

LA-UR-19-25455

Approved for public release; distribution is unlimited.

Title: Measuring the x-ray irradiated degradation of PMMA through FTIR and 2D-COS analysis

Author(s): Brett, Jack Kevin

Intended for: Term Paper for master's program.

Issued: 2019-06-12

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Measuring the x-ray irradiated degradation of PMMA through FTIR and 2D-COS analysis

Jack K. Brett*

Los Alamos National Laboratory, MST-7 Engineered Materials, Materials Science and Technology Division, Los Alamos, NM 87545

ABSTRACT: To combat issues arising from polymer aging studies which include wasting valuable time and resources, Two-Dimensional Correlation Spectroscopy (2D-COS) has been observed to identify accelerated aging conditions in materials in a very short timeframe. This study is attempting to validate 2D-COS as a viable technique for aging studies by measuring the degradation of PMMA via x-ray radiation. PMMA has been previously observed to degrade via main chain scission under x-ray radiation,^{9, 10} and similar results have possibly been seen in this study. More work needs to be done to collect reliable data, including finalizing a standard operating procedure and normalizing raw data so that noise is not recognized as spectral change by the extremely sensitive 2D-COS software.

INTRODUCTION

Polymer aging studies are performed to examine the way certain materials behave in extreme conditions for long periods of time. This information can aid in the choice of materials for certain products based on the way they behave. Accelerated aging studies are necessary to shorten the time needed to run a full-length aging study, which can take many years to complete. These aging studies do have shortcomings, as they can result in useless data while wasting a multitude of time. Also, aging studies can fail to account for all the possible chemical reasons of a material's degradation as one may have multiple degradation mechanisms.^{1, 2}

An analysis technique, Two-Dimensional Correlation Spectroscopy (2D-COS), has been seen to accurately identify accelerated aging conditions of materials. It is of importance to the Engineered Materials group at LANL to validate this technique in order to perform accurate accelerated aging studies to save valuable time and resources.

2D-COS is a technique designed by Isao Noda, which generalized Two-Dimensional FTIR to include any time-dependent variable, such as temperature, concentration, pressure, pH, or radiation dose plotted against multiple spectra that show distinct

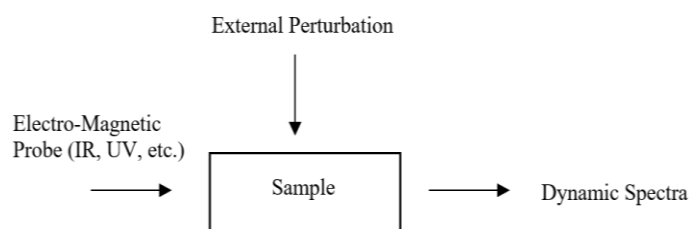


Figure 1. Diagram of the general 2D-COS process.

change in a material. This new technique shows increased resolution from traditional IR as very complex spectra can be separated and overlapping bands can be readily identified.^{3, 4}

This technique is performed by exposing a sample to a variable amount of an external perturbation (temperature, concentration, pressure, pH, or radiation dose), spectroscopically measuring in between each specified amount of the perturbation (Figure 1). As the external perturbation level is increased, unique spectral changes should be seen, which represent characteristic changes in the material. These spectra are all then used to generate a two-dimensional contour plot also known as the dynamic spectrum, through mathematical manipulation that will be explained later on.

The dynamic spectrum involves two separate contour plots, the synchronous and asynchronous spectra (Figure 2). Both of these spectra together can give information about the behavior of the material decay and even the sequence of events of the degradation. The synchronous spectrum gives insight into spectral changes that are correlated to each other. The characteristic quality of the synchronous spectrum is the diagonal. On this diagonal lie autoperks, also known as the spectral change as seen through the increasing external perturbation, where the intensity is proportional to amount of change observed in the material. On the off-diagonal, signals can be seen which are called cross peaks. Cross peaks allow for correlation squares to be drawn for signals on the diagonal, meaning that those two spectral changes are

correlated to each other. To determine the correlation, the signs of the cross peaks must be examined. Autopeaks are always positive, but cross peaks can be either positive or negative. If cross peaks are positive, it means that the two autopeaks are either increasing or decreasing together, and the opposite if cross peaks are negative.⁵

