# Standoff and Point Detection of Thin Polymer Layers Using Microcantilever Photothermal Spectroscopy

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## Abstract

Standoff detection based on optical spectroscopy is an attractive method for identifying materials at a distance with very high molecular selectivity. Standoff spectroscopy can be exploited in demanding practical applications such as sorting plastics for recycling. Here, we demonstrate selective and sensitive standoff detection of polymer films using bi-material cantilever-based photothermal spectroscopy. We demonstrate that the selectivity of the technique is sufficient to discriminate various polymers. We also demonstrate in-situ, point detection of thin layers of polymers deposited on bi-material cantilevers using photothermal spectroscopy. Comparison of the standoff spectra with those obtained by point detection, FTIR, and FTIR-ATR show relative broadening of peaks. Exposure of polymers to UV radiation (365 nm) reveal that the spectral peaks do not change with exposure time, but results in peak broadening with an overall increase in the background cantilever response. The sensitivity of the technique can be further improved by optimizing the thermal sensitivity of the bi-material cantilever and by increasing the number of photons impinging on the cantilever.

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**Key words**: Standoff detection, plastics sorting, microcantilever sensors, photothermal spectroscopy, bi-material cantilevers, infrared spectroscopy

## Introduction

In recent years, an increased awareness of the adverse environmental and human health effects of plastics has been driving the development of technologies that can have an immediate application in plastic recycling.[1-5] Recycling various plastics requires sorting them according to their molecular compositions prior to valorization.[6] For this reason, developing techniques that can provide molecular fingerprint of polymers with high sensitivity continues to be an essential component of strategies formulated for plastic recycling.[7] Arguably, the ideal method to identify plastics for sorting is employing standoff detection methods. Remote sensing, or standoff detection, is defined as detection carried out at a distance such that equipment (as well as operators) remains at a distance away from the target sample. In general, standoff detection involves collecting and characterizing spectral signatures from the target for molecular identification that can be carried out either passively (exploiting ambient light) or actively (exploiting light source of the device). Active standoff detection using spectroscopic techniques is ideally suited for mechanical sorting of plastics. Techniques such as fluorescence labeling,[8, 9] laser-induced breakdown spectroscopy (LIBS),[10-12] infrared (IR) spectroscopy,[13-18] and Raman spectroscopy[19, 20] are currently being explored for applications in sorting plastics. Currently, the primarily used sorting method of plastics relies on near IR spectroscopy. However, near IR spectra have many overtones that can impair the selectivity in polymer identification. Mid IR on the other hand, is free from overtones and is regarded as the "molecular fingerprint regime". Thus, mid-IR spectroscopic identification from a distance finds an immediate application for sorting plastic

objects on a moving conveyor belt in an industrial setting. Although highly desirable, standoff detection with high sensitivity and selectivity is a challenging task due to several operational factors. The drawbacks of traditional standoff spectroscopic techniques include slow spectral collection times, complex and bulky nature of the equipment, and poor sensitivity. For example, collecting spectroscopic signals in a reasonable allotment of time can be challenging due to the reduced power levels of scattered light reaching the optical detector for analysis. In addition, mechanical, electrical, and optical interferences from the surrounding environment in the sorting centers need to be addressed for practical implementation.

Conventional spectroscopy is based on Beer-Lambert principle which detect transmitted (scattered) photons using photodetectors.[21] Photodetectors commonly used for IR detection require cooling to suppress the dark current originating from background noise. Often, intense stray light can saturate such conventional photodetectors making sensitive detection a challenge. The photothermal spectroscopy technique, on the other hand, is a technique which detects the photons using the heat generated from photon absorption and excitation of vibrational states of target species.[22] Therefore, photothermal spectroscopy is a direct technique that can provide complementary information (calorimetric) unlike conventional photon count technique (photons that are not absorbed by the sample). The advantage of photothermal spectroscopic technique is that it can be used for standoff detection by collecting and detecting the photons scattered by the sample with a thermal sensor. A bi-material cantilever can serve as a highly sensitive thermal detector for sensing the heat generated by IR photon absorption.[23] On IR absorption, a bi-material cantilever undergoes bending because of the differential thermal expansion of bi-material elements. Typical bi-material microcantilevers have a thermal sensitivity in the order of pico

