



Two-dimensional (2D) Chemiluminescence (CL) correlation spectroscopy for studying thermal oxidation of isotactic polypropylene (iPP)

Hideyuki Shinzawa*, Hideaki Hagihara, Hiroyuki Suda, Junji Mizukado

Research Institute for Sustainable Chemistry, Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

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ABSTRACT

Application of the two-dimensional (2D) correlation spectroscopy is extended to Chemiluminescence (CL) spectra of isotactic polypropylene (iPP) under thermally induced oxidation. Upon heating, the polymer chains of the iPP undergoes scissoring and fragmentation to develop several intermediates. While different chemical species provides the emission at different wavelength regions, entire feature of the time-dependent CL spectra of the iPP samples were complicated by the presence of overlapped contributions from singlet oxygen ($^1\text{O}_2$) and carbonyl species within sample. 2D correlation spectra showed notable enhancement of the spectral resolution to provide penetrating insight into the thermodynamics of the polymer system. For example, the oxidation induce scissoring and fragmentation of the polymer chains to develop the carbonyl group. Further reaction results in the consumption of the carbonyl species and subsequent production of different $^1\text{O}_2$ species each developed in different manner. Consequently, key information on the thermal oxidation can be extracted in a surprisingly simple manner without any analytical expression for the actual response curves of spectral intensity signals during the reaction.

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1. Introduction

Chemiluminescence (CL) is a production of light induced by a chemical reaction. In general, such emission ranges over the region of 400–750 nm, while different chemical species provides the emission at different wavelength regions. By analyzing the variation of CL emission from the system of object undergoing the chemical reaction, it is possible to probe the evolutionary changes induced by the reaction. Recently, highly sensitive CL spectroscopy based on Fourier transform technique has been developed to capture the exceptionally weak CL emission at different wavelengths arising from object of interest [1–4]. The CL spectrometer provides a definite advantage in the identification of the CL species as well as the detection of weak emission as well as the over the conventional CL characterization technique which accumulates total CL intensity collected over the wide wavelength range.

While the CL spectroscopy offers interesting opportunity to derive in-depth understanding of the chemical reaction generating

weak CL emission, the analysis of CL spectra suffers from some practical limitations. For example, entire feature of the CL spectrum is often complicated by the presence of overlapped contributions from singlet oxygen ($^1\text{O}_2$) and carbonyl species within sample [3–7]. The overlapped peaks then make the identification of the subtle but significant variation of spectral intensities somewhat difficult.

In this communication, two-dimensional (2D) correlation spectroscopy was applied to sets of CL spectra of isotactic polypropylene (iPP) to demonstrate how this technique can be utilized to spread overlapped peaks or enhance spectral resolution [8–10]. A CL spectroscopic study of iPP under thermal oxidation is very attractive because of the potential for gaining more in-depth mechanistic understanding of the polymeric system. It is known that iPP undergoes spontaneous thermal transition in an aerobic condition. For example, when iPP sample is heated above the melt temperature, it essentially goes through oxidation via the cleavage or fragmentation of the polymer chains. These reactions lead to the generation of alcohol, carbonyl, ester, and carboxyl groups. The development of the reaction products of the polymer usually results in the systematic alteration of CL spectroscopic features, both

* Corresponding author.

E-mail address: h-shinzawa@aist.go.jp (H. Shinzawa).

intensities and frequencies [4,11,12]. Thus, by studying such spectral changes with generalized 2D correlation analysis, it is possible to determine the sequence of the reaction steps as well as to identify the presence of reaction products.

2. Experimental

2.1. CL spectra

Fig. 1 illustrates a schematic illustration of a CL spectrometer MS-8310 (Ueshima Seisakusyo Co. Ltd, Tokyo) used to capture weak emission induced by thermal oxidation. The CL spectrometer consists of a Savart-plate polarization interferometer and a CCD area image sensor [1]. Emission from sample goes through a Savart-plate placed between the polarizers. This Savart plate, made of a calcite crystal, works as a polarizing prism to separate the incident beam. The signals are then detected by the CCD image sensor and the difference in the optical path between the two beams, i.e. interferometer, is converted to CL spectra by Fourier-transformation. The spectral resolution is thus essentially determined by the spatial resolution of the CCD sensor. It is interesting to point out here that this Savart-plate works as a beam splitter like that used for a multichannel FT-IR spectrometer and the utilization of the Savart-plate, in turn, makes it possible to measure CLs at different wavelength, namely CL spectrum.

