Using In-process Viscometry Measurements to Predict Prepolymer Molecular Weight and to Control the Molecular Weight of Polyurethanes

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Polyurethanes, which are prepared by the reaction of an isocyanate with a polyol, are commonly employed in a broad range of applications such as paints and inks. The physical properties and the performance characteristics of the polyurethane that is formed depend on the synthetic route and the conditions that are employed. This requires that the synthetic chemist must carefully monitor the reaction conditions to obtain a product that meets the needs of the specific application. We note, for example, that the molecular weight of the polyurethane impacts, for example, the ability of the polymer to disperse pigments or to impart high strength bonds in laminations.

In most instances, the synthetic chemist frequently monitors the progress of the synthesis of the polyurethane by monitoring the free NCO concentration via a standard titration procedure. While this technique is useful, it should be noted that, in some systems, the decrease in the free NCO concentration slows down or even stops, but the viscosity of the mixture increases, suggesting that some other reaction(s) are taking place. In other words, while monitoring the free NCO concentration is a useful tool, it is not sufficient to totally characterize the progress of the synthetic reaction. Another technique is required to monitor the reaction.

In this paper, we describe a series of experiments that involve the use of in-process viscometry to follow the synthesis of an experimental polyurethane/urea prepolymer. In these experiments, the reagents (the polyol and the isocyanate) and solvent (n-propyl acetate) were added under nitrogen to a 3 L glass round bottom flask. The reaction was stirred for a period of seven hours, during which time the temperature was gradually raised to 90 ^{o}C.

The viscosity was measured on-line using a “SPL-324” viscometer (Cambridge Viscosity, Inc., Medford MA). This viscometer measures the viscosity via a single piston technology that provides extremely accurate and repeatable measurements. This system, which is depicted in Figure 1, includes a loose fitting piston which moves up and down as the viscosity of the sample changes and does not require a seal. The movement of the piston is monitored by a sensor in the viscometer head, and the absolute viscosity of the sample is reported. The viscometer incorporates a temperature detector so that the temperature corrected viscosity is reported.

Since the SPL-324 viscometer can be readily installed in the reaction flask (the entire assembly is shown in Figure 2), we are able to obtain the viscosity of the reaction mixture on a continuous basis. In order to check that the viscosity data truly monitors the progress of the reaction, we tracked the reaction by removing and analyzing an aliquot in three additional ways:

- Determination of the free NCO via ASTM D2572 (titration with di-n-butylamine/HCl).

- Determination of the molecular weight via Gel Permeation Chromatography. The sample was quenched in a solution of monoamine in THF and injected onto a series of Phenogel crosslinked polystyrene columns with THF as the mobile phase.
- Determination of the weight of non-volatiles by removing an aliquot and drying the sample in a hot air oven for 15 min at 150 C. (to verify that no solvent loss has occurred which would impact the viscosity reading, and for the free NCO calculation).

A plot of the viscosity as a function of the molecular weight (M_w) of the reaction product is presented in Figure 3. This figure demonstrates that the viscosity clearly tracks the molecular weight of the polymer (as measured by GPC) over a molecular weight range from 6,000 to 20,000. In a separate plot, we note that the % free NCO also tracks the molecular weight of the prepolymer, demonstrating that measuring the viscosity is a useful tool to monitor the progress of the reaction.

Conclusions

In-process viscometry clearly provides the synthetic chemist with a powerful tool to monitor the progress of a reaction. Since the SPL-324 viscometer can continuously monitor the reaction, the data is readily available without the need to withdraw aliquots on a periodic basis. The SPL-324 is designed to be easy to use and is reliable. We have been using the sensor for over two years without any downtime. In addition, we should note that a production scale viscometer is available. When we scale up a process, it will be easy to move to the production scale system for the production of polyurethanes. Similarly, while the reaction we are monitoring in this paper was performed at 90 ^{o}C, it should be noted that a high temperature sensor is also available, which can operate up to 370 ^{o}C.

Figure 1 Schematic Diagram of SPL-324

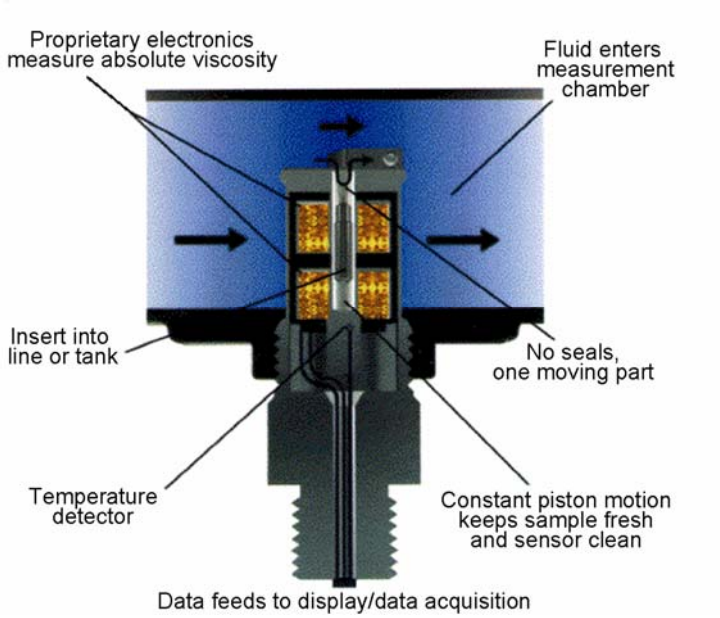

Figure 2 The SPL324 Viscometer

Figure 3 Prepolymer Viscosity as Function of Molecular

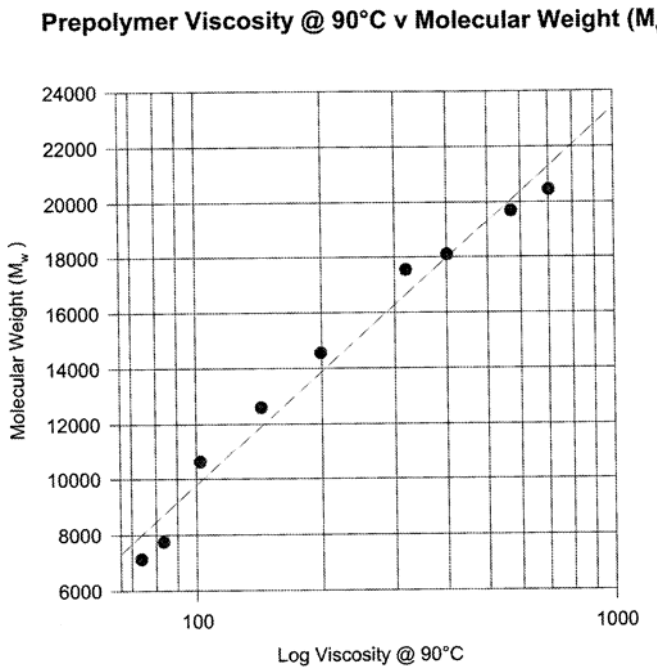

Figure 4 Prepolymer Free NCO as a Function of Molecular Weight