Photodegradation of Self-Immolating Polymers as a Potential Solution to Optical Scattering

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ABSTRACT

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Starshades and other sensitive optical devices require dust mitigation techniques to protect their surfaces. We investigate coating these surfaces with a photodegradable polymer film that will vaporize when exposed to ultraviolet light. A series of experiments was conducted in which we studied this phenomenon in vacuum after applying a photo-depolymerizing coating. Poly (2-methyl, 1-pentene) sulfone is shown to degrade in vacuum when exposed to 172 nm UV light. Future studies will examine whether the coating can be used to remove dust contaminants from sensitive optical devices upon photoirradiation.

Keywords: [Thin films, self-immolating polymers, space instrumentation, photodegradation]

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Chapter 1

Introduction

Poly(olefin sulfone) is a material that has been shown to depolymerize into its constituent monomers when exposed to ultraviolet light and heat. We investigate this polymer to further characterize the conditions under which the degradation occurs. The purpose of this investigation is to determine the potential of the polymer as a protective coating for space instrumentation used to detect exoplanets.

1.1 Motivation

Although exoplanets have been indirectly detected for many years [1], to image one is a challenge akin to finding a strand of hair on Everest. This is because they are obscured by the light of their host stars. Small, rocky planets in the habitable zones of other solar systems could be directly imaged for the first time using a developing technology called a starshade [1]. Starshades are external occulters used in conjunction with a telescope to facilitate imaging exoplanets. The starshade is useful because it suppresses the light of the host star, which is billions of times brighter than the nearby exoplanet. This works much like if an observer were to block the light of the sun with their thumb in order to better see an airplane flying by. In fact, a starshade can provide an exoplanet-seeking telescope with 10^{10} contrast [2]. This high-contrast imaging provided by a starshade would open the possibility of detecting life-sustaining conditions on other planets. The National Academies of Sciences, Engineering and Medicine (NASEM) decadal survey announced that starshades will be a priority in future missions, but they are still in need of technological development. It is stated that "a starshade with its highly desirable properties of very small inner working angle and overall larger area of high contrast. . . is rated as a medium risk with more development needed. [3]"

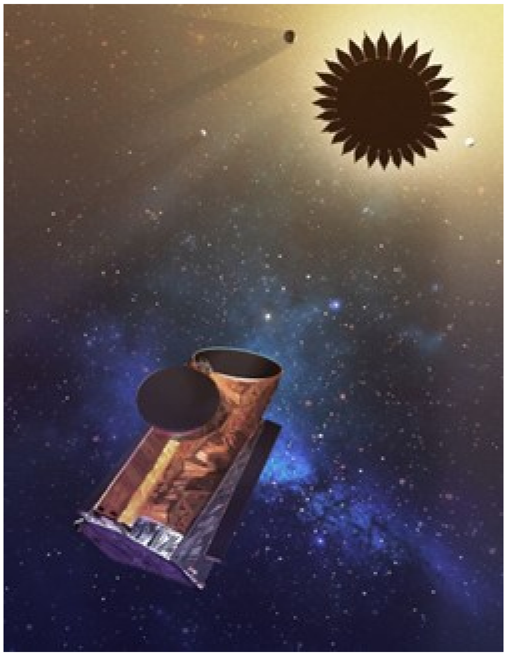

Figure 1.1 An artist's rendition of a starshade. A starshade acts as an external occultor for a telescope. [4]

The risk in using starshades is that the petal edges and planar surfaces need to be very precise to provide sufficient contrast for imaging exoplanets. Along the starshade edge, as little as four to seven square millimeters of contaminants for each five- to ten-square-meter segment will cause enough scattering to make exoplanets ten parsecs away unobservable [5]. Furthermore, the starshade petals will not necessarily be co-planar. Thus, solar glint off particulates on the surfaces would cause additional scattering. Therefore, dust mitigation techniques must be implemented on both the edges and planar surfaces of the starshade to minimize the risk of compromising the images collected by the telescope.

Although efforts are made to maintain a clean environment, it is estimated that the cleanrooms in which the starshade is assembled, manufactured, and stored contain between 10,000 and 100,000 particles per cubic foot [5]. A similar estimation of potential contamination is expected at launch.

We investigate a dust mitigation method that involves covering the starshade in a protective coating before these particulates could accumulate during manufacturing and storage. This coating will self-immolate once the starshade is deployed outside of the Earth's atmosphere, leaving a clean, precise petal.

Contemporary dust mitigation techniques, such as First Contact® Polymer, may be used [6]. However, they leave a window of time where dust can accumulate. A First Contact® Polymer coating must be peeled off by hand before launch, leaving the surface uncovered throughout the transportation process. The advantage of a self-immolating coating is that there would be no period of time between production and deployment that the starshade would be unprotected.