Joules and can detect small variations in the temperature with a sensitivity of 5-10 mK at room temperature.[24] Since thermal change is additive, it does not have any intrinsic selectivity. However, selectivity can be introduced by illuminating the cantilever sequentially with different wavelengths. This we explore and demonstrate to understand the IR absorption effects. An immediate advantage of standoff photothermal spectroscopy over conventional IR spectroscopy is that unlike conventional detectors, the bi-material cantilever-based photothermal spectroscopy offers high sensitivity and selectivity in the mid IR region without cooling.

We have used a tunable quantum cascade laser (QCL) as the light source for our experiments. For stand-off detection, the surface of a polymer sample is illuminated with mechanically chopped IR radiation from the QCL. The scattered IR photons are directly allowed to fall on a bi-material microcantilever without using any focusing optics. The cantilever surface is exposed to on/off cycles of the radiation effected by the optical chopper. Photothermal oscillations of the cantilever at the chopping frequency originate from alternate heating and cooling as a function of the chopping rate/time. The cantilever simultaneously bends from bi-material heating effect. A plot of the cantilever's oscillatory bending amplitude as a function of the IR wavelength resembles the IR spectrum of the target surface/analyte. As comparison, we also collected photothermal spectra of polymers using point detection. Point detection is carried out by using a bi-material cantilever deposited with a thin layer of polymer (in the order of 200 nm). The polymer-coated cantilever is exposed sequentially to pulsed IR radiation from a tunable QCL. A plot of the cantilever bending as a function of illuminating wavenumber resembles the IR absorption spectrum of the adsorbate. We also compare our photothermal results with Fourier Transform Infrared (FTIR) in transmittance mode and attenuated total reflection (ATR) mode.

In theory, the thermal sensitivity of the bi-material cantilever governs the sensitivity of detection of an analyte employing cantilever-based photothermal spectroscopy. Barnes et al, demonstrated sensitive photothermal spectroscopy using a bi-material cantilever with pico Joule sensitivity.[23] A thermal sensitivity of 5 femto Joules was demonstrated by Majumdar et al. using a silicon nitride cantilever.[24] The typical deflection, $z$, of a bi-material cantilever as a function of absorbed power, $P$, can be expressed as:

$$z = -\frac{3}{4}(\alpha_1 - \alpha_2)\frac{t_1 + t_2}{t_2^2 K}\frac{l^3}{(\lambda_1 t_1 + \lambda_2 t_2)w}P \quad . \qquad (1)$$

where, $l$ and $w$ are the length and width of the cantilever, $\alpha_1$ and $\alpha_2$ are the coefficients of the thermal expansion for the two layers, $t_1$ and $t_2$ are the layer thicknesses, $\lambda_1$ and $\lambda_2$ are the thermal conductivities, $w$ is the width of the cantilever (subscripts 1 and 2 refer to metal film and cantilever material, respectively). The thermal sensitivity parameter $K$ is expressed as:

$$K = 4 + 6\left(\frac{t_1}{t_2}\right) + 4\left(\frac{t_1}{t_2}\right)^2 + \frac{E_1}{E_2}\left(\frac{t_1}{t_2}\right)^3 + \frac{E_2}{E_1}\left(\frac{t_2}{t_1}\right) . \qquad (2)$$

In the standoff detection mode, the incident IR beam scattered by the target surface is detected with an optimized bi-material microcantilever.[25, 26] The microcantilever, therefore, serves as a sensitive, broad band, uncooled IR detector for the photons scattered by the target sample. The cantilever bending varies sensitively as a function of the IR absorption characteristics of the target surface when the wavelength of the IR source is changed. A sequential plot of the cantilever bending as a function of the wavelengths the target is exposed to transcribes the IR absorption spectrum of the target surface/analyte. To reduce the effects of noise and to obtain an optimized K for the geometry of the bi-material structures employed in our experiments, the incident IR beam

was chopped at 25-50 Hz. An optimized chopping frequency was determined for each analyte to record maximum cantilever deflections as detected with a lock-in amplifier. Standoff photothermal spectroscopy can also be accomplished using resonance mode.[27-29] However, in these experiments we have used bending approach based on bimaterial cantilevers.

