ton press is used to fabricate the four injection-molded pieces that are made from glass-filled PET (which can be recycled). The panels do not require painting.

An example of chemical recycling connected with the auto industry is Ford Motor Company's use of repolymerized nylon 6 in a throttle-body adapter (12). The feedstock for this part is recycled nylon carpeting and other nylon waste, which is depolymerized to caprolactam. This reclaimed monomer is then used to make the nylon 6 that goes into the adapter.

Despite the many benefits plastics in the automobile has brought, recycling these parts presents many obstacles. First, there is the diversity of plastic types found in the automobile. Second, most plastic parts in older vehicles are unlabeled as to the type of plastic. In addition, it is often difficult to remove the plastic part from the vehicle and these parts are often contaminated with other materials (13). For these and other reasons, only a small fraction of automotive plastic parts are currently recycled. Scrapped automobiles, known as end-of-life vehicles (ELVs), are processed by shredding operators. In preparation for shredding, dismantlers typically drain fluids (oils, antifreeze, air conditioner refrigerants) and remove tires. Then, following the removal of parts (engines, starters, generators) for resale, and parts (batteries, catalytic converters, radiators) for recovery of materials (polypropylene, Pb, Pt, Rh), the remaining hulk is shredded in hammer mills to permit the recovery of ferrous and nonferrous (Al, Mg, Cu) metals (13). The recovery of metals has historically been the primary focus of dismantlers. They supply two-fifths of the nation's ferrous scrap (14). The remaining by-product, which consists of glass, ceramics, fabrics, plastics and elastomers, and residual fluids and metals is called automotive shredder residue (ASR). Twenty-five percent of ELV weight is estimated to be ASR (15). Current practice in the United States is to dispose of ASR in landfills (16). ASR can also be thought of as a low-grade fuel with plastics estimated to contribute more than 40% of the heat content (17). However, ASR is contaminated with heavy metals and PCBs and without further processing ASR is unsuitable as a fuel for environmental reasons. If subjected to further processing, ASR has been proposed as a fuel for power generation when burned with municipal solid waste (MSW), and for cement and steel production (17).

Laboratory Procedure

This lab exercise spans parts of three, 3-hour lab periods. The students complete this lab in preassigned groups. Two of the five groups in a lab section are instructed to prepare dibenzyl terephthalate from PET (Method 1) and the other three groups are instructed to prepare dibenzyl terephthalate from terephthaloyl chloride (Method 2). The students are informed that they will be asked to compare their results after they have prepared and characterized their product. Method 1 takes three lab periods to complete: in week 1 the product is prepared, in week 2 it is isolated and purified, and in week 3 it is characterized. Method 2 takes two lab periods to complete: in week 1 the product is prepared, isolated, and purified; in week 2 it is characterized.

Dibenzyl Terephthalate from PET: Method 1

Three grams of PET (obtained from clear 2-L pop bottles and cut in 0.25 in. \times 0.25 in. squares) are placed in a 100-mL round bottom flask along with a Teflon-coated stir bar, 30 mL benzyl alcohol, and 0.6 g zinc acetate. After attaching a water-cooled condenser, the mixture is stirred and refluxed for 24 h. The product mixture is washed with distilled water (100 mL) and the water decanted from the mixture.⁴ After adding 50 mL of methanol to the product mixture, it is cooled in an ice bath to yield white crystals of crude dibenzyl terephthalate that are collected by suction filtration. The crude product is dissolved in 100 mL of hot methanol and a hot filtration is performed to remove insoluble impurities. The filtrate is reduced to approximately half its original volume on a hot plate and allowed to cool slowly to room temperature. After further cooling in an ice bath, the purified product is collected by suction filtration and allowed to air dry until the next lab period when it is characterized.

Dibenzyl Terephthalate from Terephthaloyl Chloride: Method 2

The students are provided a stoppered test tube containing 2.5 g of terephthaloyl chloride. To the test tube, 10 mL benzyl alcohol is added, followed by 2 mL pyridine. The mixture is placed in a hot water bath maintained at 85 °C for 15 minutes and stirred intermittently. After cooling the product mixture to room temperature, 10–20 mL of methanol is added to the test tube and the contents cooled in an ice bath. The crude product is collected by suction filtration. At this point, the purification procedure for DBT is identical to that described in Method 1.

