I-1. PROJECT RESEARCHES

Project 10

PR10

Operando system for observing the dynamic structure of polymers under ionisation

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PROGRAM OVERVIEW:

Readily available aromatic ring polymers undoped with fluorescent molecules have attracted attention for use in radiation measurements. However, the mechanism underlying the fluorescence, as the key element, has not been elucidated. When the polymers are exposed to charged particles with low intensity, optical signals that are difficult to understand from the fluorescence mechanism of traditional polymers doped with fluorescent molecules are observed. It is speculated that the signals arise from a transient change in the intrinsic properties of the polymers upon exposure to charged particles. However, this phenomenon disappears when the irradiation is stopped. Thus, there are limitations of the indirect approach for inferring the intramolecular electronic states “under ionisation” from those of the “after irradiation” polymer. To solve this problem, a direct approach is required to determine the intramolecular electronic states in the ionised state. Here, we aim to develop a system that can measure the changes in the bond strengths among the constituent elements, the arrangements of the constituent elements, and the electron distributions in polymers in real time while controlling the on/off state of the irradiation.

IMPLEMENTATION:

After extensive testing, we have hypothesised that the charged particles, resonating with the dynamic structure of the base adjacent to the aromatic ring, temporarily delocalise the intramolecular electron distributions, inducing new molecular modes and changing the intrinsic properties. According to the hypothesis, the dynamic structures of the bases adjacent to the aromatic ring should change in response to the presence of charged particles. To directly investigate the electronic states in molecules under ionisation, we are preparing to sequentially mount various radioactive sources on instruments, such as a Raman spectrometer, an infrared spectrometer, a fluorescence spectrometer, and an ultraviolet/visible spectrophotometer. The data from these instruments need to be systematically understood. The amount of space available for each instrument is different, so the mounting unit is being developed, which includes adjusting the size and shape of the radioactive source. The realisation of this new measurement environment will clarify the changes that occur in the bond strengths among the constituent elements and the intramolecular electron distributions in polymers under ionisation, and how they relate to the changes in the optical properties. In addition, clarification of the dynamic structures of polymers under ionisation could lead to the improvement of the properties of traditional polymers doped with fluorescent molecules.

ACKNOWLEDGEMENTS:

This work was supported by JSPS Grant-in-Aid for Challenging Research Exploratory Grant Number 24K21749.

R6P10

PR10-1

Elucidation of dynamic structures of polymers under ionisation

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INTRODUCTION:

Optical signals difficult to explain and are attributed to internal light have been captured in synthetic molecules irradiated with charged particles. These signals likely arise from a switching phenomenon in which exposure to weak charged particles temporarily induces changes in the intrinsic optical properties of the molecule. The phenomenon disappears when irradiation is stopped, so details have been difficult to obtain. Electronic states within the molecule appear to be switched between steady and ionised states when the irradiation is turned on or off. Changes in bond strengths between the constituent elements, the arrangement of the constituent elements, and the electron distributions are observed in real time. Here, we aim to establish the mechanism underlying this unknown phenomenon.

IMPLEMENTATION:

Polymers of undoped fluorescent molecules can temporally exhibit unknown optical signals that cannot be explained by internally generated fluorescence. This occurs only when they are exposed to environmental levels of charged particles. Through extensive verification, we developed an hypothesis that ‘ionising radiation that resonates with the dynamic structure of the base adjacent to the aromatic ring temporarily delocalises the intramolecular electron distribution, inducing a new molecular mode and modifying the inherent optical properties.’ Based on our hypothesis, the dynamic structure of the base adjacent to the aromatic ring changes depending on whether ionising radiation is present. Therefore, we used Raman, infrared (IR, and fluorescence spectrometers to directly observe intramolecular electron states sequentially exposed to strontium-90 or americium-241 radiative sources. The Raman, IR, and Rayleigh spectra for familiar polymers such as polyethylene terephthalate were obtained when the irradiation was on and off. Positions and shapes of each peak were compared, and differences led to the presence of dynamic structure transformations. In addition, singular points where the optics switches when changing the irradiation dose will be identified. In the near future, we reveal the process of changes in bond strengths between constituent elements, as well as those in the intramolecular electron distribution, and elucidate the mechanisms.