For the comparison of point sensing (local sensing) with standoff detection, a thin polymer film was deposited on a bi-material cantilever (details added below in Materials and Methods section) and exposed to different wavelengths of IR radiation. The polymer film was deposited on the silicon side of the bi-material cantilever to eliminate the reflectivity issues of the optical beam deflection measurement system. A similar sequential plot of the cantilever bending as a function of wavelength shows the IR absorption spectrum of the adsorbed polymer. Such a detection by direct heating of the bi-material is referred to as photothermal cantilever deflection spectroscopy (PCDS) in literature.[30, 31] Unlike standoff, in PCDS, the sample is in direct contact with the bi-material cantilever and here we show a comparative study of the results obtained with stand-off deflection measurements.

**Materials and Methods:**

Polydimethylsiloxane (PDMS, Sigma-Aldrich, St. Louis), polymethyl methacrylate (PMMA, KAYAKU, Westborough), polyvinyl alcohol (PVA, Sigma-Aldrich, St. Louis) and SU-8 photoresist (KAYAKU, Westborough) were used in our experiments. For standoff detection, all of the polymer thin films were prepared by spin coating method. Around 5 µL of polymer was placed on a glass slide (clean room level) and spun at 5000 rpm for 10s. From the amount of material and the surface area of the sample, a thickness of around 200 nm was estimated.

We have used commercially available silicon cantilever beams in these experiments (Nanoworld, Switzerland). The cantilevers have dimensions of 500-µm in length 100-µm in width, and 1 µm in thickness. Using an e-beam evaporator, thoroughly cleaned cantilevers were deposited with a thin film of Au with a 5 nm thick Cr film serving as the adhesion layer. The choice of Au as a bi-metallic layer rests on its high thermal diffusivity and chemical inertness allowing us to obtain optimal spectral response data. From multiple experiments, it was found that a film thickness of 300 nm provided the highest thermal sensitivity for our application. However, for purpose of comparative study we used 30 nm of gold coating in our experiments as reported here.

For the deposition of a thin layer of polymer on the silicon cantilever, the cantilever-chip was taped to a glass slide using double sided tape. The glass slide was placed in the spin coater (KW-4A SETCAS LLC). 1 µL of polymer was drop casted on the base of the cantilever using a precision micropipette (Eppendorf Thermofisher). The optimized spin coater rate was set as be 2000 rpm for 15 seconds to ensure a uniform coating of the polymer on the cantilever. After the coating, the polymer coated cantilever was placed in the furnace (Thermoscientific) at 30°C for 30 minutes to ensure a firm and uniform layer of polymer deposition on the cantilever.

A tunable QCL with a wavelength range from 7.0 µm to 8.2 µm (Daylight Solutions, CA) was used to capture the data. The average power level of the QCL was 1mW at the maximum operating current. This mid-IR region is free from overtones. The experimental arrangement is shown in Figure 1. The laser beam from the QCL was chopped at 20-50Hz using a mechanical chopper (350CD, Scitec Instruments). The target polymer sample placed at 10-15 cm away is illuminated with the mid IR photons from the QCL. The scattered IR photons from the surface was allowed to

fall on a bi-material cantilever. Because of the small distance, no IR focusing element was used in this arrangement. The deflection of the bi-material silicon cantilever was measured using a laser diode reflected off the apex of the cantilever into a position sensitive detector (PSD). The PSD signal was read using a custom-made electronic box. We have used a lock-in amplifier (SRS 865A) to detect the cantilever deflection responses.

We also carried out photothermal spectroscopy of polymer films deposited on bi-material cantilevers using spin coating. An average film thickness of 200 nm was estimated from the resonance frequency change of the cantilevers employed. In these experiments, the cantilever with polymer film was placed directly on the IR beam from the QCL. We have carried out FTIR spectrometer (VERTEX 70, Bruker) and FTIR-ATR accessory (ZnSe 025-18XX, PIKE Technologies) experiments on the same samples for comparison. The effect of UV exposure on the polymers were also carried out by illuminating the samples with UV radiation from a Black-Ray UV bench lamp (UVP, Upland).

