



# An insight into the sequential order in 2D correlation spectroscopy using polymer transitions: Boltzmann Sigmoid, Gaussian Cumulative, Lorentz Cumulative, and Asymmetric Sigmoid. Findings in experiments and simulations

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## ABSTRACT

In this paper, we found the curves of infrared spectral intensity at specific wavenumbers of several polymer transitions can be accurately fitted by one of Boltzmann Sigmoid, Gaussian Cumulative, Lorentz Cumulative, or Asymmetric Sigmoid functions. These transitions include the melting of iPP, the Brill transition of PA66, the epoxy curing, the oxidation of SBS, and the melting of HDPE. These functions were obviously different from other important functions, which were earlier introduced into generalized 2D correlation spectroscopy, such as sinusoidal, exponential, and Lorentzian. The properties of the Boltzmann Sigmoid, Gaussian Cumulative, Lorentz Cumulative functions were studied using the simulated infrared spectra. The sequential order is only controlled by the parameter reflecting the center point location, while other parameter values have no relationship. The influences of the parameters in Asymmetric Sigmoid on the sequential order were also studied using the simulated IR spectra. Within the transition range, it was found the values of several waveform parameters co-determine the sequential order. We concluded that the MW2D or PCMW2D method should first be employed to determine a rational transition range before using 2D correlation infrared spectroscopy to study the mechanism of the polymer transitions. The clear physical meaning of the sequential order is the “earlier” or “later” of the transition points. As long as the experimental range (external perturbation) is wide enough and the data precision is good, the sequential order is absolutely reliable within the transition range. The results discussed throughout this paper have proven that the sequential order rules are absolutely correct. The content of the present study will solve the controversy on the sequential order rules to a large extent.

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## 1. Introduction

Generalized two-dimensional correlation spectroscopy is a widely used spectroscopy method [1–4], which was proposed by Noda in 1993 [5]. By using this method, the resolution of the spectra is significantly enhanced and the sequential order of spectral intensity variation can be easily gained according to Noda's rules [6,7]. In Noda's early paper [5], three important functions (sinusoidal, exponential, and Lorentzian) in generalized 2D correlation spectroscopy were introduced. The clear physical meanings of the sequential order of these three functions were also described. The sequential order on sinusoidal signals is the “earlier or later” of the phase angles ( $\beta(\nu)$ ), while it represents the “faster or slower” of the rate constant ( $k(\nu)$ ) on exponential signals. Lorentzian peak signals are commonly viewed in chromatographic testing, so the

sequential order is the “longer or shorter” of the chromatographic retention time ( $\theta(\nu)$ ). However, the spectral signals are always complex in experimental data. The signals can be probably described or fitted by other functions. The exact physical meanings of the sequential order in these functions will be different from the sinusoidal, exponential, and Lorentzian.

Recently, Huang [8,9] carried out a study on the sequential order of the simulation infrared spectra. In his paper, the simulation spectra signals were based on exponential function. He found when the “local sequential order” existed; the Noda's rules sometimes had serious problems. The sequential order gained was contrary to the real “local sequential order”. Huang concluded the Noda's rules were dangerous and wrong in some situations. After Huang's study, Jia et al. [10] proposed a distinctive viewpoint. They introduced an idea of the half-life in the spectral signals' variation in generalized 2D correlation spectroscopy. In Jia's study [10], a new interpretation that the universal physical meaning of the sequential order is the “longer or shorter” of the half-life was given. In 2006, a similar idea was also reported by Czarnik-Matusewicz et al. [11]. They thought it

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should be very careful that 2D correlation was performed and interpreted correctly, because the sequential order is not easily verified by other techniques. Huang and Jia's research brought us a new understanding on generalized 2D correlation spectroscopy. After careful examination of the soundness of the theoretical ground [7], Noda himself confirmed 2D correlation spectroscopy is a robust technique broadly applicable to the analysis of spectral data.

Generalized 2D correlation spectroscopy is actually a signal-processing method based on Fourier Transform [5,7,12]. Therefore, the sequential order is certainly influenced by the cut range of the time-domain signal and the signal function. The specific physical meaning of the sequential order should be determined according to the specific situations. In our opinion, some restrictive or extra conditions (cut range and function) should be introduced when we use the Noda's rules to judge the sequential order. In Jia's paper [10], they suggested the whole process should be divided into stages in the presence of the spectral signal intersection points (the normalized plots), for each stage has its own sequential order. Their suggestion is a typical restrictive condition for 2D correlation spectroscopy application. However, it should be noticed all the research objects were based on the exponential function in Huang and Jia's study. Like the original definition in Noda's paper [5], it can be easily inferred the sequential order in the exponential function is the statistical average of the change rate speed, regardless of the "local sequential order" existence. So Huang and Jia's research cannot sum up in all cases of generalized 2D correlation spectroscopy. Other more important spectral signal functions should be studied and developed.

