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Application News

UV-2600i / UV-3600i plus UV-Vis Spectrophotometer

Diffuse Reflectance Spectrum Measurement of Thermochromic Material Using UV-Vis DiffusIR™

Y. Tange

User Benefits

- Enables evaluation of temperature-dependent color change of thermochromic materials.

■ Introduction

Thermochromism refers to the phenomenon of temperature-dependent color change in materials. This phenomenon has various causes, including isomerization of the molecular structure and the solid phase-liquid phase transition. Thermochromic materials in which thermochromism occurs are applied as thermal recording paper for receipts and as thermosensitive paints for monitoring anomalous heat generation in industrial equipment. In functional design of the thermophysical properties of thermochromic materials, it is necessary to evaluate the temperature at which color change occurs and the colors before/after the reaction. In-situ measurement of the ultraviolet-visible (UV-Vis) spectrum of powders or coated samples on a substrate under temperature control is possible by using a system consisting of a Shimadzu UV-Vis spectrophotometer equipped with a UV-Vis DiffusIR diffuse reflection accessory (PIKE Technologies), enabling evaluation of changes in the sample color due to temperature.

This article introduces an example of diffuse reflectance spectrum measurement when layered polydiacetylene (PDA) on a substrate was heated from 30 ˚C to 250 ˚C at intervals of 10 ˚C.

■ Measurement Conditions and Measurement Sample

Fig. 1 shows the appearance of the UV-Vis DiffusIR diffuse reflection accessory with a high temperature vacuum chamber used in this measurement.

The type used here enables measurement under reduced pressure vacuum and inert gas replacement conditions in addition to heating. Highly accurate measurement of the sample temperature is possible by attaching a thermocouple to the underside of the sample part.

Table 1 shows the detailed measurement conditions, including the heating conditions.

Table 1 Measurement Conditions

Instrument	: UV-2600i UV-Vis DiffusIR
Wavelength range	: 350 nm - 750 nm
Sampling pitch	: 1.0 nm
Scanning speed	: Low
Slit width	: 5.0 nm
Temperature range	: 30 ˚C - 250 ˚C
Temperature interval	: 10 ˚C

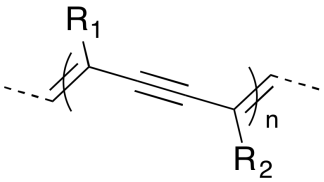

Fig. 2 General Structural Formula of PDA

Fig. 2 shows the general structural formula of the PDA used in the measurement. The main chain (backbone) of PDA has a conjugated structure consisting of mutually alternating multiple bonds and single bonds. When heat or other external stimuli is applied to PDA, the side chains are disordered, and the effect of this disorder in the side chains on the three-dimensional structure of the conjugated backbone causes the color of the polymer to change [1].

In this experiment, layered PDA on a substrate was processed to a size that could be fitted into the heating chamber as shown in Fig. 3, and was then measured.

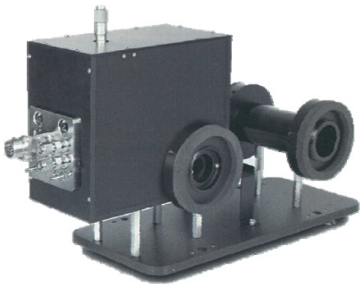

Fig. 1 UV-Vis DiffusIR Heating and Vacuum Type Diffuse Reflection Measurement Accessory