The asynchronous spectrum then provides information on the individual changes in the material, and is the reason for the large resolution increase seen in 2D-COS from traditional IR measurements. This spectrum shows the spectral changes that are not correlated to each other. It represents the individual changes in the material that are due to the differing levels of the perturbation. Differing from a synchronous spectrum, an asynchronous spectrum has no autopeaks, only cross peaks. These cross peaks appear when two spectral signals change in an out-of-phase relationship with one another. Even if dealing with very close/overlapping spectral bands, as long as the variation patterns at a certain signal are substantially different due to the perturbation variable, a signal will form in the asynchronous spectrum.⁵

Another key use of the asynchronous spectrum is that it can be used to identify the sequential order of events of the material decay. Noda developed a set of rules to determine the order of events that has been seen to be very reliable.⁴ These rules mainly pertain to the signs of the cross peaks and how they relate to correlating peaks in the synchronous spectrum for the same signal. For example, if a cross peak is positive with a higher intensity at a certain wavenumber, then it is the first occurring step, but only if the sign of the signal in the asynchronous spectrum is the same as the autopeak in the synchronous spectrum for that particular signal. If the sign between this cross peak and the autopeak in the synchronous spectrum are opposite, then that rule is flipped.

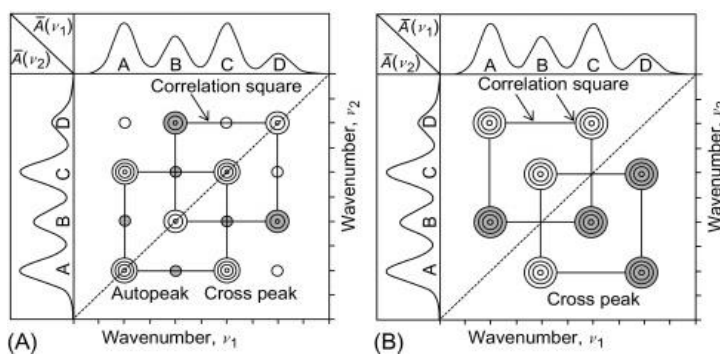


Figure 2. Example dynamic spectrum showing the Synchronous (A) and Asynchronous (B) Contour Maps.

For this study, 2D-COS is currently being utilized to analyze the degradation of Poly(methyl methacrylate), PMMA, (Figure 3) with an external perturbation of x-ray radiation. PMMA is of large interest for this study because it is well known to degrade under multiple environmental conditions, including heat and ionizing radiation.⁶⁻⁸ The importance of the study is tailored towards the validation of 2D-COS as an analytical technique, so having a material that is well documented to show spectral change is important because it should be readily confirmed by 2D-COS.

It has been documented that through x-ray and other high energy irradiations, that PMMA is susceptible to main chain scission. X-ray irradiation has also been found to be the most efficient radiation source for PMMA, in terms of the efficiency of chain scission without the removal of ester groups.^{9, 10} These known results give a benchmark for material degradation that should be readily observed through 2D-COS, which would serve as a validation of the analysis technique if similar results are seen.

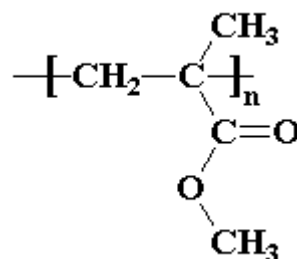


Figure 3. Chemical structure of PMMA.

EXPERIMENTAL

The PMMA film samples used in this study have been purchased from Goodfellow and spectroscopically measured using the Bruker 800 instrument at LANL. Initially for this study, the goal was to utilize transmission FTIR to measure the changes due to irradiation, but once experiments were performed on the material, the 50 μ m PMMA film appeared to be too thick, as some important spectral signals were saturating, so an ATR attachment was used, which only samples the surface of a sample, where transmission measures through the entire sample.

In order to dose the PMMA thin film samples, a Mo-target x-ray source that operates at 50 kV and 40 mA was utilized. The PMMA samples were attached to IR cards and placed on a stainless steel plate to be hit by the ~25 keV x-ray beam for a dose rate of 0.8 Gy/s in room temperature conditions. Measurements taken up to this point have been exploratory, as many bounds of the experiment have to

be set in order to introduce a standard operating procedure. For example, in order to properly do a 2D-COS experiment, the interval of external perturbation for each measurement taken must be the same. For example, a measurement would need to be taken 100, 200, 300... etc. Gy, and that interval cannot change. The progress in the study thus far exudes change in the PMMA film that is believed to be caused by the radiation.