**Results and Discussions**

Figure 3 shows the standoff photothermal spectra of PDMS, PMMA, PVA and SU-8 taken with our setup for a standoff distance of 10 cm. The spectra in these figures are the normalized amplitude variations of the cantilever as a function of IR wavelength used for illuminating the sample surface. The extent of bending is proportional to the IR radiation scattered off the polymers on the sample. The spectra show absorption peaks characteristic to respective polymers. All peaks observed as a function of cantilever bending match very well with the published IR absorption spectra of the respective polymer. The observed photothermal bands at 1140 $cm^{-1}$ -1240 $cm^{-1}$

exhibit the characteristics of C-O-C stretching vibration,[32] and the bands at 1260 $cm^{-1}$ –1259 $cm^{-1}$ is $CH_3$ deformation[33] in Si-$CH_3$. The main peaks of PVA were observed at 1425 $cm^{-1}$ -1324 $cm^{-1}$. These peaks are assigned to C–H bending vibration of $CH_2$, C–H deformation vibration.[34] Finally, the C–O–C stretching of epoxy rings[35] in the SU-8 spectrum correspond to the peak band observed at 1245 $cm^{-1}$.

The relative intensities of the peaks vary slightly for the photothermal spectra as compared to conventional IR spectra. In addition, some peaks that are not very prominent in conventional IR spectra appear to have a higher intensity in the photothermal spectra. This probably stems from the complementary thermal change effected by the coupling of the excited vibrational modes of the analytes and their consequent non-radiative decay with the phonon-states of the microcantilever. The coupling results in generation of heat reflected as cantilever deflection due to bi-material effect. The cumulative effect of the residual time in the excited states and subsequent non-radiative transition time dictate the thermal response time constant of the cantilevers employed and their dynamic response. This is evident from the responses as a function of the chopping frequencies (Figure 2). At high enough chopping frequencies, the apparent change in heating from the non-radiative decay is low effecting a smaller change in cantilever deflection. Chopping frequencies in the order of ~25-50Hz provide us with good sensitive ($\sim 10^2$ $ng/mm^2$) deflection data that we report here. The observed intensities of the cantilever deflections are directly proportional to the absorption characteristics of the polymer as evident from the curves depicting different slopes for different polymers. It is also a function of the incident IR power, the absorption vibrational mode excited in the adsorbate, and the thermal sensitivity factors of the cantilever as expressed in equation 2 above. From the figures presented, it is obvious that the standoff spectral peaks are broader than the ones obtained with FTIR and FTIR-ATR. This

observed broadening has its origin in the vibrational modes and their respective decay time-constants that the bi-material cantilevers are susceptible to. The cantilevers used in our experiments were longer in length with low resonance frequency. Effectively the decay time constants at low resonance frequency and low Q are expected to be small, i.e., the cantilevers are expected to radiate out the generated heat quickly resulting in less deflection signal. Consequently, for high enough chopping frequencies, the effective thermal change becomes negligible and so does the response change (Figure 2).

Figure 4 depicts the comparison of the standoff spectra with spectra obtained with PMMA, PDMS film deposited on the cantilever. Comparison of the standoff spectrum with the spectrum obtained using polymer film deposited on the cantilever (PCDS or point sensing) shows a broadening of peaks due to dynamic changes involved. For the standoff technique, the bi-material cantilever serves as a photon detector which reflects average density of photons that are adsorbed by the polymer samples. However, in the PCDS case, the bi-material cantilever serves as a sensitive calorimeter reflecting the heat produced when the polymer absorbs specific photons. The time involved in the first case is longer than that of the second one from the fact that IR photons have a higher penetration depth in Si. This is expected to excite acoustic phonon states in Si that correspond to the operational chopping frequency, with their consequent non-radiative decay coupling to thermal phonon states generating heat, invoking a plausible explanation of the apparent broadening phenomenon. Further dynamic studies are being done to understand the phenomenon and will be communicated elsewhere.

