Monitoring the effect of initiator concentration on molecular weight and intrinsic viscosity of polyvinyl pyrrolidone (PVP) using ACOMP

Abstract

Automatic Continuous Online Monitoring of Polymerization Reactions (ACOMP) was used to monitor the free radical polymerization of polyvinyl pyrrolidone (PVP) throughout the reaction. Two batch reactions were run at 1.5% and 2.5% initiator concentration to monitor the effect of a small change in initiator concentration on reaction kinetics, weight average molecular weight and intrinsic viscosity. The physical properties of a polymer such as brittleness, conductivity or solubility are dictated by the molecular weight distribution (MWD) and its various averages, especially weight average molecular weight (M_w). Online monitoring of polymerization reactions is important in many industrial and research applications from new product development and pilot reactions scale-up to optimization of existing processes and quality control.

Introduction

ACOMP was used to monitor the free radical polymerization of vinyl pyrrolidone using UV/Vis, viscometry and multi-angle light scattering (MALS). This technique is suited for many processes including solution, bulk, emulsion and inverse emulsion polymerizations as well as post-processing steps such as hydrolysis and quaternization.

Polyvinyl pyrrolidone is a versatile water-soluble polymer that is used in many applications including beer filtration, pharmaceutical tablet coatings, binder in personal care products, dishwasher soap packaging, inks and coatings. PVP has existed for more than 70 years. Increased demand for this versatile polymer calls for the advanced fusion of analytical, sensor and process data yielding correlations that can optimize product quality and increase plant throughput while simultaneously reducing energy and feedstock consumption.

This application note describes how ACOMP is used to monitor the polymerization of vinyl pyrrolidone under small changes in initiator concentrations.

ACOMP System Configuration

A UV/Vis detector was used to measure the concentration of vinyl pyrrolidone monomer at 260 nm. A Fluence Analytics' proprietary viscometer was used to measure the intrinsic viscosity, and a proprietary 5-angle light scattering (MALS) detector was used to measure weight average molecular weight. The ACOMP system interfaced with the reactor through a recirculation loop ensuring a representative sample of the reactor contents was analyzed. The reactor recirculation loop was continuously sampled at 0.5 ml/min and diluted with de-

ionized water to the appropriate detector concentrations using ACOMP's proprietary sampling and conditioning technology. The sample was diluted 12 times to the viscometer and 80 times to the UV/Vis and MALS detectors. ACOMP dilutions range from 10x to 1,000x dilution depending on the reactor concentration and properties of the polymer.

Methodology and Results

The reactions were conducted at 3% vinyl pyrrolidone (VP) and a constant temperature of 45°C.

Figure 1 shows the ACOMP Raw Signals for the UV/Vis, viscometer and light scattering of the polymerization of vinyl pyrrolidone using 2.5% initiator (VA-044). The raw data are analyzed in real time and available to the user through the ACOMP HMI. This information is also available to the process and quality engineers through the plant distributed control system (DCS). A baseline, indicative of the reactor conditions prior to polymerization, is collected for all the detectors. Once the reaction is initiated, UV/Vis decreases with monomer consumption as displayed in blue, and viscometer and light scattering increase throughout the polymerization as depicted in red and green, respectively.

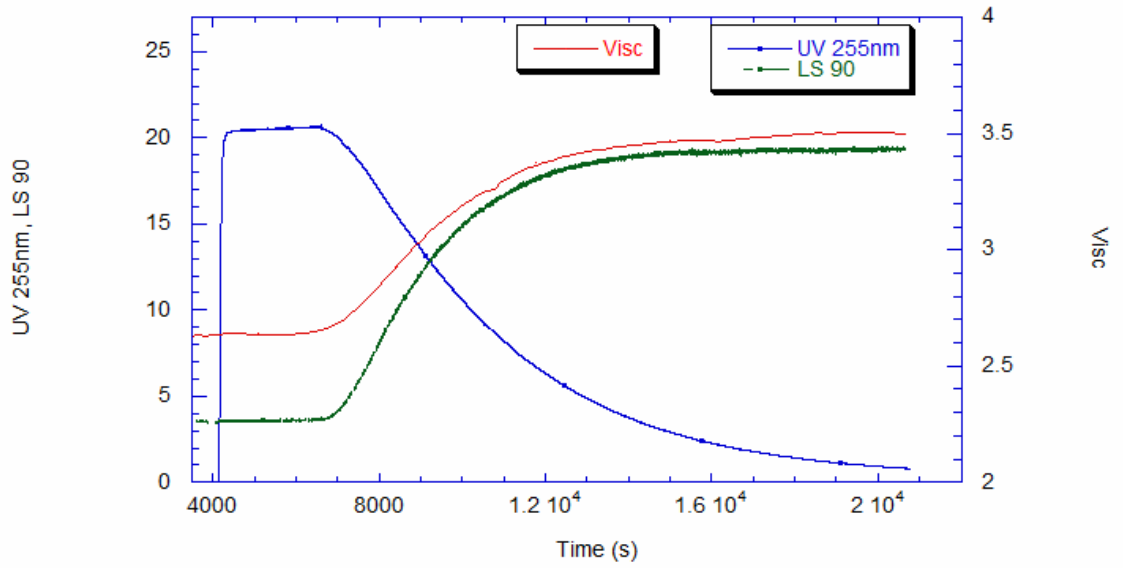

Figure 1: Raw ACOMP Data PVP 2.5% Initiator

Reaction Kinetics

Figure 2 exhibits the polymer concentration as measured by the UV/Vis. As expected, the reaction with 2.5% initiator shows much faster kinetics.

