"New" Compounds from Old Plastics: Recycling PET Plastics via Depolymerization

An Activity for the Undergraduate Organic Lab

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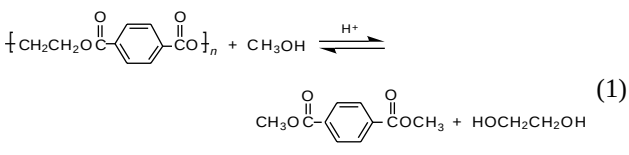
There is recognized value in including experiments in the undergraduate chemistry lab that illustrate chemistry of the "real" world. Such experiments are particularly attractive if they are also truly related to topics discussed in the chemistry lecture. Reported here is such an activity, which can be adjusted to fit either one or two typical organic lab periods. We discuss how the depolymerization of the widely used plastic polyethyleneterephthalate (PET) can be accomplished in one lab period via an ester hydrolysis reaction. A second lab can be used to conduct an esterification reaction of the terephthalic acid obtained from the PET hydrolysis of the first lab. Prelaboratory discussion accompanying these experiments can include not only the chemistry involved, but also the important societal issue of plastics recycling. These experiments are best done during the second semester organic lab after ester chemistry and S_N2 reactions have been studied in lecture.

Many plastic products, particularly those used for packaging, have a short period of usefulness and are soon discarded. It is estimated that each year in the United States about 140 billion pounds of plastic products are discarded; that is about 600 pounds per person (*1*). Currently about 80% of discarded plastic ends up in landfills, with the consequence that plastics account for nearly 25% of the volume of landfill refuse (*2*). Since many areas are experiencing critical shortages of landfill space, considerable effort, including incentives for waste recycling, has been made to reduce the volume of landfill wastes.

Among the many products made from PET plastic are the familiar 2-liter soft drink bottles. The recycling of most PET bottles is done by a physical process in which they are washed, shredded, melted, and remolded to give various new products. However, if higher-quality products are needed, the used PET may be depolymerized to give monomers that are then purified and repolymerized.

Du Pont Chemical depolymerizes post-consumer PET by an acid-catalyzed transesterification reaction with methanol, a reaction that is possible only under conditions of high temperature and pressure. There are sufficient traces of acid in the PET to catalyze the reaction as shown in eq 1.



(1)

While PET can be depolymerized industrially via transesterification to give ethylene glycol and dimethylterephthalate, we found that this was not possible under conditions available in the undergraduate organic lab. Refluxing PET in methanol in the presence of a catalytic amount of sulfuric acid gave very little reaction even over extended periods.

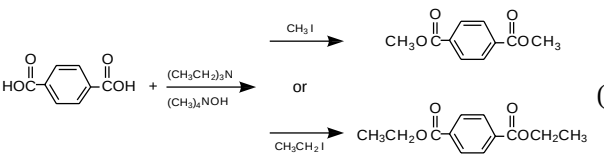
Although Williamson reports in his popular lab book (*3*) that PET "is remarkably resistant to hydrolysis" and "there will be no apparent reaction" when PET is refluxed with aqueous acid or base, we found that PET can be readily depolymerized via hydrolysis, as an alternative to transesterification, by refluxing it with either potassium *tert*-butoxide (*4*) or potassium hydroxide in pentanol. If one wishes to devote only a single lab period to this activity, it may be terminated at this point by characterizing the terephthalic acid obtained from the hydrolysis. However, terephthalic acid doesn't melt, but sublimes at temperatures above 300 °C. Still, it is possible to obtain an IR spectrum using a Nujol mull (*5*) or an NMR spectrum using DMSO-d_6/$CDCl_3$ (*6*).

However, since both esterification and S_N2 reactions are included in many undergraduate organic labs, it may be advantageous to use a second lab period to convert the terephthalic acid obtained into a diester (e.g., the dimethyl or diethyl ester) either via a Fischer esterification reaction or by the S_N2 reaction of a diammonium terephthalate salt with an alkyl halide. These diesters can be readily characterized by melting point, IR, and NMR.

Brief Summary of Procedure

Students are assigned articles on plastics and recycling (*1*, *2*, *7*) to be read before the first lab period. To save lab time, they are also instructed to bring their own PET sample already cut into small pieces. Since ester chemistry has already been covered in lecture, only a short review of ester hydrolysis is given in the first prelab along with a brief discussion of "anhydrous hydroxide" (*4*). In the first lab the PET is hydrolyzed by refluxing with either potassium hydroxide or potassium *tert*-butoxide/water (anhydrous hydroxide) in pentanol or the mixed isomers of commercially available amyl alcohol.

The second prelab includes a short review of ester syntheses including the Fischer esterification reaction and S_N2 reactions of carboxylate salts with alkyl halides. In the second lab period either the dimethyl or diethyl ester of terephthalic acid is readily prepared via the S_N2 reaction of a diammonium salt of terephthalic acid with methyl or ethyl iodide in a polar aprotic solvent such as acetonitrile (eq 2).



(2)

The needed diammonium salt is prepared from the reaction of terephthalic acid with either triethylamine (*8*) or tetramethylammonium hydroxide (*9*). Alternatively, the familiar Fischer esterification can be used to prepare these esters, but yields are significantly lower. Both diesters are readily characterized by melting point and ^{1}H or ^{13}C NMR.

Summary

The activities described here provide students an opportunity to observe one way in which PET plastic may be recycled as they successfully conduct common organic lab reactions: base-promoted ester hydrolysis and ester synthesis (either the Fischer esterification reaction or the S_N2 reaction of carboxylate salts). Our students have expressed satisfaction in converting discarded ketchup and soda bottles into "new" organic compounds and have indicated that the issue of recycling plastic products has become more meaningful to them.

Chemicals used in the experiments that some chemistry departments may not have include potassium *tert*-butoxide and tetramethylammonium hydroxide. However, alternate procedures are described that do not require their use.

Note

[W]An expanded version of the text and detailed experimental procedures for the instructor and for the students are available on *JCE Online* at *http://jchemed.chem.wisc.edu/Journal/issues/1999/Nov/abs1525.html.*

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PET Procedure:

In a 100 mL RBF placed 5.0 g of PET (0.052 mol), 35 mL of 1-pentanol, and 4.4 g of KOH (0.079 mol). The reaction was rapidly stirred and refluxed using a flask heater. After a short time a thick white suspension results. The white suspension may become too viscous then add more solvent to RBF. The reaction was reflux for 1.5 hr.

The reaction mixture was allowed to cool and 25 mL of distilled water was added to the RBF. Filter the solution to remove any un-reacted PET by suction filtration. Place solution into separatory funnel and remove the aqueous layer. Wash the alcohol layer with an additional 25 mL of distilled water. Combine all aqueous extracts. Add slowly while stirring diluted hydrochloric acid to acidify the aqueous extracts. Use suction filtration to collect the terephthalic acid. Use acetone to wash the crystals for faster drying.