A commercial iPP was supplied by Wako Chemicals Company and used without any further purification. Total 0.5 g of the iPP sample in an aluminum pan was placed on heater equipped in the CL spectrometer. Time-dependent CL spectra of the iPP sample were collected around at its melt temperature (180 °C) and well above it (240 °C) by accumulating the emission for 30 min. The measurements were carried out for 480 min.

3. Result and discussions

3.1. CL spectra

The time-dependent CL spectra collected at 180 °C and 240 °C are shown in Fig. 2(A) and (B), respectively. Note that the spectral resolution in this wavelength region is uneven because of the conversion from wavenumber to wavelength. For example, the resolution becomes approximately 25 nm in the longer wavelength

region. In fact, such low spectral resolution in this region results in a problem for analyzing the CL spectra later. Tentative assignments of observed CL peaks based on references are listed in Table 1. Unfortunately, the detailed mechanism for the origin of emission observed in this region is not fully understood yet. Thus care must be taken in the assignment of the CL peaks. For example, in Fig. 2(A), the spectra show the continuous increase of the CL intensity around 600 nm. Several studies have reported that this band is associated with the $^1\text{O}_2$ from the reaction products, reflecting a fact that the iPP sample substantially undergoes thermally induced oxidation and eventually generate emission species [5–7]. While the further discussion is needed, we tentatively assign it to the $^1\text{O}_2$ in this article. Additional fine feature is also observed around at 490 nm. It is noted that the spectral intensity around at 490 nm shows an initial increase during the first 180 min and subsequent decrease. Such trends mostly represent the variation of chemical species showing a unimodal change in the quantity. It is tentatively assigned to the carbonyl species which arises from the reaction products appeared at the very onset of the reaction and are consumed during the subsequent process [4,11,12]. On the other hand, the entire feature of the CL spectra shown in Fig. 2(B) is somewhat different. For example, the carbonyl species observed at 490 nm show an initial increase only during the first 60 min, suggesting the rapid consumption of the component. It is, therefore, likely that the reaction process is substantially influenced by the change in the temperature.

The changes in the spectral feature shown in Fig. 2(A) and (B) reasonably reflect the alternation of the iPP caused by the applied temperature. Thus, the detailed analysis of the spectra, in turn, reveals not only the development of the reaction products but also effect of temperature on the reaction dynamics. It is, however, rather difficult to identify from such 1D spectra the subtle changes of spectral features. Especially, this task is even more challenging in elucidating the difference in the time-dependent behavior among the spectra. For example, it is obviously difficult to sort out the difference in the way the spectral feature changes between Fig. 2(A) and (B). Thus, the enhancement of the CL spectra becomes essential to elucidate such subtle but pertinent information present in the data.

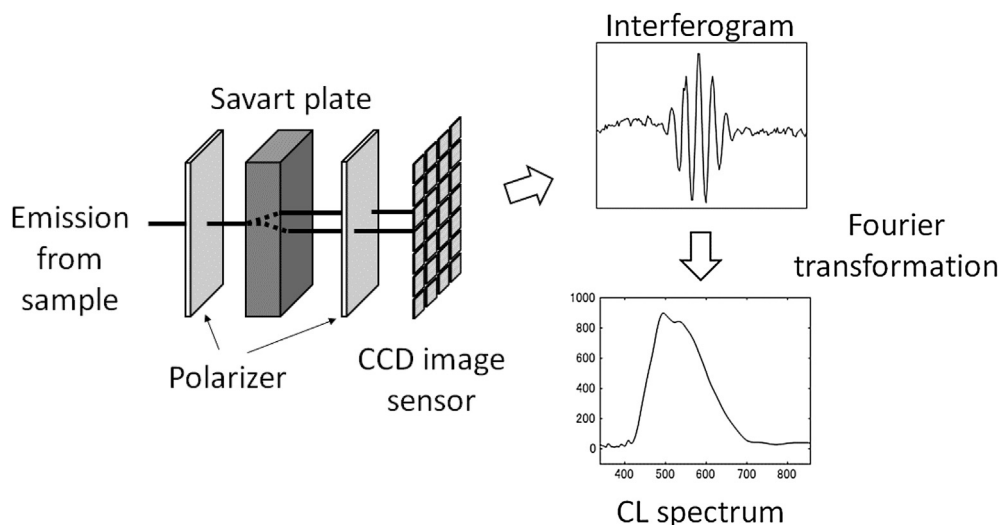


Fig. 1. Schematic illustration of CL spectroscopy based on CCD image sensor and Fourier transformation.

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