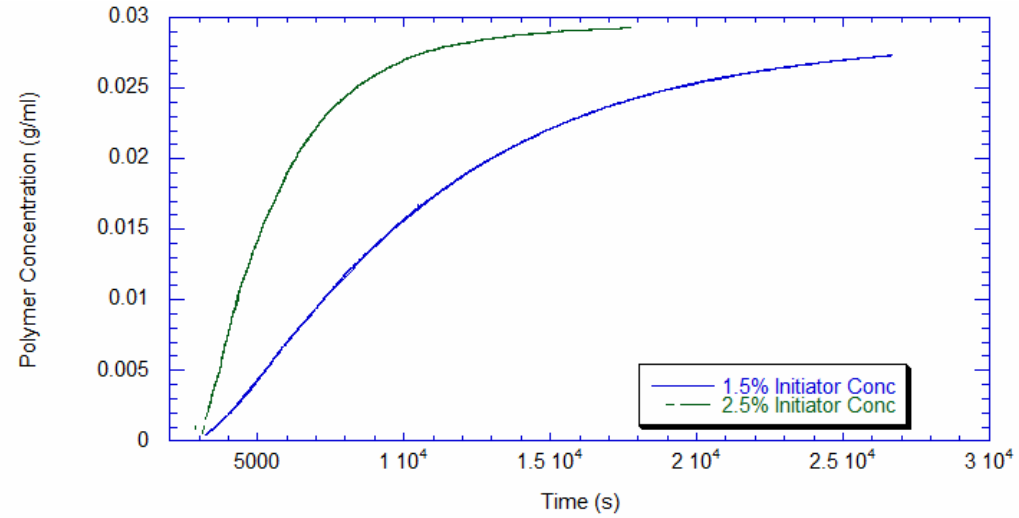

Figure 2: PVP concentration vs. time as measured by the UV/Vis

Intrinsic Viscosity and Molecular Weight

Figure 3 displays the intrinsic viscosity as measured by the viscometer. The higher initiator concentration leads to a 10% decrease in intrinsic viscosity.

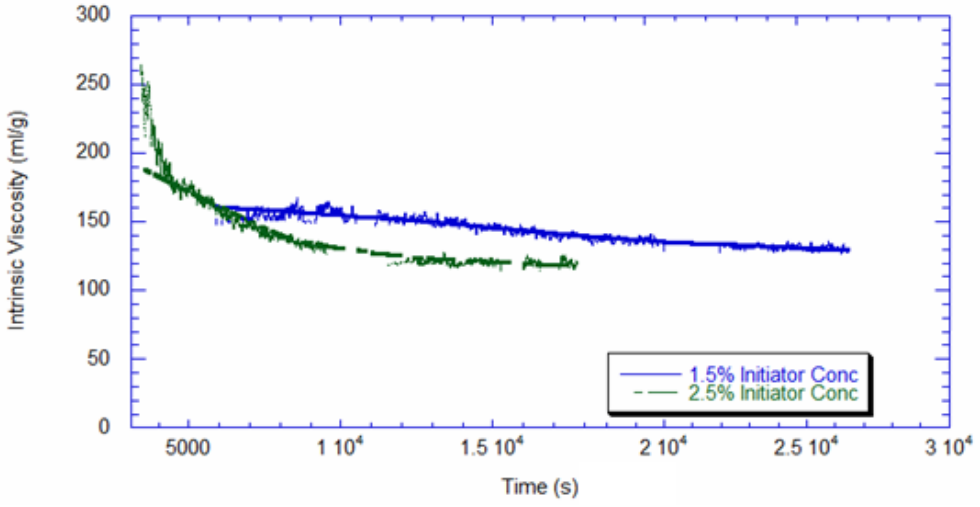

Figure 3: PVP Intrinsic Viscosity vs. time

Figures 4 and 5 present the weight average molecular weight as measured by the light scattering detector, combined with the UV concentration detector. The higher initiator concentration leads to a 23% decrease in molecular weight.