In the present study, we found three functions (waveforms) from the temperature-dependent infrared spectra of polymer transitions, including Boltzmann Sigmoid, Gaussian Cumulative, and Lorenz Cumulative. These three functions have "S" shape and have been widely used in various science fields. In polymer fields, these functions are also usually faced. In DSC curves [13], the polymer glass transitions are always "S" shape. The dynamic modulus-temperature curves in DMTA are also "S" shape [13]. In TG testing, weight change-temperature curves still have "S" shape [13,14]. Wang and Sun et al. [15–17] also observed the shapes of IR spectral variation in polymer transitions can be described by Boltzmann Sigmoid.

Recently, we have found the infrared spectral intensity variation of many polymer transitions can be precisely fitted by these three functions, as long as the experimental conditions and the external perturbation was reasonable and credible. The features of the sequential order of these three functions in 2D correlation spectroscopy were necessary to be investigated. We also would like to find out the clear physical meaning of the sequential order in these functions. The moving-window 2D correlation infrared spectroscopy (MW2D) [18–23] was employed to determine the transition points and the transition range. The temperature-dependent infrared spectra within the transition range were used for generalized 2D correlation analysis. We found the sequential order of the infrared spectra within the transition range were fully consistent with that of the transition points determined by MW2D. It was also found the clear physical meaning of the sequential order in the generalized 2D correlation analysis is the "earlier" or "later" of transition points under an external perturbation.

Judging from the experiments, we did not meet the problems reported in Huang's paper [8]. The sequential order in the generalized correlation analysis is identical with that of true observations. In order to confirm the performances of Boltzmann Sigmoid, Gaussian Cumulative, and Lorenz Cumulative function in the generalized correlation analysis further, the properties of these three functions are studied using the simulated infrared spectra.

During the studies mentioned above, we also found the infrared spectral intensity variation of some polymer transitions can be

described by another new Asymmetric Sigmoid function. The property of this function is fully different from that of Boltzmann Sigmoid, Gaussian Cumulative, and Lorenz Cumulative. Although only a small portion of polymer transitions appears in this form, we still feel its importance. It is necessary for us to study in detail. In this paper, we show the course of finding Asymmetric Sigmoid from the experimental infrared spectra data. The properties of Asymmetric Sigmoid in 2D correlation spectroscopy were also explored using the simulated infrared spectra.

## 2. Experimental

### 2.1. Materials

In the present study, the isotactic polypropylene (iPP) was kindly supplied by Baling Petrochemical Industry Co., Ltd of Sinopec. Polystyrene-block-polybutadiene-block-polystyrene block copolymer (SBS) was also supplied by Baling Petrochemical Industry Co., Ltd. Nylon 66 (PA66) used for experiment was LEONA 1300S, which was bought from Asahi Kasei Co. The epoxy oligomer diglycidyl ether bisphenol-A (CYD-128) was bought from Baling Petrochemical Industry Co., Ltd. The epoxy curing agent was a low molecular weight polyamide (650, liquid), and its weight-average molecular weight is 600–1100 g/mol. High-density polyethylene (HDPE) used for experiment was 6098, which was bought from Qilu Petrochemical Industry Co., Ltd of Sinopec. All the materials were directly used in experiment without further purification. The structures of Nylon 66, SBS, the epoxy oligomer, and the epoxy curing agent are shown in Scheme 1.

### 2.2. FTIR spectroscopy

#### 2.2.1. iPP

1 g of iPP was placed between two PET sheets. The iPP film was directly prepared from heating pressing the iPP sandwiched between two PET sheets at 190 °C in a hot press, and then was naturally cooled to room temperature. The heating pressing time was 2–3 min and the pressure of the hot press was 20.0 MPa. The best iPP film thickness is 10–20 μm. After that, the film was annealed in the nitrogen atmosphere at 120 °C for 6–8 h. The annealed film was cut to a circular shape (diameter = 0.5 cm) by a cutter. The iPP film was sandwiched between two small KBr windows to prevent the high-temperature flow and was finally placed into a homemade in situ pool (program heating instrument). FTIR spectrometer was Bruker Tensor 27. It was equipped with a deuterated 1- $\alpha$ -alaninedoped triglycine sulfate (DLATGS) detector. The temperature-dependent absorbance IR spectra were collected. The scans of each were 20, and the spectral resolution was 4 cm<sup>-1</sup>. During the measurement, the iPP film sample was protected by high-purity nitrogen gas (99.999%). The IR spectra were collected from 60 °C to 195 °C at approximately 2 °C increments. The total number of the spectra collected was 67. The heating rate in the measurement was 5 °C/min.

#### 2.2.2. PA66

1 g of PA66 was placed between two aluminum foils. The PA66 film was directly prepared from heating pressing the PA66 sandwiched between two aluminum foils at 260 °C in a hot press, and then was naturally cooled to room temperature. The heating pressing time was 3–4 min and the pressure of the hot press was 20.0 MPa. The best PA66 film thickness is 10–20 μm. After that, the film was annealed in the nitrogen atmosphere at 185 °C for 6–8 h. The annealed film was cut to a circular shape (diameter = 0.5 cm). The PA66 film was sandwiched between two small KBr windows to prevent the high-temperature flow and was finally placed into a homemade in situ pool. FTIR spectrometer was Bruker Tensor

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