SPECTRACORR SOFTWARE

To perform 2D-COS on collected FTIR data, the Thermo Fisher software SpectraCorr was purchased. It can easily and quickly translate a series of spectra into both synchronous and asynchronous spectra. The theory behind the calculations first involves subtraction of the reference spectrum $\bar{y}(v)$ (Equation 1) from the raw data, producing the dynamic spectrum, where j represents the quantitative measure of the external perturbation, and m represents the max number of external perturbation measurements taken.

$$\bar{y}(v) = \sum_{j=1}^m \frac{y(v, t_j)}{m} \quad (1)$$

The synchronous correlation spectrum can then be calculated from the dynamic spectrum by

$$\Phi(v_1, v_2) = \frac{1}{1-m} \sum_{j=1}^m \tilde{y}_j(v_1) \cdot \tilde{y}_j(v_2) \quad (2)$$

While slightly more complicated, the asynchronous spectrum is calculated by

$$\Psi(v_1, v_2) = \frac{1}{1-m} \sum_{j=1}^m \tilde{y}_j(v_1) \cdot \tilde{z}_j(v_2) \quad (3)$$

Where $\tilde{z}_j(v_2)$ is the discrete orthogonal spectrum and defined as

$$\tilde{z}_j(v_2) = \sum_{k=1}^m N_{jk} \cdot \tilde{y}_k(v_2) \quad (4)$$

N_{jk} is known as the Hilbert-Noda transformation matrix. This matrix term allows for an orthogonal correlation to be created, which is just a cross-correlation with the dynamic spectrum where the phase of each Fourier transform component is shifted by 90°. This method has been observed to be much faster and more efficient than the previously used fast Fourier transform approach.¹¹

When the dynamic spectra is displayed for sample data included with the software (Figure 4), the user also has the opportunity to select the reference spectrum under the "Source" tab to be plotted against the correlation which can be seen above the displayed contour plot. The tabs above the plot allow for easy access and transition through the possible spectra labeled as "Sync Correlation", "Async Correlation", and "Global Phase." There are user-friendly ways of changing display options by right-clicking inside the plot display which allow the user to change from a