The intent of our experiment was to offer a potential solution to optical scattering from starshades by characterizing a photodegradable polymer film that will evaporate when exposed to ultraviolet light outside of Earth's atmosphere. However, this technique could be useful for a variety of applications, including telescopes, other kinds of sensitive optical equipment, and surfaces that need to be dust-free in space.

1.2 Background

To identify a polymer film that could protect a surface until it was outside of Earth's atmosphere, we investigated self-immolating polymers. Specifically, if a polymer is sensitive to UV-C light (100-280 nm), which is readily available in space, then the polymer film would not dissociate until the object being protected is already outside of Earth's atmosphere. According to extraterrestrial solar irradiance spectrum, we can expect up to 0.293 W m^{-2} nm^{-1} at these wavelengths [7].

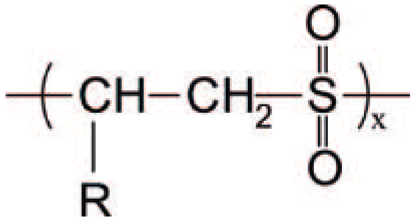

Figure 1.2 Structure of poly(olefin) sulfone. [8].

Certain photopolymers has been previously shown to depolymerize when exposed to UV-C light. The specific photopolymer that we investigated is poly(olefin sulfone). Poly(olefin sulfone) is a 1:1 alternating copolymer of olefin monomers and sulfur dioxide, as shown in Fig. 1.2. Previous characterization has indicated that “they possess sulfonyl groups (-SO_2-) in the main chain and are easily synthesized by radical polymerization of an olefin monomer in a liquefied sulfur dioxide” [8]. The sulfonyl group is electron-withdrawing, attracting the electrons from the adjacent carbon atoms. This leaves an acidic proton that can be easily abstracted by a base. When this happens, a chain depolymerization reaction then occurs that reverts the poly(olefin sulfone) back into its subunits of sulfur dioxide and olefin monomers.

Experiments have shown that poly(olefin sulfone) degrades when mixed with a photobase generator (PBG) upon irradiation with UV-C light and subsequent heating [9]. The PBG is physically altered when subject to 254 nm light so that it acts as a base for the depolymerization chain reaction [10]. It was found that using an [(o-nitro benzyl)oxy]carbonyl moiety as the PBG was the most effective for depolymerization [11].

Sasaki, et. al. investigated the photoinduced depolymerization of poly(olefin sulfone) mixed with a photobase generator, comparing various olefin monomers [9]. The results of this comparison are shown in Fig. 1.3. After irradiation, poly(2-methyl 1-pentene sulfone) (PMPS) had the lowest residual ratio of all the monomers that were tested. Residual ratio is a critical consideration in our experiment. According to Sasaki's publication, "the extent of PMPS irradiated at 600 mJ/cm^2 followed by heating at 150°C for 15 minutes was estimated by the change in absorption spectra to be 95%" [9]. For this reason, our experiment focuses on characterizing the depolymerization conditions of PMPS in particular.

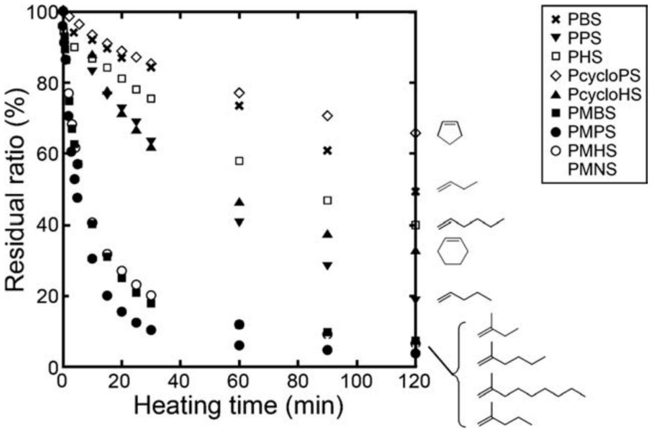

Figure 1.3 Previous experiment done on poly(olefin sulfone). PMPS had the lowest residual ratio after irradiation [9].

1.3 Determining the Conditions of Self-Immolation

Based on Sasaki's investigation of PMPS, we know that the polymer can degrade after irradiation and subsequent heating. We aim to further determine the conditions and characteristics of self-immolation of PMPS. Poly(olefin sulfone) has been studied for use in composite photoresists to allow for dry photolithography methods [12]. Our study focuses on use in optical equipment in space, such as starshades and telescopes. Therefore, we want to understand how the polymer degrades in space-environment conditions: in vacuum and exposed to UV-C light. Furthermore, we investigate whether the heating step that Sasaki used in his experiments is necessary to achieve degradation under these conditions. At the end of this thesis, I will address the following three questions:

1. Does PMPS degrade in vacuum without heat?
2. Is the photobase generator (PBG) necessary?
3. Does PMPS degrade under the conditions necessary for space applications?

