

# Investigations into the Mechanism of Energy Transfer between Aromatic Microplastics and Pollutants during Photolysis

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## Overview

**Purpose**  
To determine if and how light energy is transferred between plastics containing aromatic polymers and absorbed pollutants during photolysis.

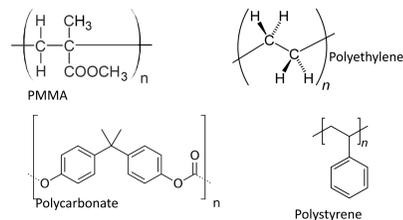
**Methods**  
Absorption and Fluorescence spectroscopy of triclosan absorbed to different plastics is studied.

**Results**  
Aromatic plastics reduce the rate of photolysis of triclosan relative to non-aromatic plastics because they can quench triclosan.

## Introduction

Plastics are a widely versatile and durable material resulting in their widespread use in various industries today. Discarded plastics do not remain in their original form but rather degrade in the environment into pieces too small to recycle. Microplastics are defined as plastic particles that are less than 5mm in diameter [1]. Microplastics present a unique challenge in that they cannot be recycled and can pass through the wastewater filtration system. Microplastic pollution is of concern to the environment due to the low solubility and rapid bioaccumulation in aquatic species [2]. Toxic compounds may concentrate on the surface of plastic particles and then transfer these toxins to aquatic animals by ingestion of these microplastics, resulting in the absorbed toxins to be spread throughout the food chain to humans eventually [3].

Past research has demonstrated that triclosan will undergo photolysis at a faster rate on the surface of plastics that do not absorb sunlight such as polyethylene and polymethylmethacrylate than it does in water with no plastic present [4]. We have also observed that the decomposition of triclosan is almost twenty times slower when absorbed onto plastics that are capable of absorbing sunlight such as PS and PC [4]. We have hypothesized that the aromatic polymer plastics will quench the triclosan after it absorbs light thus slowing the rate of photolytic decomposition. We are interested in investigating if and how light energy is transferred between triclosan and aromatic plastics. The goal was to carry out absorption and emission spectroscopy studies for these varying types of plastic to find evidence of energy transfer between triclosan and PE or PC.



**Figure 1:** Structures of polymers that make up the plastics Polymethylmethacrylate (PMMA), Polyethylene (PE), polycarbonate (PC), polystyrene (PS) that are used in this study.

## Materials

The plastic particles for PMMA and PS were acquired from Cospheric in Santa Barbara, CA. PE plastic particles were obtained from Sigma Aldrich. The polycarbonate particles were made in our lab by pipetting 5 uL of saturated PC solution in THF into cold (0°C) nanopure water. The triclosan used for these studies was obtained from Sigma Aldrich.

## Instrumentation

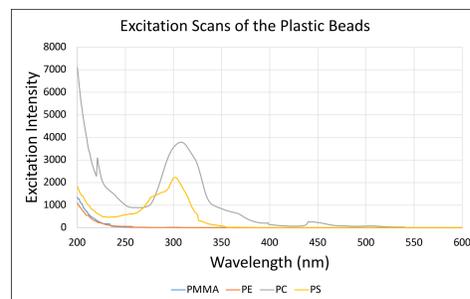
Absorption and Emission Spectra were obtained on the FP-8300 Series JASCO Fluorescence Spectrometer. Solutions were studied in a 0.25cm path length cuvette. The parameters of scans included 600V scan sensitivity, 1nm data interval, 200nm/min scan speed, no filter, and Xe light source.

## Sample Preparation

About 10 mg of PE, PS, PMMA, and PC were prepared in water for fluorescence analysis. Then, plastic beads were treated with 5uL of 22.0mg/mL TCS and diluted with 4995 uL of nanopure water and allowed to soak for 48 hours so that the triclosan would absorb on the beads. The solutions were then loaded in the cuvette and absorption and emission spectra of the solution were determined. Absorption and emission spectra of triclosan were acquired in methanol at concentrations of 0.01 mg/mL and 0.1 mg/mL.

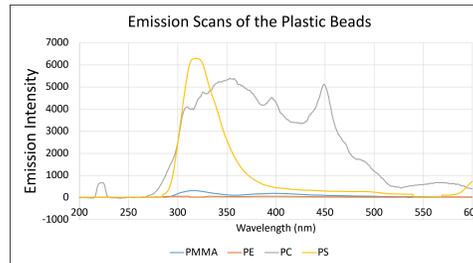
## Results and Discussion

We acquired absorption spectra of the PC, PS, PMMA, and PE beads in water to see if any of these plastics absorbed light in the 300 or 350 nm range (the wavelengths used for our photolysis studies). There absorption spectra are shown in Figure 2.