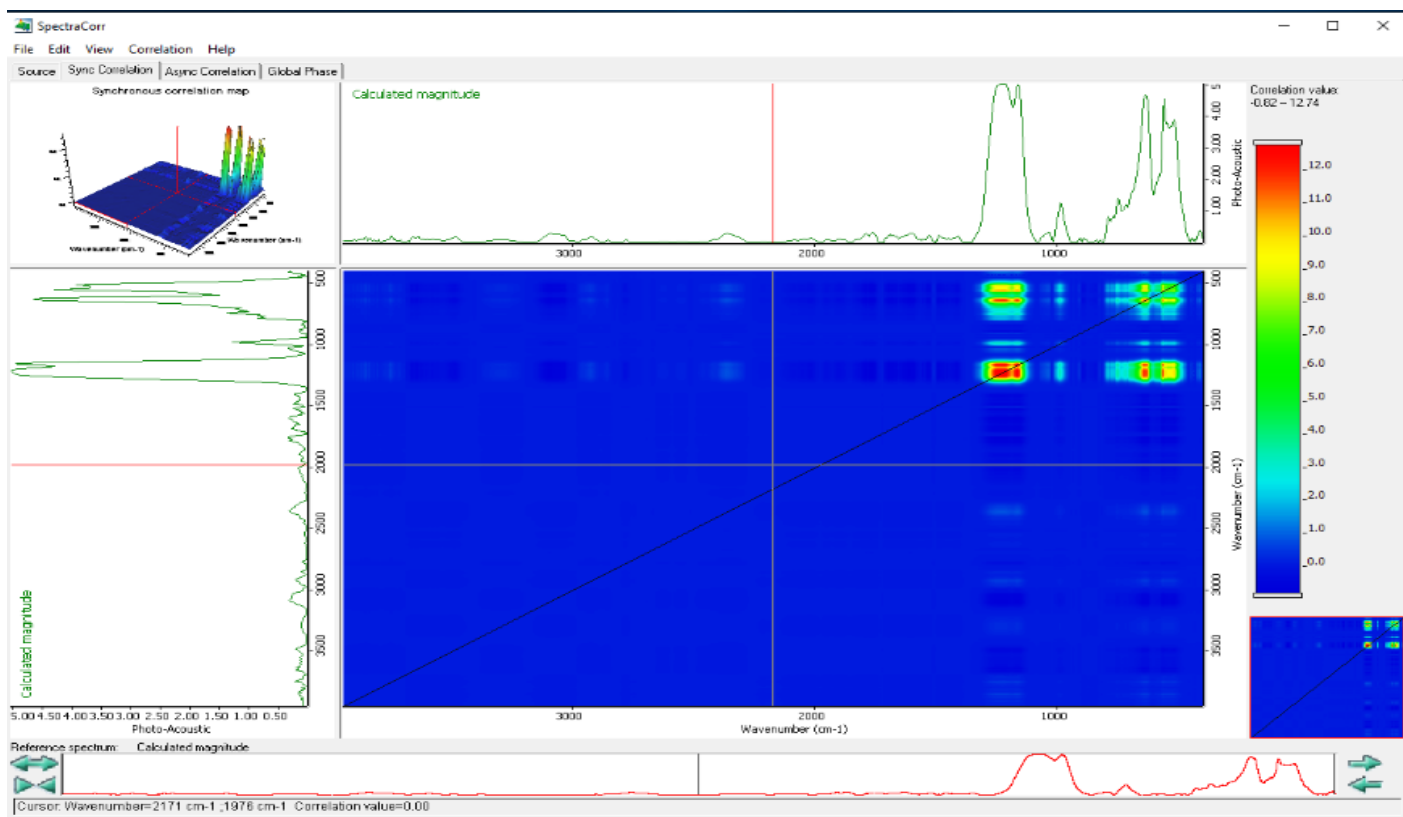


Figure 4. Output display of synchronous spectrum from the SpectraCorr software.

color fill plot or a conventional contour plot, or both, depending on the user preference.

A useful feature of SpectraCorr is the 3D display of the correlation that can be viewed on the upper-left side of the screen. On the right side of the display the correlation value can be seen. This value defines the intensity of a signal, or showing the strength of a correlation. This value can also be used to calculate a moving window plot, which plots the external perturbation levels against the overlay spectrum.

RESULTS AND DISCUSSION

One experiment that has been performed shows the FTIR spectrum of a sample of PMMA subject to a radiation dose from 0-12,000 Gy (Figure 5). For a normal study that utilizes 2D-COS, Noda recommends that the level of the perturbation be the same each time it is applied, but for this test, the level was changed as to cover a larger amount of dose in less time. For final, reportable data, a defined dose must be decided upon for each separate measurement. Only the range of 500-1900 wavenumbers are displayed in Figure 5 because there were no other spectral changes observed throughout the rest of the spectrum. The main peaks of interest in this experiment exist at ~ 1720 and 1140 cm^{-1} , as the 1720 cm^{-1} peak represents the C=O stretch and the 1140 cm^{-1} peak represents the C-O-C stretch in PMMA. These spectral changes are summarized in Table 1.

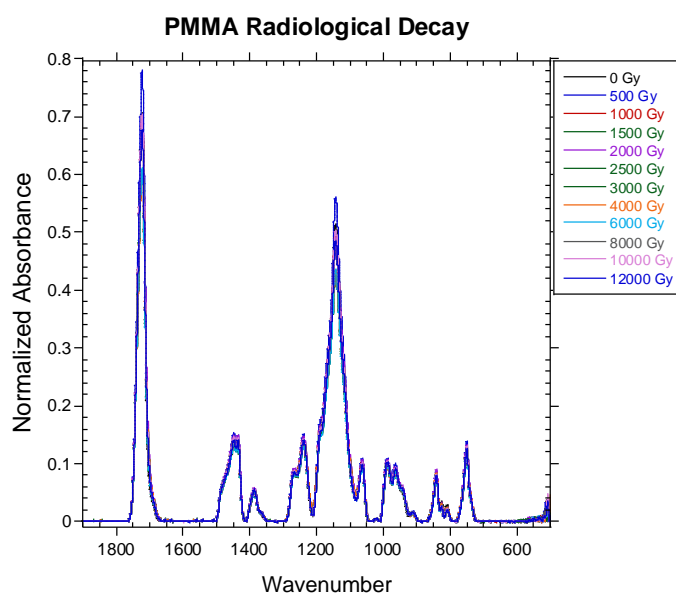


Figure 5. Overlay FTIR spectra of PMMA from 0-12,000 Gy.

This overlay FTIR data was then input into the previously mentioned SpectraCorr software to obtain both the synchronous and asynchronous contour maps. The zoomed-in synchronous spectrum with the same range as Figure 5 can be seen in Figure 6.