We have also investigated the effect of UV radiation on the photothermal response of the polymers. UV radiation over time causes photooxidative degradation which typically results in the breaking of polymer chains, generating free radical and reduction in molecular weight.[36] This leads to deterioration of their mechanical integrity forming useless material of no apparent monetary value. Plastics that go through recycling conveyors may often be exposed to UV radiation and thus their degradation percentage needs to be considered while developing a new viable sensor. Exposing the polymers including physical plastic material (LDPE, PVC) to 365 nm UV radiation for 20 minutes does not change the peaks observed with standoff and point detection. Figure 5 shows the effect of UV exposure on low density polyethylene (LDPE) as an example. A decreasing response trend with apparent no change in the spectral peak position is observed for these polymers as a function of the exposure time. However, the peaks broaden with an overall increase in the background deflection, suggesting degradation. This can serve as a viable in-situ quality control and monitoring tool which present techniques are not able to deliver. Figure 6 summarizes the effect of UV radiation for different polymers. We plot response intensity for each material at 8000 nm. The curves showed a decreasing trend with different slopes, an indication of varying degradation rates of the polymers on exposure to UV.

The standoff photothermal spectroscopy technique has many advantages over conventional IR spectroscopy using cooled IR photodetectors. Bi-material cantilevers detect IR at room temperature and therefore do not require cooling. Also, intense stray light that could normally damage or give false positive results in a conventional IR detector, apparently does not affect photothermal results of bi-material cantilever. The cantilever detector is miniature and can be packaged into a small device with less energy consumption for seameless operation. The

sensitivity of this technique could be further improved through optimizations, e.g., using stronger tunable IR sources and more sensitive plasmonic nanostructured cantilevers. The standoff distance could be increased by using a mirror to collect and focus scattered light onto the cantilever. QCLs operating at different wavelength-band windows are now commercially available. These lasers offer higher power ratings at individual wavelength-bands which could increase signal-to-noise ratio multi-fold. Consequently, at higher QCL IR power, larger standoff distances can be achieved. Optimized designs of the cantilever and judicial choice of bi-material elements can significantly improve the thermal time constant of the cantilevers. Enclosing the cantilevers in partial vacuum could increase the Q-factor and sensitivity of detection. Also, by coating the cantilever with special materials, it is possible to make cantilevers extremely sensitive to certain IR wavelength-bands targeting specific materials of interest.

**Conclusions:**

In conclusion, we have demonstrated a microcantilever-based standoff detection technique for sensitive and selective identification of polymers exploiting photothermal spectroscopy. Various plastic components were detected by illuminating target surfaces with an IR source and sensing the scattered beam using a bi-material cantilever. A plot of cantilever bending as a function of the incident wavelength resembles the IR absorption spectra of the target surface/analytes. Point detection of polymers were also carried out by depositing a thin layer of polymer on the cantilever. The standoff spectra and the point spectra match very well with those obtained with FTIR and ATR. The absorption peaks obtained with the standoff technique were broader compared to that of point sensing, as well as those from ATR and FTIR. We demonstrated sensitivity in the order

of $10^2$ ng/mm$^2$ for different polymers showing promise of achieving even higher sensitivity at longer standoff distances by employing higher IR power sources and improved cantilever designs.

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**FIGURE CAPTIONS**

Figure 1. Schematic diagram of the stand-off detection setup. A bimaterial cantilever with a 200 nm polymer coating was illuminated with chopped IR beam from a tunable quantum cascade laser (QCL). The deflection of the cantilever was monitored using an optical beam deflection method using a lock-in amplifier.

Figure 2. Photothermal cantilever response as a function of chopping frequency.

