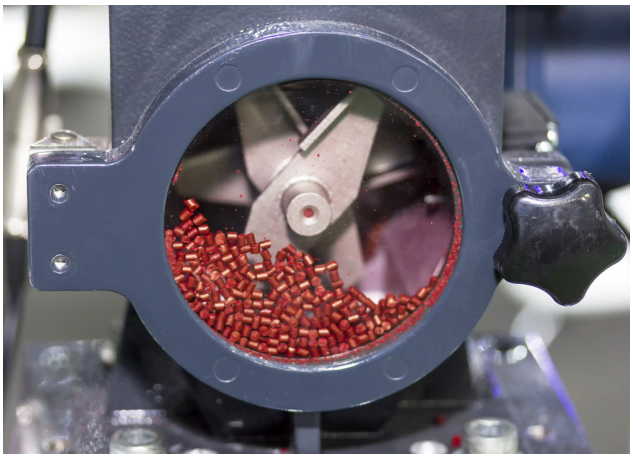
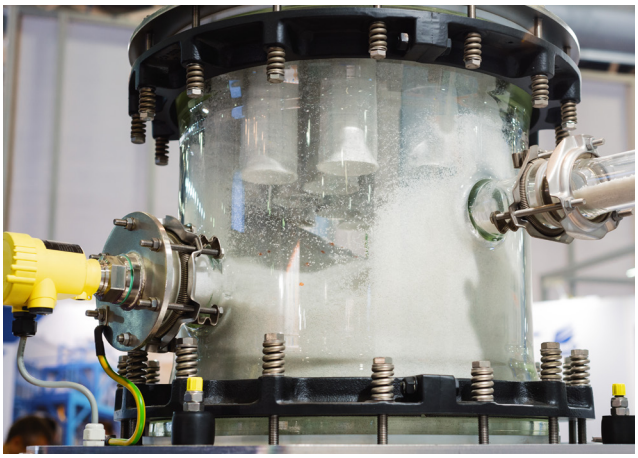
Optimizing polymerization inhibitor concentration with UV-Vis Spectroscopy

Given that a significant proportion of the world's plastics and synthetic fibers are made from polymerization processes, there is a huge need for process optimization and control methodologies compatible with this type of chemistry.

Although there are different classes of polymerization reactions, typically, all of these involve an initiation step to trigger the polymerization process and the growth of the polymer chain. This may be the addition of a chemical species or the use of high temperatures or even light, in the case of photoinduced polymerization reactions.

The growth of the polymer chain is known as propagation, and this process will continue until chain termination is achieved and the reaction stops. This may occur through unwanted side reactions of radical initiators, undesirable auto-polymerization or, more intentionally, by reaction with an inhibitor.





Inhibiting Polymerization

The length of a polymer chain has a direct impact on its physical properties and applications. Controlling this chain length in a targeted synthesis is usually achieved via the intentional addition and control of the concentration of inhibitor species.

Achieving optimum concentrations of inhibitors is a complex problem. Too little inhibitor and unwanted reactions can occur, too much inhibitor and it can be challenging to get the monomers to polymerize at all.

This is why for many polymerization reactions, process analytical technologies (PATs) are incorporated into the process workflow. With the correct calibrations, techniques such as Ultraviolet-visible (UV-Vis) absorption spectroscopy can be used to monitor both the concentration and spectral profile of polymer and inhibitor alike, and this output can be integrated into process control systems.

UV-Vis spectroscopy generally has excellent sensitivity (below 10^{-5} molar) for the measurement of different types of compounds in the reaction vessel and can be used for both quantitative and qualitative measurements. It is compatible with a wide range of compounds and sample types and is a proven PAT for monitoring polymerization reactions.

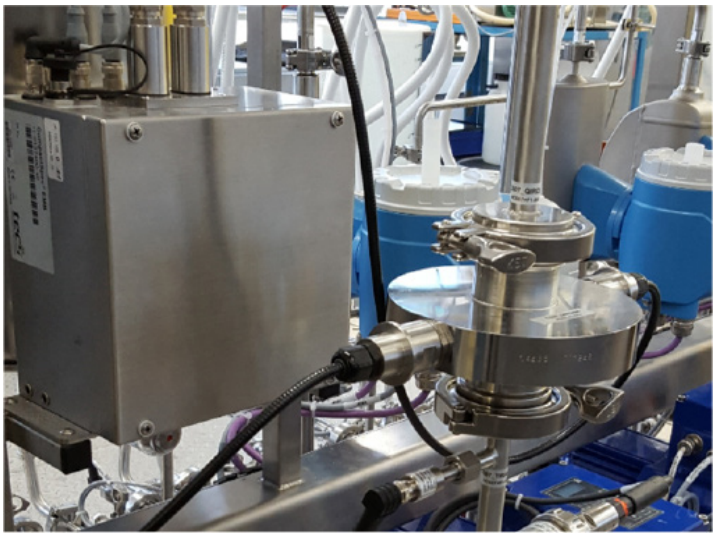
Online UV-Vis Analyzer Design

PAT for inhibitor concentration control needs to be capable of rapid online measurements in the reaction vessel. tec5USA, with extensive expertise in the design and implantation of process spectroscopy, offers an online UV-Vis Spectrometer with the Polymer extruder sample probe option for exactly this purpose.