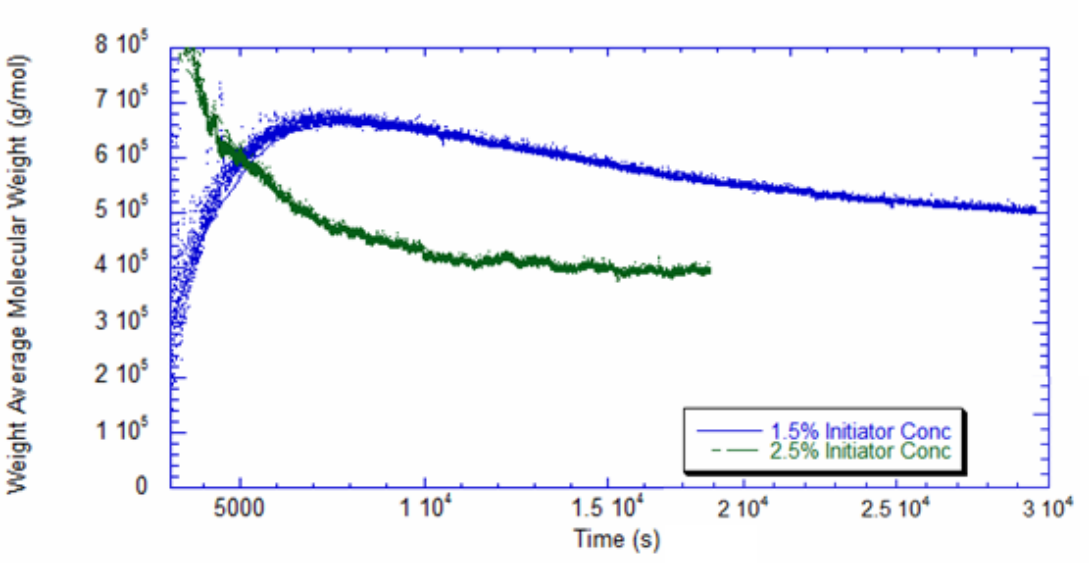

Figure 4: PVP weight average molecular weight vs. time

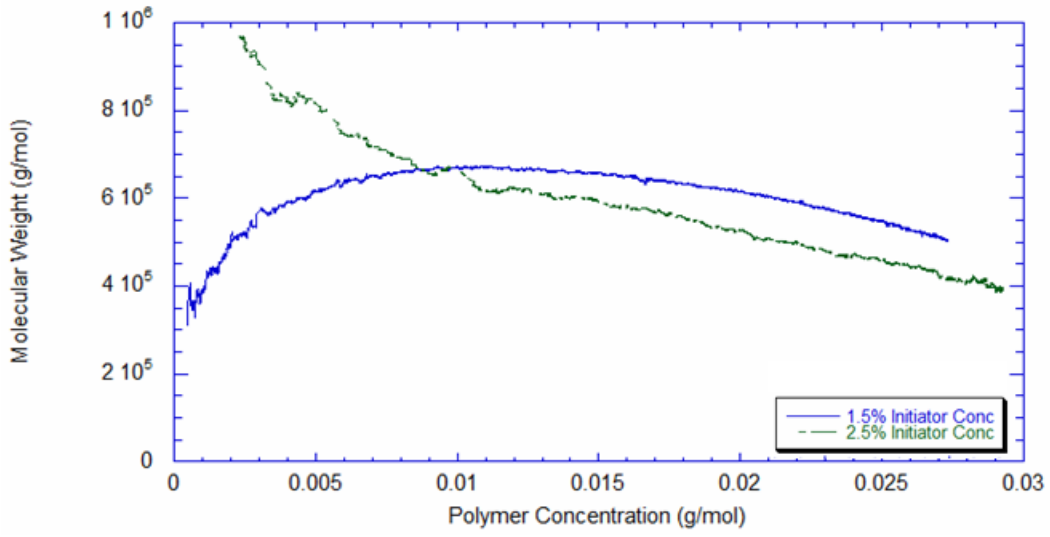

Figure 5: PVP weight average molecular weight vs polymer concentration

Summary of Results

Table 1 compares the final weight average molecular weight and intrinsic viscosity for the final product as measured by ACOMP.

Table 1: Summary of final MW and IV for PVP

Reaction ID	VP (%)	VA-044 (%)	MW(g/mol)	IV (ml/g)
PVP A	3	1.5	501,900	128
PVP B	3	2.5	386,400	115

Conclusion

ACOMP can successfully monitor the polymerization of PVP under varying initiator concentrations. In monitoring the evolution of the polymerization, the operator can identify and mitigate off-spec batches much sooner in the event of an undesirable process condition as seen with a small change in initiator concentration. ACOMP technology is also compatible for online monitoring of radius of gyration, molecular weight distribution and copolymer composition. Additional analysis of ACOMP data can lead to insight and correlations to Mark-Houwink parameters, hydrodynamic volume, degrees of branching and crosslinking.

For further reading on ACOMP

Reed, W.F. "Automated Continuous Online Monitoring of Polymerization Reactions (ACOMP) and Related Techniques." *Encyclopedia of Analytical Chemistry*, 2013, 1-40, DOI: 10.1002/9780470027318.a9288.

Florenzano, F. H., Strelitzki, R., & Reed, W. F. (1998). Absolute, On-Line Monitoring of Molar Mass during Polymerization Reactions. *Macromolecules, 31*(21), 7226-7238. doi:10.1021/ma980876e

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