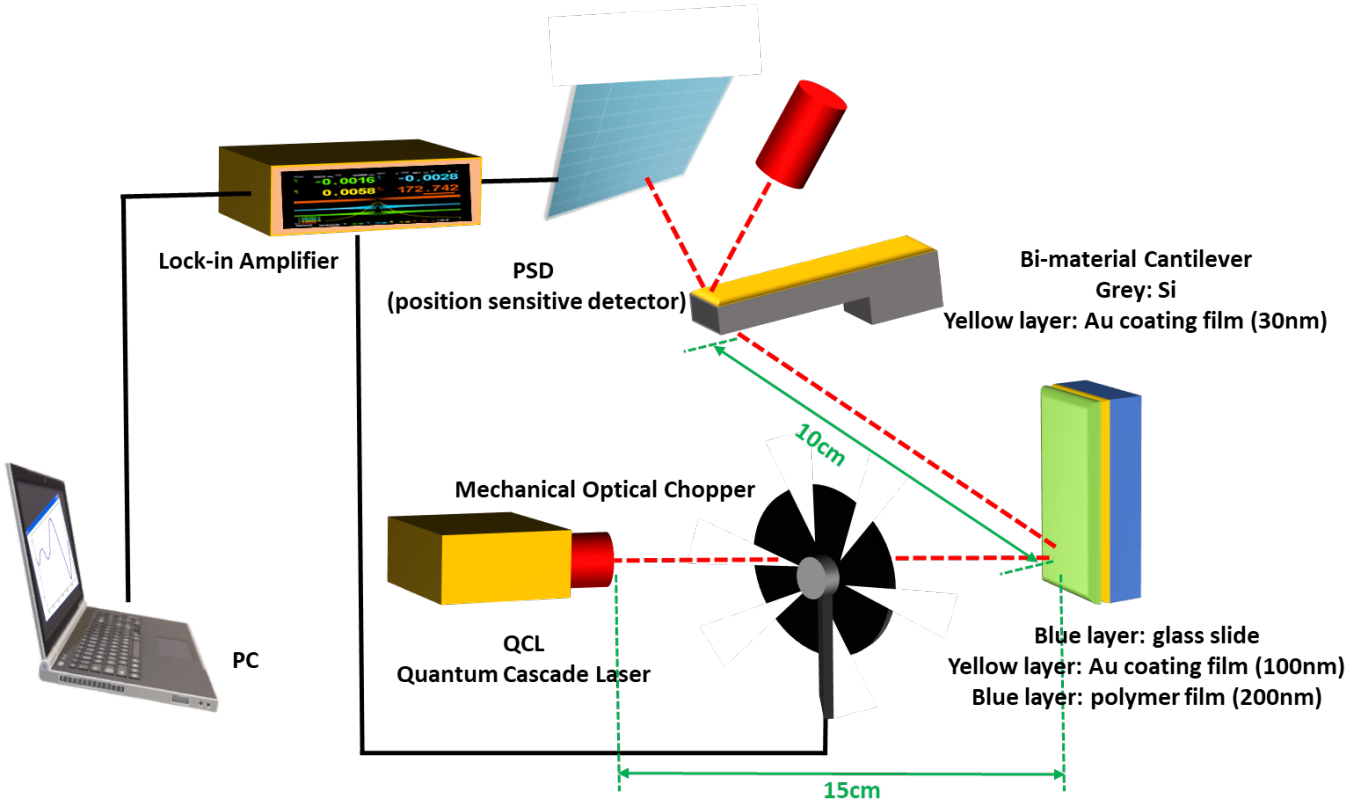
Figure 3. Standoff photothermal spectra and comparison with traditional FTIR and ATR spectra for different polymers; a) PDMS, b) PMMA, c) PVA, d) SU-8. As the target polymers absorb the IR radiation as a function of wavelength, the energy remitted to the cantilever detector is lowered resulting in a decrease in the cantilever heating/bending. The inverted absorption peaks in the plots are therefore found at the wavelength corresponding to the peaks in molecular IR absorption of the target species.

Figure 4. Comparison of the standoff spectrum with spectrum obtained with PDMS film deposited the cantilever. (a) PDMS (b) PMMA

Figure 5. The effect of UV exposure on the standoff photothermal spectrum of LDPE. The background increases with exposure time making the peaks to appear smaller.

Figure 6. Standoff Cantilever response after the polymer sample was exposed to UV light for different time intervals. All polymers show a saturation after 10 minutes of UV exposure.