Data have been collected for twenty-five student samples of dibenzyl terephthalate, ten of which were made by Method 1 and the remaining fifteen by Method 2. Every attempt to make dibenzyl terephthalate by these two methods was successful. The yield of the product made by Method 1 ranged from 32 to 82% and averaged 44%, while the yield of product made by Method 2 fell between 11–40% and averaged 26%. The melting points of the products made by Method 1 fell between 89–93 °C and between 86–89 °C for ten out of fifteen samples made by Method 2. Two of the remaining samples had a lower mp, while three had a mp between 94–96 °C. When these samples were recrystallized a second time from methanol, the melting point increased to 95–96 °C, which agrees closely with the literature value of 96.5–97 °C

(18). The IR spectrum of the product was recorded as a thin film (from a CH_2Cl_2 solution) deposited on a NaCl plate. The C=O stretch of the ester group occurred at $1718.5 \pm 1 \text{ cm}^{-1}$ for all the samples prepared by Method 1. The C=O stretch of the ester group fell over a slightly broader range for the samples prepared by Method 2. The product was also examined by TLC. TLC was performed on oven-dried plates⁵ using 3:1 dichloromethane/cyclohexane as the developing solvent. Samples were spotted as a dichloromethane solution and developed plates were viewed under a UV lamp. The R_f value of samples prepared by Method 1 fell between .42 and .47, while samples prepared by Method 2 gave R_f values of .39 to .48. Small amounts of a second species were observed in some of the samples prepared from both Methods 1 and 2. When DBT samples prepared by Methods 1 and 2 were recrystallized a second time and then reexamined by TLC, the second species was absent. Yields, melting points, IR stretches, and R_f values were collected from each group and distributed to the entire class prior to submission of a lab report.

Our general chemistry students were not asked to characterize their products by NMR. However, in more advanced settings this additional means of characterization may be desirable. The ^1H NMR spectrum of DBT in CDCl_3 consists of a singlet at 5.35 ppm owing to the methylene hydrogens and a multiplet at 7.40 ppm and a singlet at 8.10 ppm owing to the aromatic hydrogens. The ^{13}C NMR spectrum of DBT in CDCl_3 consists of eight peaks: the methylene carbon occurs at 66.95 ppm, the carbonyl carbon at 165.37 ppm, and the aromatic carbons at 135.53, 133.80, 129.51, 128.49, 128.25, and 128.11 ppm.

Hazards

All the chemicals (except PET) used in this lab should only be handled in a well-ventilated hood while wearing gloves and safety goggles. Benzyl alcohol is an irritant. Zinc acetate is both an irritant and toxic. Terephthaloyl chloride is corrosive and a lachrymator. Pyridine is a flammable liquid and an irritant and has an unpleasant odor. Methanol is a flammable liquid and toxic. It is readily absorbed through the skin. Wear gloves when handling it. Methanol should only be heated in a well-ventilated hood. Cyclohexane is a flammable liquid and an irritant. Dichloromethane is both an irritant and toxic.

Conclusion

This experiment achieves many goals. The students work with a real sample, the ubiquitous pop bottle. Many of the problems inherent in polymer synthesis are avoided by this alternative approach, yet synthesis involving a polymer is still achieved. Post-lab questions lead the students to better understand the distinction between addition polymers and condensation polymers and the realization that the former can be only be physically recycled, while the latter potentially can be both physically and chemically recycled. The important role plastics play in the construction and operation of the automobile is showcased. The students are introduced to the concept of green chemistry and better appreciate the challenges associated with recycling plastics especially from a consumer product as complex as the automobile. The students

are surprised to discover the pop bottle is not as inert a material as they originally thought and marvel at the notion that they can transform the clear plastic pop bottle into a fluffy white powder that could be used to make a new batch of PET. Making DBT by two different methods and comparing the properties of the two sets of samples illustrates a classical approach to establishing the correct identity of a compound. Finally, by their own admission, many engineering students state that they begin to appreciate the relevance of organic chemistry and polymer chemistry to their professional aspirations when these topics are linked to commercial products like the pop bottle and the automobile.

Acknowledgments

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^uSupplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

Notes

1. For example, the nylon 6,6 rope demonstration experiment; polystyrene; the cross-linked polyester glyptal and polyurethane foam.

2. Pop is synonymous with soda and soft drink.

3. Private communication with Karl D. Hattopp, Clean Tech, Inc., Dundee, MI.

4. Addition of water to the product mixture typically leads to formation of an emulsion. However, complete removal of the water is not crucial to the successful recovery of DBT and may actually facilitate it.

5. Selecto Scientific flexible TLC plates (Silica Gel 60, F-254, 200 micron thickness) were used.

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