Chapter 2

Methods

We characterized the degradation of poly(olefin sulfone) by making PMPS thin films. These films were placed in vacuum and exposed to 172 nm UV light to perform the experiment with a space-like environment. The change in film thickness was determined using ellipsometry.

2.1 Sample Preparation

The thin film samples were prepared by dissolving 1 gram of PMPS in 10 mL of tetrahydrofuran (THF). Some samples were mixed with approximately 10% by weight of a photobase generator. The polymer mixtures were stored in a freezer until ready to be spun onto a sample substrate. The polymer solutions were made into thin films by applying 60 drops to a silicon wafer, spreading the solution to the edges with the tip of the eyedropper, then spinning it at 8,000 rpm for 30 seconds. This process resulted in a film thickness of about 80-200 nm. A typical coated sample is pictured in Fig. 2.1.

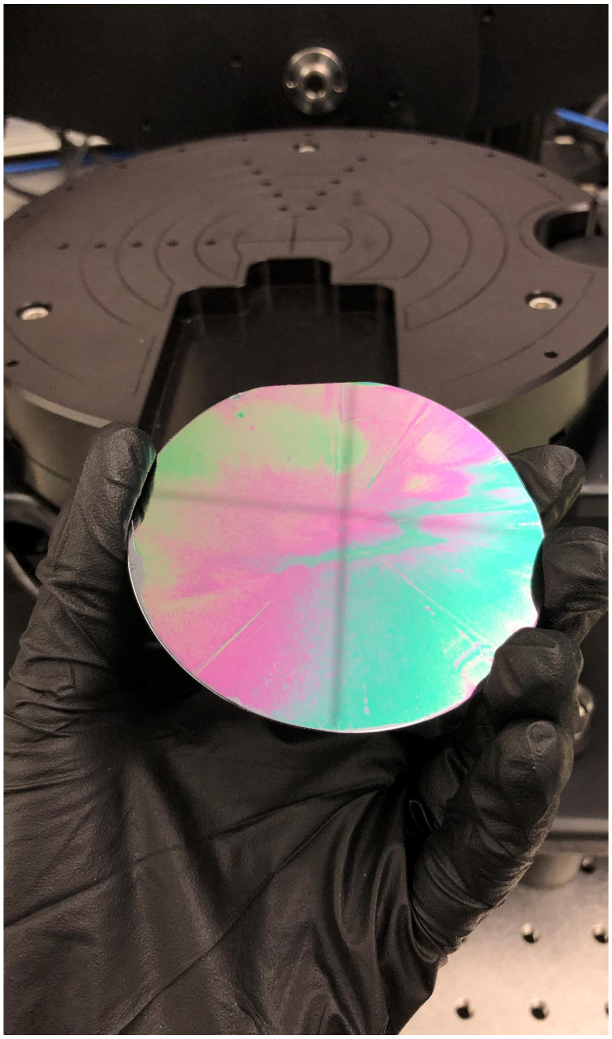

Figure 2.1 PMPS thin film sample. The PMPS thin film causes interference colors on this silicon substrate. As the PMPS degrades, the thickness decreases, and the color of the film changes.

2.2 Synthesis of PMPS

Our initial samples were made using PMPS that was provided to us by Dr. Takeo Sasaki. Later, our group synthesized our own PMPS. This polymerization was done according to the standard procedure outlined by the literature [9]: The volatile monomer, 2-methyl-1-pentene, was added to tert-butyl hydroxide, and then cooled to liquid nitrogen temperatures. Next, we added pentyl methane and pumped out the air with vacuum. Then, the volume was backfilled with nitrogen gas. This was repeated three times. Next, the polymer was dissolved in liquid SO_2 and put into an ethanol/dry ice bath, allowed to warm to -70°C, and then to room temperature. The polymer was maintained at this temperature for one hour. Subsequently, it was dissolved in acetone and poured into a beaker of methanol. Finally, the polymer solution was left in vacuum until the solvent evaporated, at which point it could be characterized by nuclear magnetic resonance (^{1}H NMR) spectroscopy. We used the ^{1}H NMR spectra to compare our polymer to Sasaki's and confirm that we successfully produced our own PMPS. Our results are shown in Fig. 2.2.

2.3 Experimental Setup

The goal of our experiment was to test the PMPS in a space-like environment, so we needed the samples to be placed in vacuum and exposed to ultraviolet light simultaneously. We built a vacuum system connected to a quartz tube. Quartz is transparent to UV light [14], so samples placed in the quartz tube could be in vacuum while irradiated by a UV light outside the tube. While in the tube, the samples are 2-4 cm away from the light source. For this experiment, we used a 172 nm xenon excimer lamp (Resonance Ltd, Barrie, ON).