ACKNOWLEDGEMENTS:

This work was supported by JSPS Grant-in-Aid for Challenging Research Exploratory Grant Number 24K21749.

PR10-2

Development of an operando ionisation measurement system

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INTRODUCTION:

In radiation measurements, the research focus on polymer-based scintillation materials has begun to shift from fluorescent-molecule-doped to undoped fluorescent polymers. Hence, emission is conventionally interpreted in terms of a ladder model based on electronic transitions within the molecular structure. However, pulsed fluorescence emission, different from that predicted when measuring environmental-level charged particles, has been repeatedly observed. This only occurs in the presence of charged particles. The key to elucidating this observation is via operando measurements to observe changes in intermolecular bond strengths and intramolecular electron distributions when turning the irradiation on and off.

IMPLEMENTATION:

There is a strong desire to elucidate the mechanism of radiation-induced luminescence in undoped fluorescent polymers. However, there are limitations to indirectly inferring the molecular electronic states ‘during irradiation’ from the polymer luminescence ‘after irradiation.’ We identify the singular point at which the optical properties of the polymer change under charged particle irradiation (approximately ten of Bq) as it is turned on and off. To realise operando measurements to investigate the properties of polymers under ionisation, support stands for mounting samples and radiation sources were developed for several spectrometers. This allowed us to directly monitor molecular states exposed to the charged particles. After documenting inherent characteristics of fluorescence and ultraviolet-visible absorption spectrometers equipped with a radiative source, excitation, fluorescence and absorption spectra were obtained for versatile aromatic ring polymers, such as polyethylene terephthalate, polyethylene naphthalate, polystyrene, polyvinyl toluene, polycarbonate and polyether sulphone under conditions with or without charged particles. The comparisons identify singular points where orbital energies change and optical properties switch. These results elucidate the process by which bond strengths between constituent elements and the electron distributions within molecules change under ionisation.

ACKNOWLEDGEMENTS:

This work was supported by JSPS Grant-in-Aid for Challenging Research Exploratory Grant Num-ber 24K21749.

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PR10-3

A radioactive source unit for an operando ionisation measurement system

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INTRODUCTION:

Recently, polymers with aromatic rings have been used as radiation detection elements for safety management in radiation facilities and nuclear reactors. The triggering event for their use is the ionising effect of radiation. Knowledge of macroscopic reactions that occur after polymer ionisation has been well developed over a century. However, there is still little known about microscale re-sponses during ionisation. Thus, this project established an operando measurement system that can investigate microscale changes in polymers in real time during irradiation. One of the core technologies was to adjust the shape of the radiation source installed inside the equipment.

IMPLEMENTATION:

To investigate intramolecular electronic states in polymers under environmental-level charged particle irradiation, it was necessary to mount both a polymer sample and a radiative source in instruments such as an X-ray diffractometer, as well as Raman, infrared, fluorescence and ultravio-let-visible absorption spectrometers. However, the amount of available space on each piece of equipment varied, and the measurement conditions had to be standardised to understand the data obtained from each piece of equipment. Commercially available radiation sources have fixed shapes and dimensions, which limit incorporation into the equipment. These difficulties were overcome by adjusting the size and shape of the radioactive sources. We established a simple method for developing a radiation source that offers a high degree of freedom. A three-dimensional printer will eventually solve these problems, where samples will be made by mixing a radioactive standard solution into the printer solution resin, with full knowledge of the resulting printer contamination. In the meantime, as a cold test, we prepared a potassium chloride solution to create a prototype radioactive source that emitted beta particles. The surface profiles of the prototype radioactive sources were evaluated with a tabletop scanning electron microscope. Then source samples with different doses by controlling the amount used of standard radioactive solution (strontium-90) will then be fabricated.

ACKNOWLEDGEMENTS:

This work was supported by JSPS Grant-in-Aid for Challenging Research Exploratory Grant Number 24K21749.