Table 1. FTIR spectral change summary.

FTIR Peak	Absorbance at 0 Gy	Absorbance at 12,000 Gy
C-O-C (1720 cm^{-1})	0.71	0.61
C=O (1140 cm^{-1})	0.52	0.44

What can immediately be seen are the two autopeaks on the diagonal and by looking at the wavenumbers on each axis, these autopeaks can be confirmed as the spectral changes seen from the C=O and C-O-C bonds. Cross peaks can readily be seen on the off-diagonal from the two autopeaks, meaning that these two spectral changes share some kind of correlation. Since the cross peaks are positive, this means each of these spectral changes are increasing or decreasing together and since Table 1 shows the peak intensity decreased during increased doses, it can be concluded that these two autopeaks are decreasing together throughout the degradation.

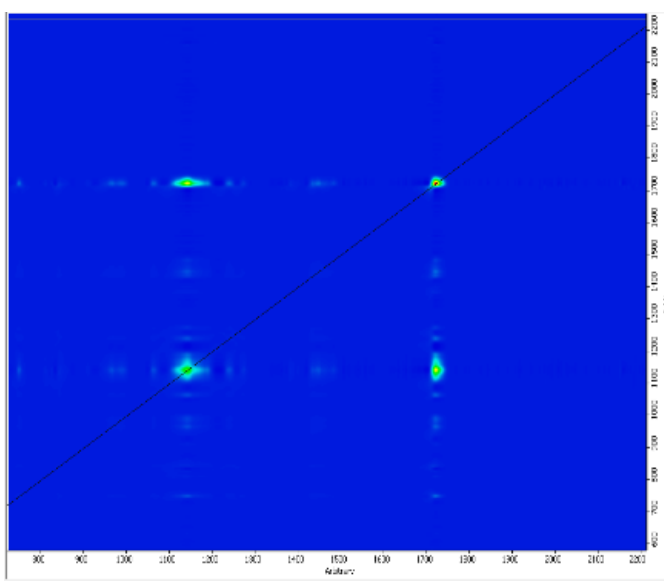


Figure 6. Synchronous spectra of PMMA overlay data from 0-12,000 Gy.

The next step in this process would be to analyze the asynchronous spectrum. Unfortunately, at this point in the study, there is no proper asynchronous spectrum to analyze. The generated spectrum has too much noise which results from issues in the

raw data (Figure 7). Because the asynchronous spectrum can identify so many tiny spectral changes which allows complex/overlapping bands to be separated, signals are being created for small changes in the background that are not actually spectral changes. Because of this, more work needs to be done to further correct the raw data of the scans before they are run through the SpectraCorr software in order to obtain a proper asynchronous spectrum and complete a full 2D-COS analysis.

Although a full analysis cannot yet be completed, a possible proposition can be made based on what has already been discussed. Since the C=O stretch and the C-O-C stretch appear to be decreasing together as the amount of radiation increases, it appears the polymer may be breaking down via the carbonyl (Figure 3), possibly agreeing with the chain scission reported in the literature.

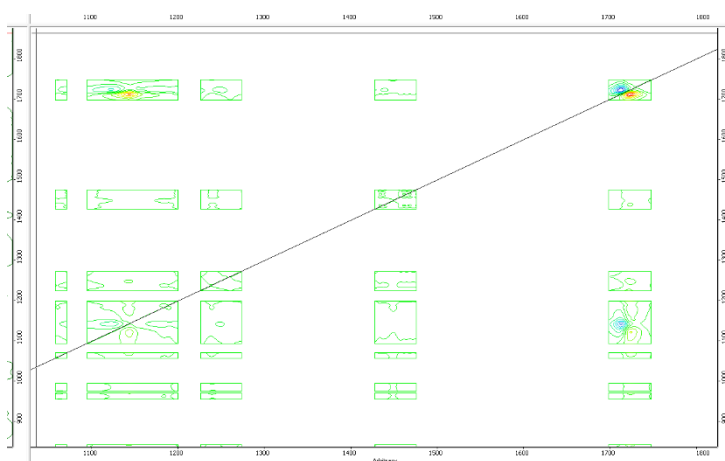


Figure 7. Asynchronous spectra of PMMA overlay data from 0-12,000 Gy.