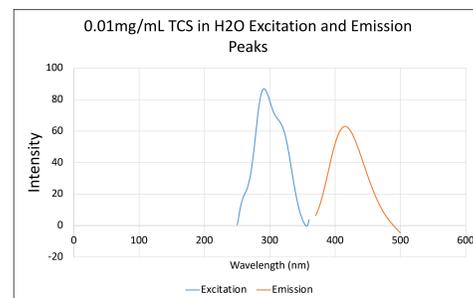
**Figure 2:** Absorption spectra of the four plastic beads in a solution of nanopure water.

The spectra demonstrate that only polycarbonate (PC) and polystyrene (PS) absorb the wavelength used for photolysis (300 nm) Polyethylene and PMMA showed no significant absorption at any wavelength compared to the PC and PS. These results suggest that PC and PS can absorb light energy used for photolysis. We then acquired emission spectra for the PC, PS, PMMA, and PE beads in water. Their spectra are shown in Figure 3.



**Figure 3:** Emission spectra of the four different plastic beads in nanopure water acquired at an excitation wavelength of 300 nm.

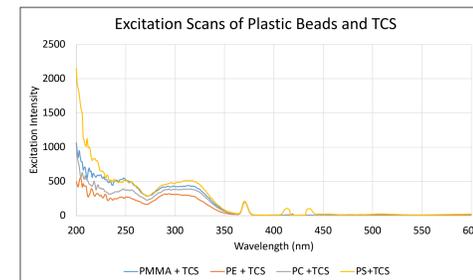
The Figure 3 emission spectra show that the PS and PC aromatic plastics will emit light over wide range of wavelengths; PS (300 to 400 nm) and PC (300 to 500 nm). PE and PMMA do not so any significant emission compared to the aromatic polymers.



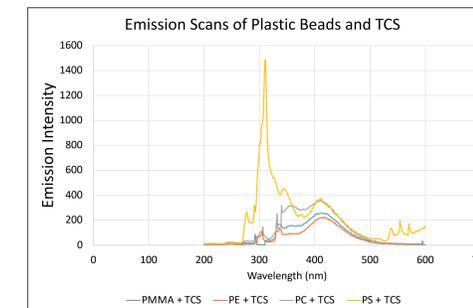
**Figure 4:** Absorption and emission spectra of a 0.01 mg/mL solution of triclosan in water. The blue line represents the absorption spectrum, and the orange line represents the emission spectrum (emission spectra not to scale).

The Figure 4 spectra show that triclosan will absorb at 280 nm and that this absorption may lead to emission at 415 nm. This suggests that energy transfer between triclosan and PC or PS may occur when photolysis is carried out at 300 nm.

We also acquired absorption spectra of PE, PMMA, PC, and PS coated in TCS and diluted in water. These spectra of this study is shown in Figure 5. The similarity of the spectra suggests that triclosan is absorbing the light, not the PC or PS.



**Figure 5:** Absorption spectra of the four plastics beads coated in triclosan in a water solution.



**Figure 6:** Plot of excitation wavelength versus total emission intensity for the 4 different plastic beads coated in triclosan in a water solution.

Emission spectra of PE, PMMA, PC, and PS coated in TCS and diluted in water are shown in Figure 6. The PS and PC beads with triclosan show more emission at 405 nm than do the PE and PMMA beads, suggesting that these beads are acquiring energy from triclosan than the PE and PC beads.

The Figure 6 emission spectra show that PC and PS beads will emit more light than PE and PMMA beads when all four are coated with triclosan. This result strongly suggests that the triclosan molecules absorbed onto PE and PMMA will have more energy to support photolysis-induced fragmentation than the triclosan absorbed to PC and PS which appears to be more prone to lose energy via the emission of a photon.

## Conclusion

The results of our studies suggest that the primary reason why the photolysis of triclosan absorbed to plastics made from aromatic polymers proceeds at a rate up to 20 or 30 times slower than when absorbed to plastics composed of aliphatic polymers is because aromatic polymers quench the triclosan prior to fragmentation. Triclosan absorbed to PS or PC will transfer light energy to the plastic and thus have less to induce fragmentation. Triclosan absorbed to PE or PMMA will not transfer light energy to the plastic, thus energy will build up in the absorbed layer during photolysis and increase the rate of degradation to 2,8-DCDD.

## References

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3. Andrad, Anthony L. "Microplastics in the Marine Environment." Marine Pollution Bulletin 62.8 (2011): 1596-1605. Web.
4. Martinez, X.; Renyer, K; Chiarelli, M.P. "Plastic catalyzed photolysis of emerging contaminants in aqueous environments" Environ. Sci. Technol.