**FIGURES**

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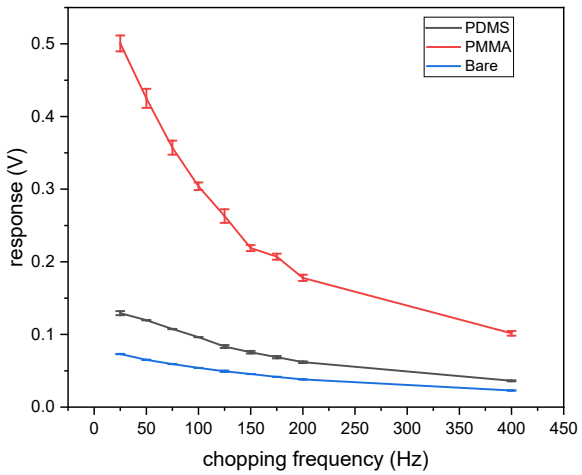


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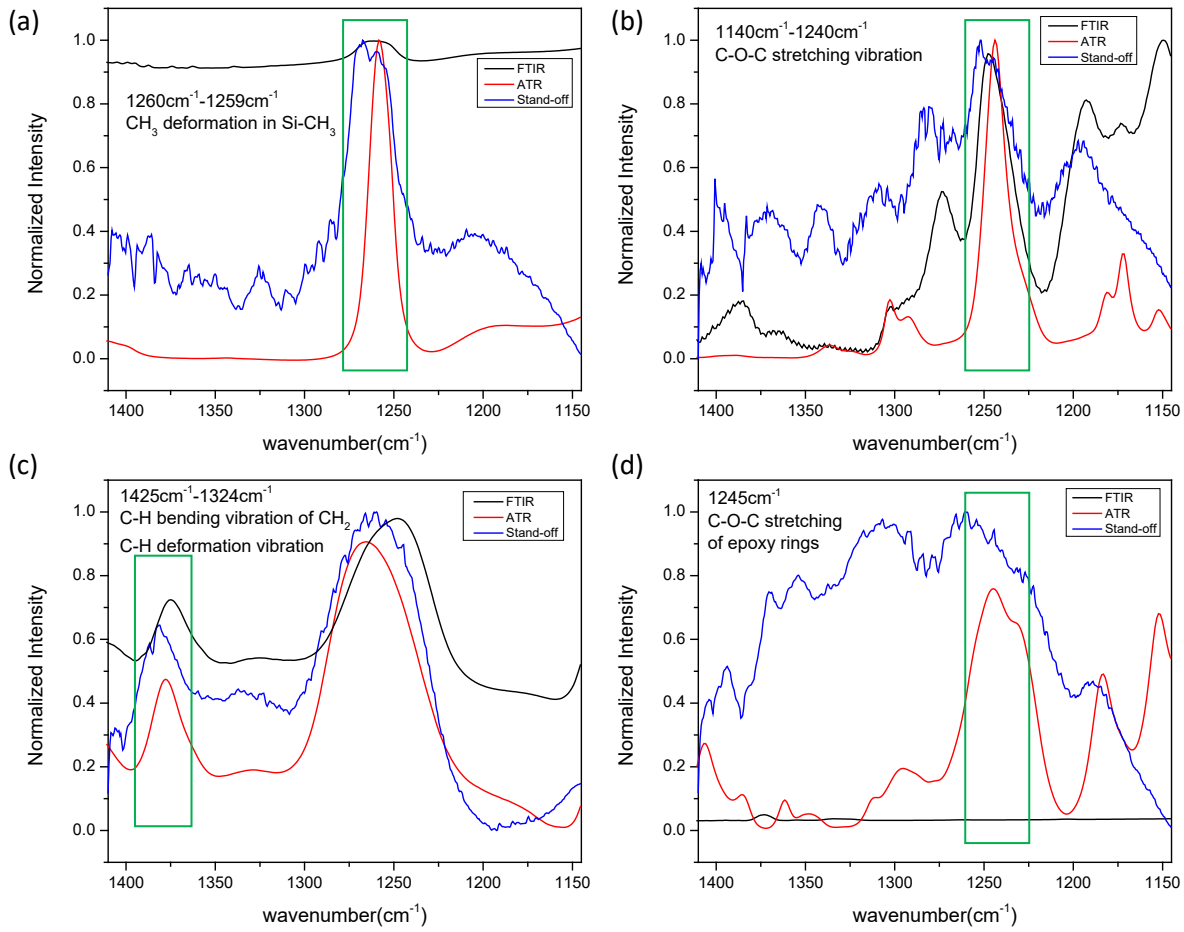