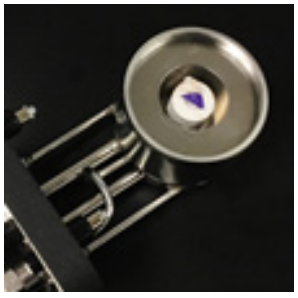

Fig. 3 Condition of Layered PDA on Substrate Set in Heating Chamber

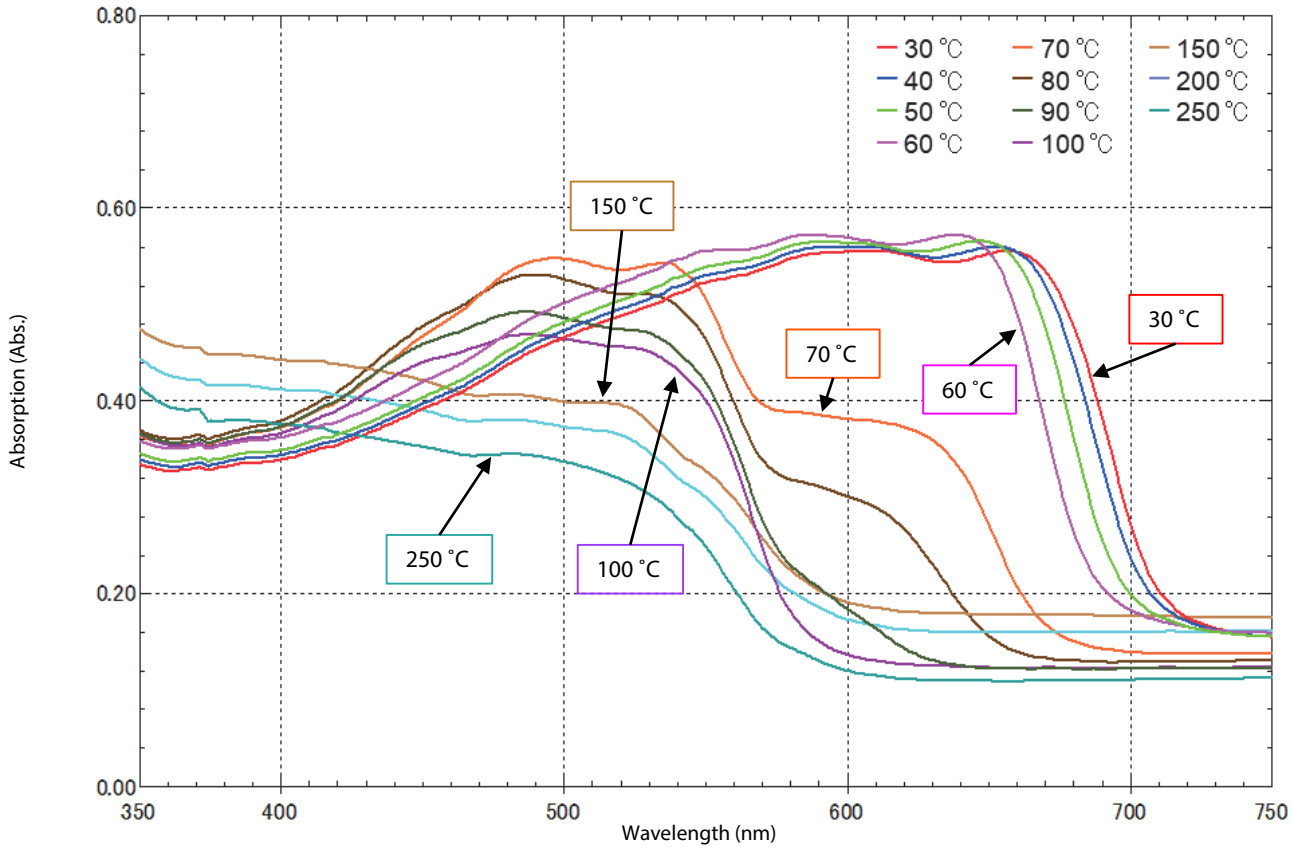

Fig. 4 Change of Diffuse Reflectance Spectrum by Heating

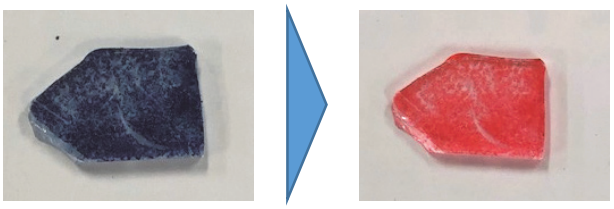

Fig. 5 Change of Appearance by Heating
Deep blue: before heating, red: after heating

■ Change of Diffuse Reflectance Spectrum by Heating

Fig. 4 and Fig. 5 show the changes in the diffuse reflectance spectrum and external appearance of the sample due to heating, respectively. The peak at around 660 nm gradually shifted to the short wavelength side from 30 ˚C to 60 ˚C, and a large change in the shape of the spectrum was observed from 60 ˚C to 70 ˚C. This coincides with the temperature region where the layered PDA transitions from a blue phase to a red phase [(2)]. (The transition temperature of layered PDA is 65.4 ˚C.) From 70 ˚C to 140 ˚C, shifting of the peak to the short wavelength side with increasing temperature gradually weakened, but another large change in the shape of the spectrum was seen at 150 ˚C. Following this change, the absorption of the entire measured wavelength spectrum gradually decreased until 250 ˚C, and the sample lost its color.

Because use of the UV-Vis DiffusIR makes it possible to continue measuring the same point on the same sample, the changes in the spectrum accompanying increasing temperature can be confirmed in detail.

■ Conclusion

The diffuse reflectance spectrum of the thermochromic material PDA under progressively higher temperatures was measured by using a UV-2600i UV-Vis spectrophotometer equipped with a heat chamber-type UV-Vis DiffusIR diffuse reflection accessory which supports measurement under heating/vacuum environments. More detailed analysis of thermochromism is possible by using the heat chamber-type diffuse reflection accessory introduced here, as this device enables continuous measurement of the same point on the same sample during the heating process.

<References>
(1) Xuemei Sun, Tao Chen, Sanqing Huang, Li Li and Huisheng Peng .“Chromatic polydiacetylene with novel sensitivity”. Chem. Soc. Rev., 39:,4244–4257, (2010).
(2) Machi Takeuchi, Karthikeyan Gnanasekaran, Heiner Friedrich, Hiroaki Imai, Nico A. J. M. Sommerdijk, and Yuya Oaki “Tunable Stimuli-Responsive Color-Change Properties of Layered Organic Composites”. Adv. Funct. Mater., 28, 1804906, (2018).

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