2.4 Ellipsometry

The thickness of the samples was determined using ellipsometry. Ellipsometry data was acquired using a J.A. Woollam RC2 variable-angle, spectroscopic ellipsometer (J.A. Woollam Company, Lincoln, NE, USA). The analysis was performed with CompleteEASE® instrument analysis software. We used a general oscillator ellipsometry model to evaluate the thickness of the PMPS. The Cody-Lorentz dispersion equation [15] best fits the thin film sample. The rest of the layers' optical constants are from the CompleteEASE® database: NTVE-JAW2, INTR-JAW2, and Si-JAW2 [16].

2.5 Measurements

PMPS sample degradation was studied using the following procedure. First, the thin films were placed in the quartz tube under vacuum. The base pressure inside the vacuum system was typically on the order of 10^{-7} torr. The film was irradiated by the 172 nm lamp for about 20 minutes. Next, the sample was removed, and the thickness was measured using ellipsometry. Finally, we returned to exposing the sample, and the process was repeated until a degradation pattern was observed. Samples of each type, with and without photobase, were also subjects of control experiments: vacuum-only and heat-only. By testing each of these experimental groups, we were able to draw conclusions about the need for a photobase generator, the previously reported heating step, and the ability of PMPS to degrade in a space-like environment.

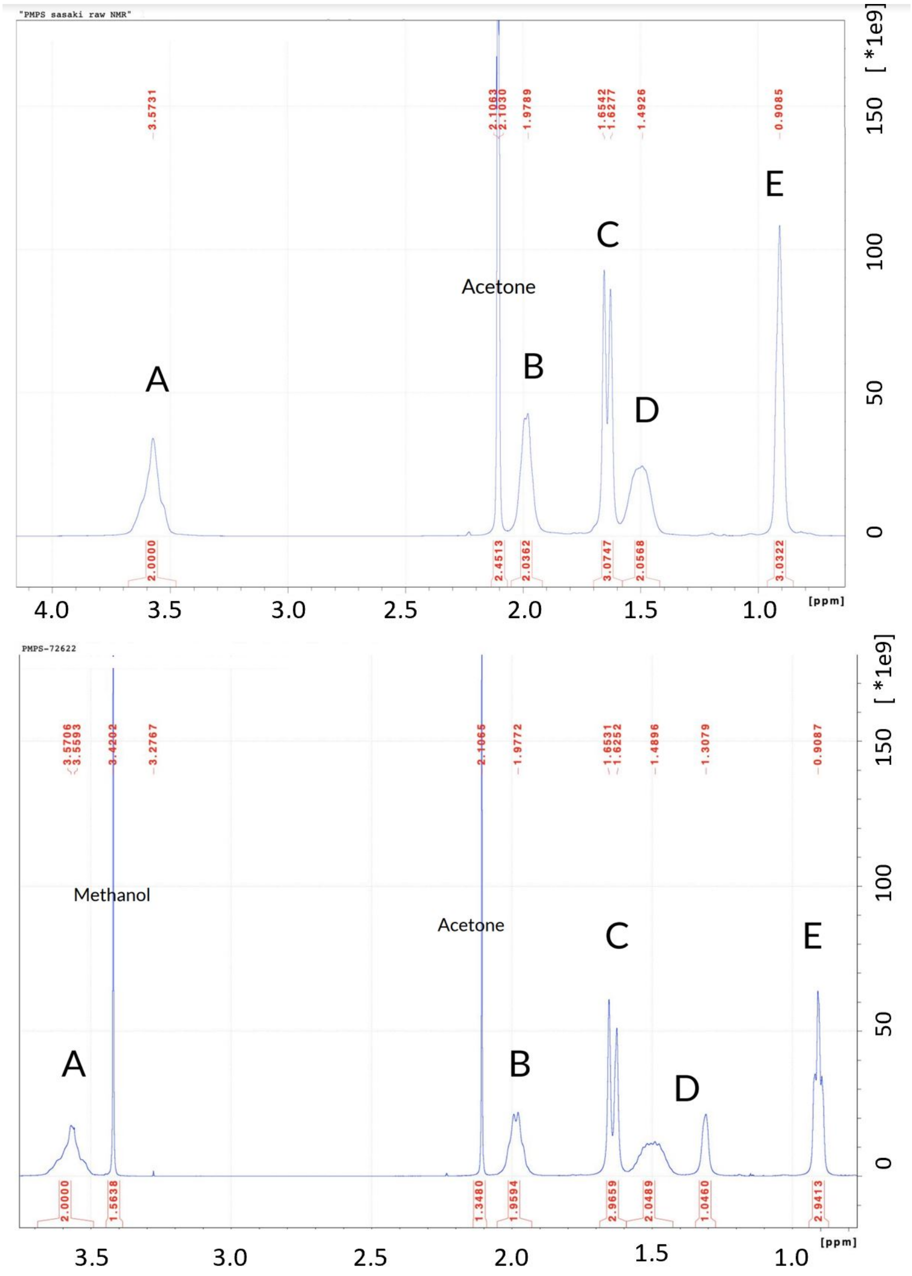

Figure 2.2 NMR Spectra. The ^{1}H NMR spectrum on the top shows the data from Sasaki's PMPS. The bottom spectrum shows our results [13]. Since the peaks (labeled A, B, C, D, and E) appear where we expected, the spectra indicate that our PMPS is comparable to Sasaki's.

