

Monitoring emulsion polymerization reactions

Benefits at a glance

- Monitoring in an aqueous environment
- Probe located outside reaction vessel
- Correlations with chromatographic and gravimetric data

Introduction

Emulsion polymerization is an important process for the production of a wide range of polymeric materials, including paints, adhesives and synthetic rubbers. The reaction is performed within an aqueous environment where the monomer species is maintained within a single phase with a suitable surfactant or emulsifier. The surfactant concentration is maintained above the critical micelle concentration (CMC), with the unsaturated monomer retained in the center of the micellar structure to form a stable emulsion. Polymerization proceeds as a classical double bond addition reaction, initiated via a free-radical mechanism. One or more monomer species may be used and the resultant polymer or copolymer is produced as a stable suspension, in the form of a latex.

Two benefits of producing polymers in a latex form are that the impact of the viscosity increase due to the formation of the polymeric species is minimized, and that the heat generated by the reaction is readily dissipated. Furthermore, high molecular weights are achieved by this process without the need to reduce the reaction rate and temperature, as required by other methods of polymerization. An important practical benefit of the aqueous-based emulsion is that the medium is environmentally friendly, and does not involve the use of organic solvents. For many applications, such as paints and adhesives, the material may be applied in the final latex form.

It is important to be able to monitor the rate of consumption of the monomer species or the relative rates of consumption of the comonomers, when more than one monomer is

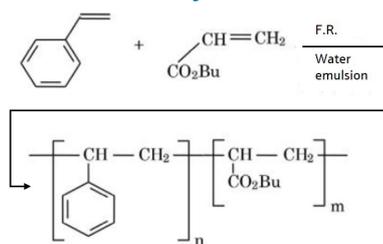
used. This is necessary to ensure that the desired rate of formation of the product occurs. Also, if more than one monomer is involved, that the relative rates of reaction are consistent with the formation of the desired product. Another issue is residual monomer, as detected by the presence of unreacted double bonds. Raman spectroscopy is well suited for monitoring these reactions insofar as it is sensitive for the measurement of specific double bonds, and it does not suffer with interference from the aqueous matrix. Furthermore, in studies with glass reaction vessels it is possible to monitor the reaction from outside, through the reactor walls.

Experimental

Emulsion polymerizations featuring acrylic-based reactions are common, and in this current example the formation of a styrene-butyl acrylate copolymer are studied (see reaction summary). A 3L glass reactor was used with the Raman fiber optic probe mounted externally, and with the laser radiation focused on the reaction mixture. The reaction mixture consists of the two monomers, styrene and butyl acrylate, dispersed in a solution of dodecylbenzene sulfonate (surfactant), with small quantities of sodium hydroxide, sodium sulfate, ammonium persulfate (initiator) and tert-dodecyl mercaptan (moderator). The mixture is stirred at a constant rate, and the reaction is maintained at a constant temperature of 55 °C by an external water bath, with ice being added for additional cooling, as required. The reaction is monitored with a Raman analyzer with a 785 nm laser excitation. The Raman scattered radiation is collected with a multi-element lens system, and is returned to the spectrometer via a fiber optic cable.

① All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

Reaction Summary



Results

Example spectra are provided in Figure 1, where the broad feature in the region 1100 to 1800 cm^{-1} is assigned to interference from the glass of the reactor walls. The overall reaction is monitored by observing the decrease in intensity of a band at 1631 cm^{-1} , which is jointly assigned to the 1631 cm^{-1} C=C band of styrene overlapping the 1639 cm^{-1} C=C band of butyl acrylate. Variations in overall measured intensity, observed during the reaction, are compensated from the ratio of the 1631 cm^{-1} band and the intense styrene, aromatic ring band at 1000 cm^{-1} . In the experiment described, the residual double bond concentration was independently determined by GC analysis of grab samples. A correlation is obtained between the ratioed Raman intensities and the GC data, as indicated in Figure 2. This procedure provides a measure of the reaction as a function of the total unsaturation. The consumption of the styrene monomer can be deduced by monitoring the ratio of the 1412 cm^{-1} vinyl C-H band to the 1000 cm^{-1} ring band, and the butyl acrylate concentration may be inferred by difference. The overall monomer-to-polymer conversion is presented in Figure 3, with independent results from GC and gravimetric measurements being superimposed.

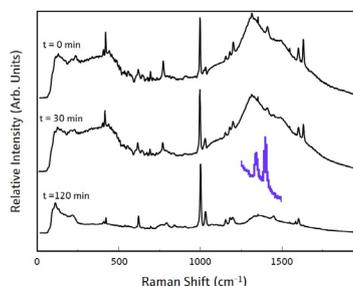


Figure 1: Monitoring changes in unsaturation of monomers

Discussion

The results provided demonstrate the utility of Raman for monitoring addition polymerizations, and in particular emulsion systems, where the aqueous environment does not present a spectral interference for the measurements. Comparable experiments with FTIR are generally fraught with difficulties. In particular, the high absorbance of the aqueous medium, and the inability to observe the experiment through the reactor walls make the experiment generally impractical.

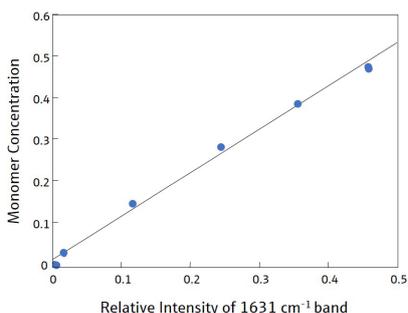


Figure 2: Total monomer concentration: Raman vs. GC

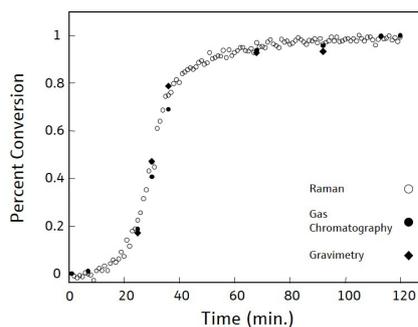


Figure 3: Conversion profile for styrene-butyl acrylate emulsion polymerization

Reference

1. Al-Khanbashi, A. Dhamdhare, M., and Hansen, M., "Application of In-line Fiber-Optic Raman Spectroscopy to Monitoring Emulsion Polymerization Reactions," *Applied Spectroscopy Reviews*, Vol. 33, No. 1&2, 1998.