Monitoring and control of a semi-batch polymerization with Raman spectroscopy

Introduction

Semi-batch reactions offer several advantages over traditional batch reactions, such as greater selectivity of products, gradual addition of reactants for better process control, and the ability to isolate product as it is formed. Polymerizations are often done in semi-batch mode because it offers the ability to carefully control the composition of the product in order to create high-performance materials with fine-tuned custom properties.

However, one significant challenge of semi-batch reactions is that the concentrations of the reactants constantly change, in both relative and absolute senses. If uncontrolled, this variation in the concentrations of reactants can easily result in unwanted properties in the product. So, this reaction mode requires continuous real-time monitoring of the concentrations of the reactants. Simply adding the reactants in the correct ratios is insufficient.

Additionally, batch-to-batch consistency is essential for high-performance materials with finely tailored properties. And in many manufacturing plants the same process equipment must be capable of producing a wide variety of high-performance materials, so the process-control method must be both precise and flexible.

Raman spectroscopy offers several advantages for real-time process monitoring of semi-batch polymerizations: It can identify bands specific to particular functional groups, such as the vinyl and alkyl moieties common to polymerization monomers, and it offers both easy sample interfacing and fiber-optic coupling of the probe to the base unit for flexible placement of the base unit relative to the process line.

Experimental

In this experiment a semi-batch polymerization reaction was carried out using three proprietary monomers, designated monomers A, B, and C. A schematic of the system is shown in Figure 1.

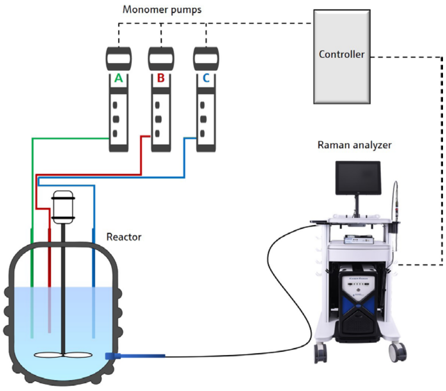

Figure 1: Schematic diagram of process control system for semi-batch polymerization

A Raman analyzer was used to deliver and collect 785 nm near-infrared radiation from a laser. A non-contact optic was used to perform the analysis through a pressure and temperature-rated sapphire viewport in the wall of the reactor. Each sample acquisition consisted of 60 seconds of illumination of the reactor contents using 125 mW of laser radiation followed by a 20 second pause. Five to seven data points from each monomer were used to generate quantitative Raman data for real-time process control.

Benefits at a glance

- Optimization of a sensitive semi-batch reaction
- Real-time data analysis for reliable process control
- Non-contact optics for minimal disturbance to the reaction system

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

In this reaction a vinyl functional group in each of the three monomers changes to an alkyl group during the polymerization. Raman is sensitive to this, whereas traditional infrared spectroscopy is much less so. Chemometric modeling in this case was based on the Raman signal for the vinyl region in all monomers, the C–H wag in monomers A and B, and the lactone region in monomer C.

Results and discussion

The polymerization reaction was performed under both open-loop (in which spectroscopy is used only for process monitoring, not for feedback control) and closed-loop (in which spectroscopy is used for process monitoring and real-time feedback control) conditions. Figure 2 shows the concentrations of each of the three monomers over time in the open-loop experiment. As expected, the concentrations of the monomers vary widely over the course of the reaction.

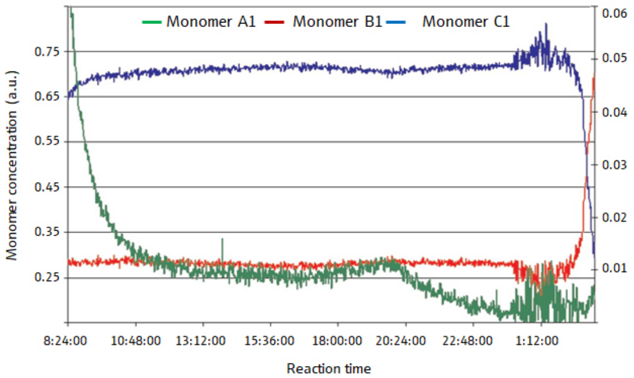

Figure 2: Monomer concentrations in an open-loop (process monitoring only) semi-batch polymerization reaction. The concentrations of the monomers, especially monomer A, vary widely over the course of the reaction. *(Reprinted with permission from Ref. 1. © 2006 Compare Networks Inc.)*

Figure 3 shows the concentrations of the three monomers in the closed-loop experiment, in which the Raman spectral data are used in real-time feedback control of the process. In this case the concentrations of the monomers are much more constant because the process control system ensures that each monomer is added to the system when needed, and only when needed. The black and gray plotlines in the middle of the figure indicate the feed flowrates determined by the process control system using the Raman spectral data.

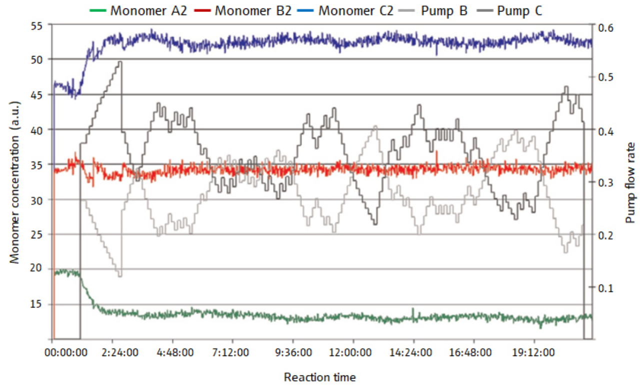

Figure 3: Monomer concentrations in a closed-loop (process monitoring and control) semi-batch polymerization reaction. The concentrations of the monomers remain very constant over the course of the reaction. The plotlines in back and gray at the center of the plot represent the feed flowrates determined dynamically using Raman data. *(Reprinted with permission from Ref. 1. © 2006 Compare Networks Inc.)*

Furthermore, consistency between batches was high, with average molecular weights of the products varying between 28700 and 30200 Daltons and polydispersity varying between 1.79 and 1.84.

Conclusion

Raman spectroscopy was demonstrated to be a simple, accurate, and effective method of process analysis for the purpose of real-time monitoring and control of a semi-batch polymerization. Raman data were able to be used for real-time feedback control of the process to maintain ideal process conditions in a closed-loop reaction system and to produce a highly consistent product between batches, ensuring consistent quality of sensitive high-performance materials.

References

1. Müller, J. et al. "Semi-Batch Polymerization Analysis by Multi-Point Raman Spectroscopy." *Process Analytical Technology*, **September/October 2006**, 1–6.