FUTURE DIRECTIONS

As previously mentioned, the data collected in this study so far has been to finalize a standard operating procedure for this technique. The data taken has been to show the fact that PMMA is changing with respect to radiation dose. The future scope of the project will first deal with experimentally determining a proper dose amount for each time the PMMA film is dosed and measured. This will be decided on by observing the dose in which the film structurally shows changes and choosing a dose amount that can accurately capture those moments of material change.

In order to account for the purchased film being too thick (50 μm), two alternatives are being considered. The first being to purchase a thicker sample and attempt to cut a 10 μm slice using a cryogenic mi-

crotope located at LANL. The other option is to synthesize the film using a spin-coating technique. Although this seems reasonable, it is preferred that the film be commercially purchased since that is more likely to be used in consumer products/parts.

The next step would be to then address the previously mentioned issue of data correction. The asynchronous spectrum is so sensitive to spectral changes that any noise in the background will trigger a signal, which is the issue with the asynchronous spectrum in Figure 7. Data normalization is a key issue for this analytical technique, so more work with the raw data will need to be completed.

A 2D moving window plot will also be generated which plots the radiation dose vs. the overlay of the spectral changes. The correlation value that is displayed via the SpectraCorr software can be used to generate this plot which is useful because it determines the level of dose that the material changes occur at, not just that the material is changing.

And finally, there are plans in place to use 2D-COS to analyze PMMA degradation with different external perturbations such as temperature and humidity. Measuring with different perturbations will allow for a more in-depth understanding of the material itself and prove the worth of 2D-COS analysis.

CONCLUSION

Polymer aging studies are extremely important because of the predictive nature they can expose about materials. But, because of some characteristic flaws, these tests are not always reliable and can waste a lot of valuable time. 2D-COS has been observed to identify accelerated aging conditions in materials and could help save time and resources needed to run an aging study. In this paper, the progress of an experiment using 2D-COS to measure the degradation of PMMA with respect to x-ray radiation is described. Validating 2D-COS as a viable tool to confirm accelerated aging conditions would aid the Engineered Materials group at LANL for multiple studies in the future. To this point, it appears that PMMA may be degrading via main chain scission, which would agree with previously reported literature. More work needs to be done to draw final conclusions, including developing a standard operating procedure and data cleaning.

REFERENCES

- (1) Gillen, K.T., Bernstein, R., Celina, M. Challenges of Accelerated aging techniques for elastomer lifetime predictions. *Rubber Chemistry and Technology* **2015**, (88), 1-27.

- (2) Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science. (U.S. Department of Energy, 2015).
- (3) Noda, I., Ozaki, Y., Two-Dimensional Correlation Spectroscopy: Applications in Vibrational and Optical Spectroscopy; John Wiley & Sons LTD, 2004.
- (4) Jung, Y.M., Noda, I., New Approaches to Generalized Two-Dimensional Correlation Spectroscopy and Its Applications. *Applied Spectroscopy Reviews* **2006**, 41 (5), 515-547.
- (5) Noda, I. Chapter 2 – Advances in Two-Dimensional Correlation Spectroscopy (2D-COS). *Frontiers and Advances in Molecular Spectroscopy*. Elsevier **2018**, 47-75.
- (6) Beetz T., Jacobsen C. Soft X-ray radiation-damage studies in PMMA using a cryo-STXM. *J Synchrotron Radiation* **2003**, (10), 280–283.
- (7) Moore, J.A., Choi, Jin O. Degradation of Poly(methyl methacrylate). *ACS Symposium Series* **1991**, (475), 156-192.
- (8) Bennet, F., Hart-Smith, G., Gruendling, T., Davis, T.P., Barker, P.J. Degradation of Poly(methyl methacrylate) model compounds under extreme environmental conditions. *Macromolecular Chemistry and Physics* **2010**, (211), 1083-1097.
- (9) Buchwalter, L.P., Czornyj, G. Poly(methyl methacrylate) degradation during x-ray photoelectron spectroscopy analysis. *Journal of Vacuum Science & Technology A* **1990**, (8), 781-784.
- (10) Choi, J.O., Moore, J.A., Corelli, J.C., Silverman, J.P., Bakhru, H. Degradation of poly(methyl methacrylate) by deep ultraviolet, x-ray, electron beam, and photon beam irradiations. *Journal of Vacuum Science & Technology B: Microelectronics Processing and Phenomena* **1988**, (6), 2286-2289.
- (11) Noda, I. Determination of two-dimensional correlation spectra using the Hilbert transform. *Applied Spectroscopy* **2000**, (54), 994-999.