Chapter 3

Results

Poly(olefin sulfone)'s ability to photodegrade has been previously demonstrated; however, there is a general lack of information about the extent to which the depolymerization proceeds in a vacuum. In this chapter, we present the results of our experiment, characterizing the effects of a space-like environment on PMPS.

3.1 Evidence of Degradation

Due to the partially transparent nature of the thin films, we can visually observe the results of exposing the samples to UV light in vacuum. When white light is incident on a thin film, certain colors are observed depending on the thickness of the film material due to thin film interference. As the samples degrade, the film gets thinner, and the interference colors change. Fig. 3.1 demonstrates how the samples change color as the thin films degrade and as the degradation products evaporate. This is the initial evidence that PMPS degrades in space-like conditions.

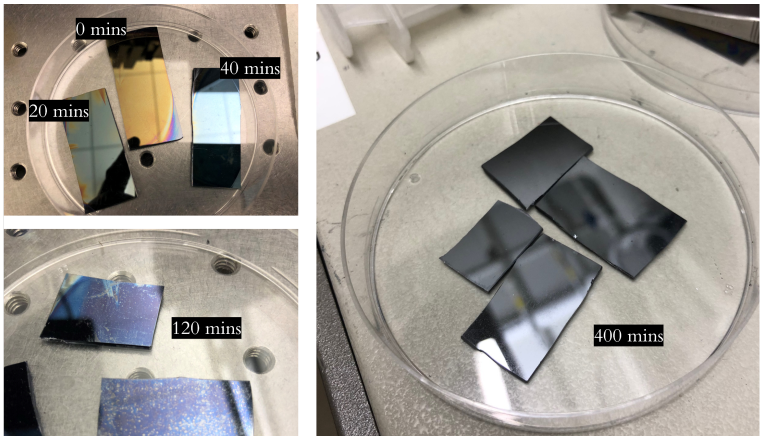

Figure 3.1 Visual evidence of thin film degradation. The pictures show the progression of the thin film degradation. The film exhibits thin film interference producing different colors associated with each film thickness. We can see the color changes with time. Eventually, we can only see the silver-colored silicon substrate.

3.1.1 PMPS with a Photobase Generator

First, we present the results of this experiment on the samples that include the photobase generator. These are the same types of samples that Dr. Sasaki used in his experiment [9]. They were kept in vacuum while exposed to 172 nm UV light. The thickness of the thin film samples was measured using ellipsometry, and the results are plotted in Fig. 3.2 against exposure time. In each iteration of this experiment, samples had an initial thickness of about 200 nm and reached near-zero thickness after about 520 minutes.

In order to confirm that the polymer is stable until exposed to the UV light, we completed a control experiment in which the same type of samples were placed in vacuum. The results are given in Fig. 3.3. We see that there is minimal degradation over a long period of time.

Another control experiment tested the effect of heat on the stability of the polymer. We exposed the same type of samples, PMPS with PBG, to 120 °C, but without UV light or vacuum. The results are shown in Fig. 3.4. We see that there is a small decrease in thickness.

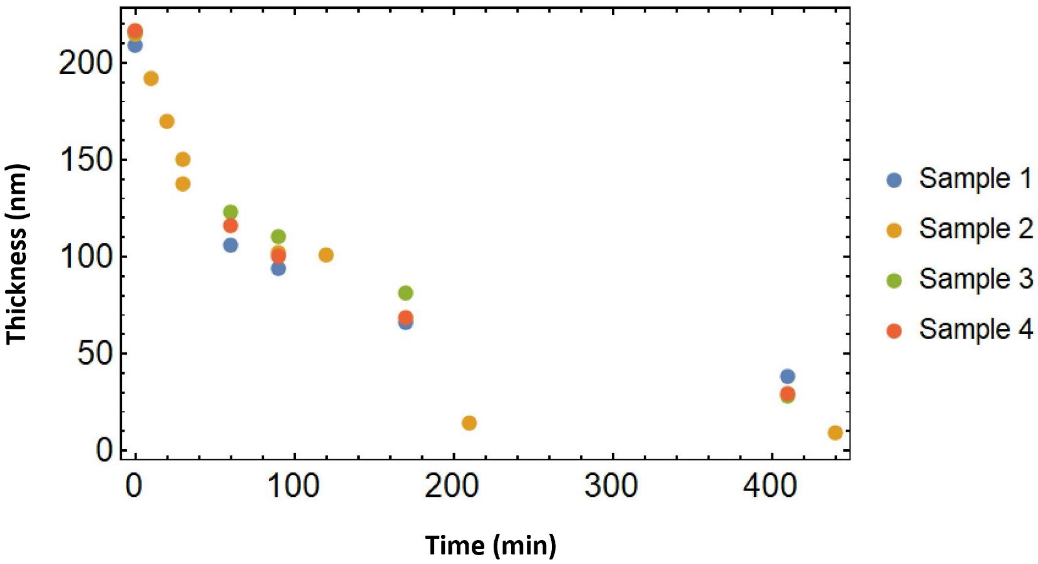

Figure 3.2 Thickness of the PMPS with PBG films over time. Samples 1-4 are individual thin film samples that experienced the same treatment. They were each exposed to 172 nm light while in vacuum. The samples start with a thickness of about 200 nm, then degrade to nearly 0 nm after approximately 520 minutes.