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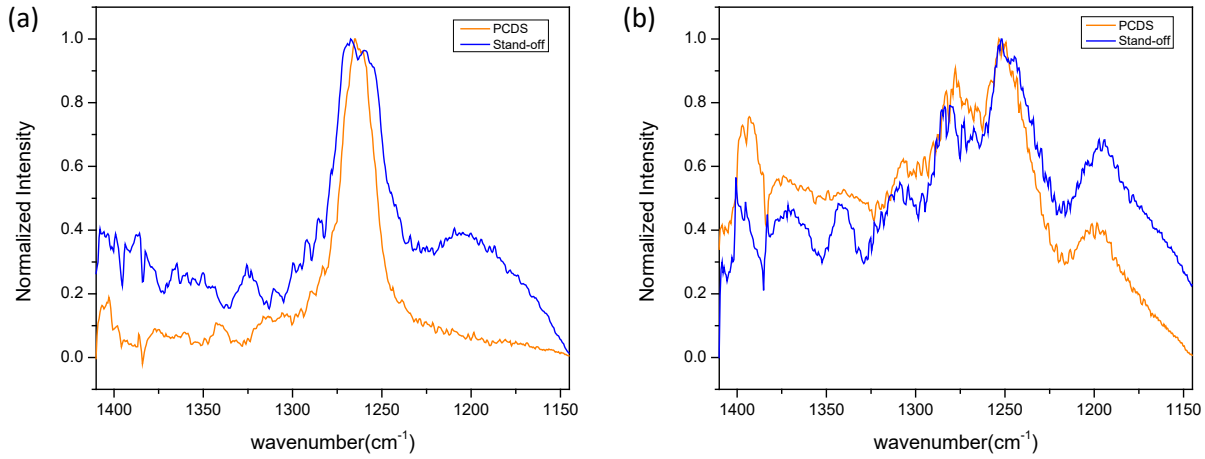


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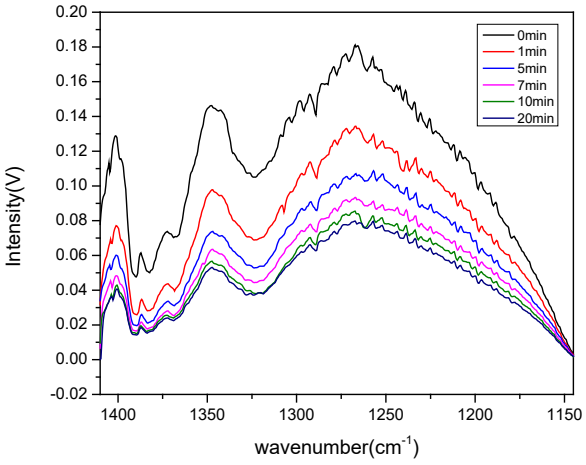

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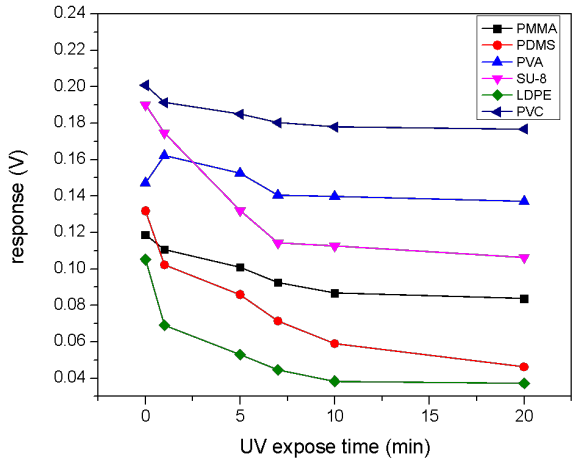


Figure 6. Standoff Cantilever response after the polymer sample was exposed to UV light for different time intervals. All polymers show a saturation after 10 minutes of UV exposure.

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