The spectrometer offers an impressive S/N of ~ 20,000 and comes with options to cover a spectral range of 190 – 1100 nm. This wavelength range is sufficient for nearly all commonly used polymerization inhibitors. For example, a common inhibitor Cupferron has strong absorption between 210 - 490 nm, so its concentration can be monitored at in this wavelength range. Many longer chain polymer species typically have absorption more towards the near infra-red region, so it can be advantageous to monitor a range of spectral regions to disentangle the complex reaction mixtures.

The detection system consists of a high dynamic range silicon diode array detector with 256 pixels. With a wavelength accuracy of 0.2 – 0.3 nm and permanent wavelength calibration, this means UV-Vis measurement of the reaction mixture are both reliable and accurate. The detector is also exceptionally thermally stable, so environmental changes will not affect the sampling quality.

With the tec5USA UV-Vis Spectrometer, the spectral acquisition times are short enough so that samples can be taken of the reaction mixture as frequently as every few milliseconds. This means that, should unwanted auto-polymerization occur, or other rapid reactions, the real-time concentration information can be used to adjust and optimize the process as necessary.



[tec5USA Online UV-Vis Analyzer]

[Excalibur HD Extruder Probe]

The tec5USA UV-Vis Spectrometer has a modular design making it highly flexible and offering the possibility of customization to the particular needs of a given reaction. Essential for PAT, it has no moving parts making it a maintenance-free device, reducing operating costs and production losses associated with regular maintenance downtime.

Process control communications options include Modbus, 4.20 mA and OPC and the spectrometer can be interfaced as part of a closed-loop control connection to DCS/SCADA systems.

Sampling Options

Polymerization reactions often occur under harsh conditions, higher temperatures, UV-irradiation and many of the radical intermediate species formed are highly reactive. This means any materials used for probes or reaction vessels need to be very chemically inert to avoid degradation and contamination.

tec5USA uses the Excalibur HD Extruder Probe to handle harsh sample environments. Capable of withstanding temperatures up to 300 °C, pressure up to 300 bar, with chemically-resistant sapphire windows and a titanium barrel, the Extruder probe is a robust sampling probe suitable for direct insertion in polymer extrusion mixes. In addition, there are a variety of transmission measurement tips available, with path lengths of 1 – 10 mm depending on the expected concentrations and signal intensities expected for the chemical species of interest.

The tec5USA UV-Vis Spectrometer is a highly flexible, robust device for on-line measurements in the challenging environments associated with polymerization reactions. Find out how tec5USA's instruments and extensive expertise in process control spectroscopy could be used to enhance and optimize your processes.

About tec5USA

tec5USA is the North American subsidiary of tec5 AG, who belong to the publically traded company Nynomic AG, an international photonics group and leading manufacturer of products for permanent, non-contact and non-destructive optical measurement technology.

Rather than waiting for time-consuming laboratory measurements, tec5USA's instruments rapidly measure time-critical chemical and physical parameters to react immediately to deviations in the production line, permitting real-time process verification. This hence enables consistent quality, waste minimization and rework reduction, yield maximization, end-to-end supply chain optimization and pay per content.

Industries tec5USA serves are semiconductor manufacturing equipment, thin film technology, chemistry, petrochemistry, environmental technology, the mining industry, biotechnology and pharma, food, feed and beverages as well as agriculture.

Works Cited

1. Zivic, N., Bouzrati-Zerelli, M., Kermagoret, A., Dumur, F., Fouassier, J. P., Gigmes, D., & Lalevée, J. (2016). Photocatalysts in Polymerization Reactions. ChemCatChem, 8(9), 1617–1631. https://doi.org/10.1002/cctc.201501389

2. Roncali, J., Garnier, F., Lemaire, M., & Garreau, R. (1986). Poly mono-, bi- and trithiophene: Effect of oligomer chain length on the polymer properties. Synthetic Metals, 15(4), 323–331. https://doi.org/10.1016/0379-6779(86)90081-0

3. Su, W.-F. (2013). Principles of Polymer Design and Synthesis, Lecture Notes in Chemistry 82. Principles of Polymer Design and Synthesis (Vol. 82).

4. tec5. (2021) Products. https://www.tec5.com/en/products, accessed 10th March 2021

5. tec5. (2021) Multi-Spec UV-vis. https://www.tec5usa.com/multispec-system, accessed 10th March 2021

6. NIST (2021) Cupferron, https://webbook.nist.gov/cgi/cbook.cgi?Spec=C135206&Index=0&Type=UVVis&Large=on, accessed 10th March 2021