3.1.2 PMPS without a Photobase Generator

Next, we show the results of this experiment on the samples that do not include the photobase generator. These are different from the samples that Dr. Sasaki used in his experiment [9], since he included the PBG. Again, these samples were kept in vacuum while exposed to 172 nm UV light. The thickness of the thin film samples were measured using ellipsometry, and the results are plotted in Fig. 3.5. In each trial, samples had an initial thickness of about 80 nm and show a similar pattern of degradation to the samples with PBG.

Just as in Sec. 3.1.1, we conducted control experiments using vacuum and heat for PMPS samples without a PBG. In order to confirm that the polymer is stable until exposed to the UV light, control samples were placed in vacuum for an extended period of time. The results are given in Fig. 3.6. We see that there is negligible degradation over a long period of time. Another control experiment examined the effect of heat on the stability of the polymer. Fig. 3.7 shows that there is

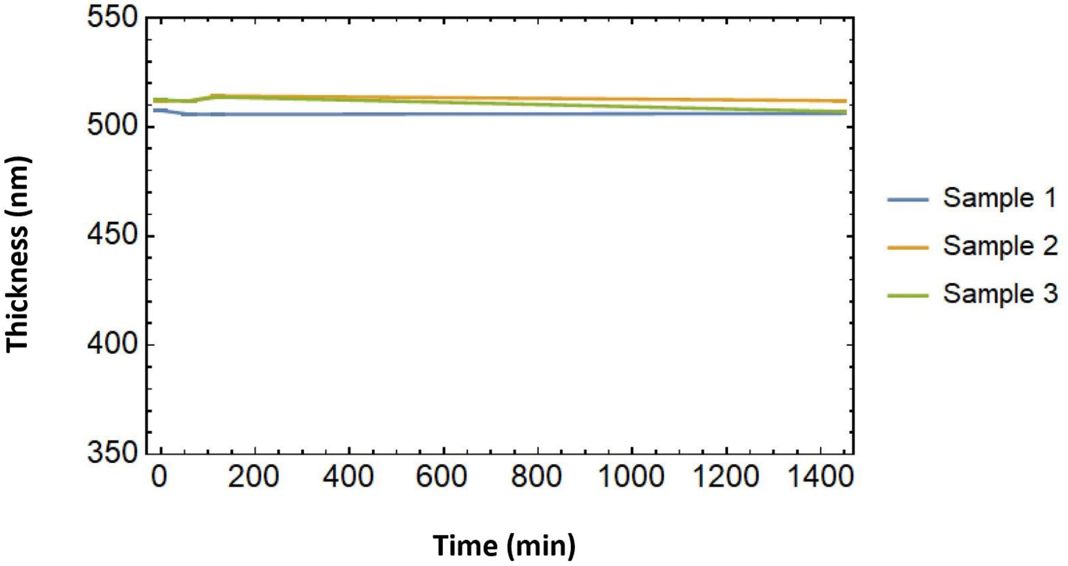

Figure 3.3 Thickness measurements from PMPS samples with PBG stored in vacuum. Samples 1-4 are individual thin film samples all that experienced the same treatment, but both were measured for reproducibility. They were not subject to either UV light or heat. We see that there is no degradation.

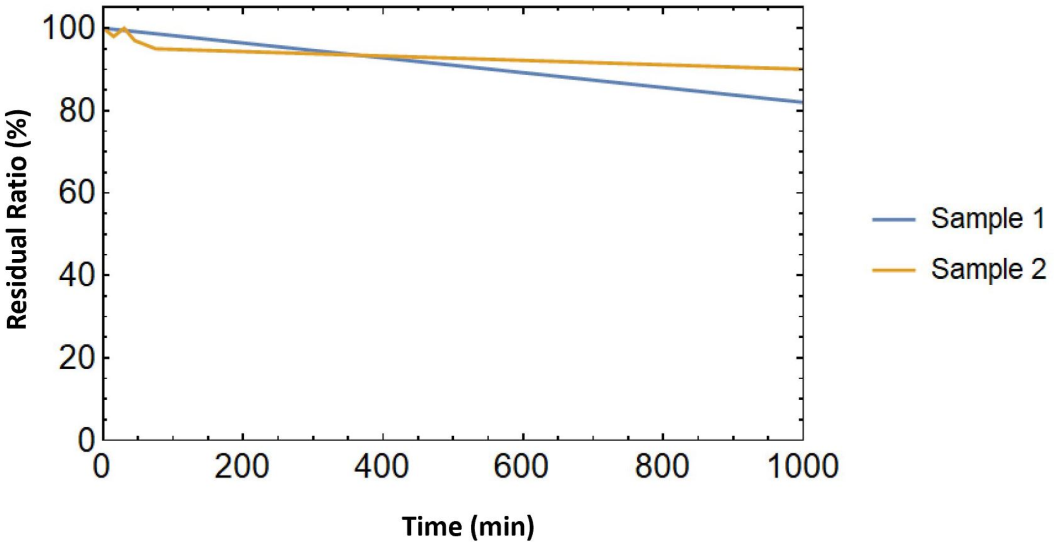

Figure 3.4 Thickness measurements from two PMPS samples with PBG were heated to 120°C in air. Samples 1 and 2 are individual thin film samples that experienced the same treatment, but both were measured for reproducibility. There is a small amount of degradation over 1000 minutes.

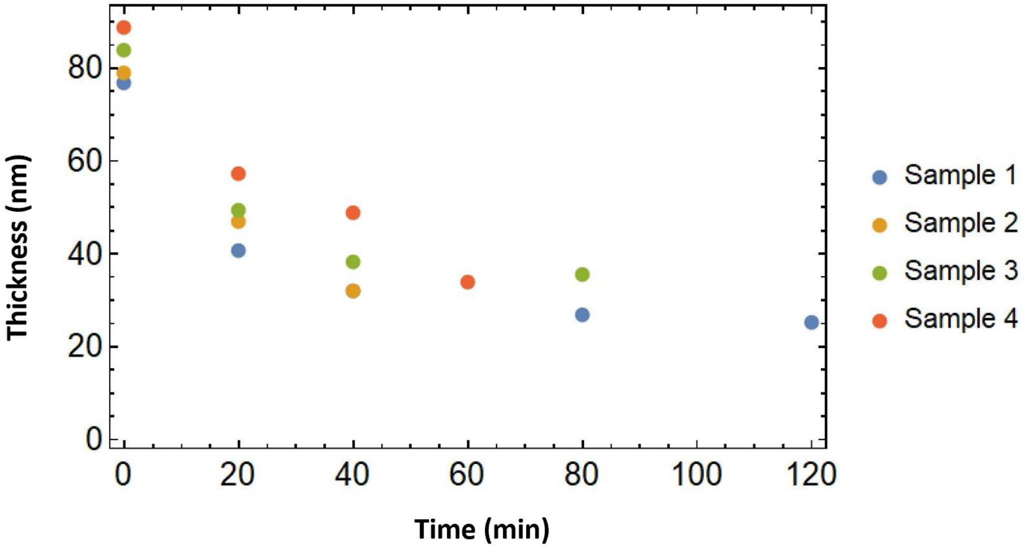

Figure 3.5 Thickness of the PMPS (without PBG) films over time subjected to UV light and stored in vacuum. Samples 1-4 are individual thin film samples that experienced the same treatment, but all were measured for reproducibility. The samples start with a thickness of about 80 nm, then degrade to less than 50% of its original thickness after just 120 minutes.

degradation at 120 °C, but the degradation is much slower than when exposed to UV light.

3.2 Conclusion

We return to the questions that this experiment was designed to investigate:

1. Does PMPS degrade in vacuum without heat?
2. Is the photobase generator (PBG) necessary?
3. Does PMPS degrade under the conditions necessary for space applications?

We can conclude that PMPS photodegrades in vacuum. However, the polymer will remain stable in a low-pressure environment until exposed to UV-C light. Once in UV light, the PMPS samples photodegrade significantly. Importantly, we have proven that the heating step that has been used in previous experiments is not necessary. PMPS can degrade in vacuum without heat when subjected

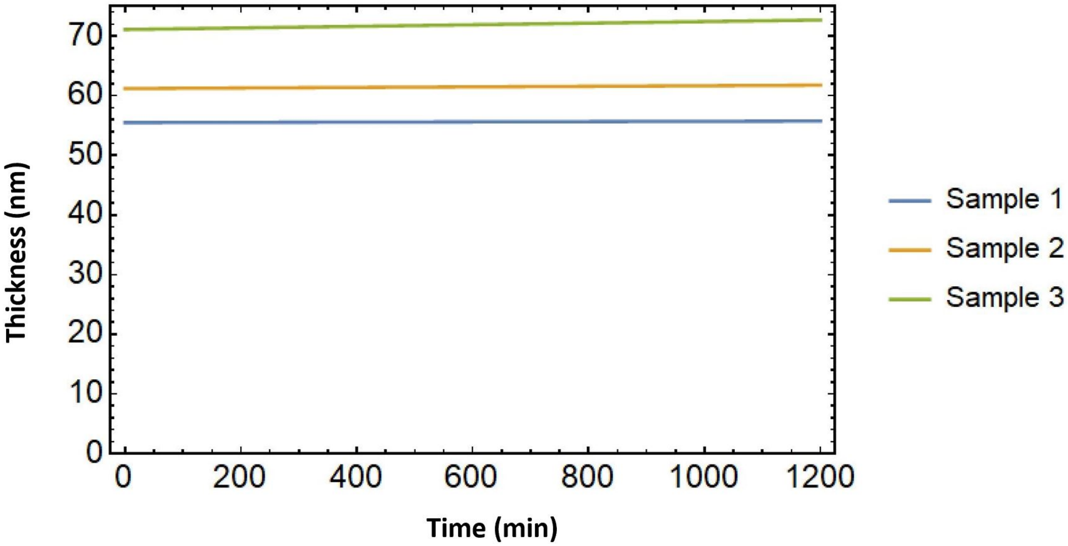

Figure 3.6 Thickness measurements for PMPS samples without PBG stored in vacuum. They were not subject to either UV light or heat. Samples 1-3 are individual thin film samples that experienced the same treatment, but all were measured for reproducibility. Each color represents a different sample. We see that there is no degradation.

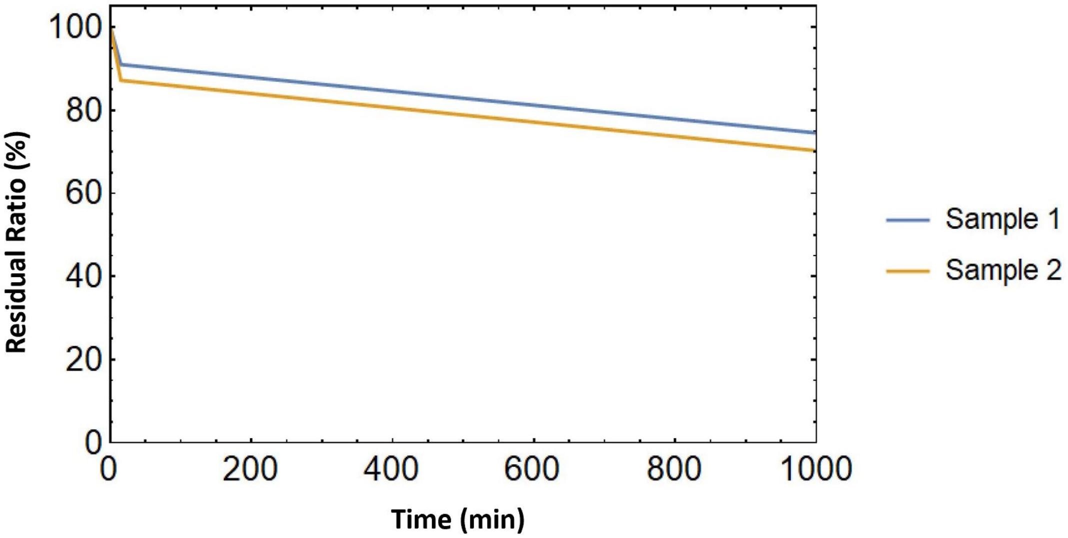

Figure 3.7 Thickness measurements from two PMPS samples without PBG that were heated to 120°C in air. Samples 1 and 2 are individual thin film samples that experienced the same treatment, but both were measured for reproducibility. We see that there is a small amount of degradation over 1000 minutes.

to UV light.

We have observed degradation under the same conditions whether the PMPS is mixed with PBG or not. From the data in Fig. 3.2 and Fig. 3.5, we can conclude that PBG may not be necessary under the timescales and conditions in which we are interested. However, this may not be the case for longer wavelengths than 172 nm. To fully understand the effect of the PBG, we will repeat this experiment with other wavelengths in the future. Although it appears that PMPS with PBG degrades at a faster rate than those without PBG, the PMPS without PBG film also had a smaller starting thickness. Therefore, degradation rate may be more dependent on starting thickness than on PBG content. We will need to investigate further to quantify this pattern.

In summary, this experiment demonstrated that poly(olefin sulfone) can photodegrade in vacuum without the need for a heating step. This alone is a notable accomplishment since there are many potential space applications of protective coatings which self-immolate in the light from the sun outside of earth's atmosphere. Our results indicate that PMPS does degrade under the conditions necessary for space applications.

3.3 Future Work

We can conclude from our experiment that PMPS, and possibly other self-immolating polymers, may have potential as protective coatings. In our future work, we plan to quantify the residual polymer left on the substrate after irradiation and the coating's ability to mitigate dust particulates. We also plan to determine whether other polymers and other PBG compositions potentially produce a lower residual ratio in vacuum. Characterizing PMPS degradation was the first step in showing that these coatings could be used to protect space instrumentation such as starshades.

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